Comparison of several glycerol reforming methods for hydrogen and syngas production using thermodynamic analysis

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Abstract
This paper focuses on the comparison of different glycerol reforming technologies aimed to hydrogen and syngas production. The reactions of steam reforming, partial oxidation, autothermal reforming, dry reforming and supercritical water gasification were analyzed. For this, the Gibbs energy minimization approach was used in combination with the virial Equation of state. The validation of the model was made between the simulations of the proposed model and both, simulated and experimental data obtained in the literature. The effects of modifications in the operational temperature, operational pressure and reactants composition were analyzed with regard to composition of the products. The effect of coke formation was discussed too. Generally, higher temperatures and lower pressures resulted in higher hydrogen and syngas production. All reforming technologies demonstrated to be feasible for use in the production of hydrogen or synthesis gas. The proposed model showed good predictive ability and low computational time to perform the calculation of the combined chemical and phase equilibrium in all systems analyzed here.

Keywords: Reforming processes, Gibbs energy minimization, Hydrogen, Syngas.

1. Introduction
In the past decades, biomass has received a great deal of attention as a new source for clean energy because it is renewable, alternative and producing less carbon dioxide than fossil fuels [1]. In the last decade, biodiesel has been becoming a major substitute for fossil diesel, as its environmental benign characteristics can reduce carbon dioxide emission pollution and mitigate climate change problems [2,3].

Glycerol is obtained as a by-product in biodiesel production using vegetable oils by a base-catalyzed transesterification reaction. Glycerol of high purity is an important industrial feedstock for applications in food, cosmetics, pharmaceutical and other industries [4]; however, it is costly to refine crude glycerol, especially for medium and small-sized plants.

In any case, since glycerol production and utilization have a notable impact on the economics and sustainability of biodiesel production, the development of novel processes for glycerol valorization is essential. Among all possible routes, glycerol conversion into valuable gases like as hydrogen and syngas as an energy carrier using different reforming processes are one of the most attractive ways to aggregate value in the glycerol [4].

The reforming processes used to produce hydrogen and syngas from glycerol include some methods, and in the literature, it is possible to find some articles about then. The articles principally discussing the catalytic behavior of the systems, the main related methods for glycerol reforming are steam reforming (SR) [5-11], partial oxidation (or oxidative reforming) (PO) [12-14], autothermal reforming (ATR) [12, 14] and Supercritical Water Gasification (SCWG) [15-19]. Other methods like as dry reforming (or CO\textsubscript{2} reforming) (DR) [20,21], dry autothermal (a combination between dry, oxidative and steam reforming) [22] and pyrolysis [23], also, were evaluated as possible routes for glycerol conversion.
Normally catalysts were used to promote and accelerate these reforming processes. Ni, Co and noble metals like as Pt, Pd and Rh based catalysts were related to promote the reforming process. Among them, the Ni based catalysts are the most commonly used [5, 9].

In this paper, we focused on the comparison of several glycerol reforming technologies. The SR, PO, ATR, DR and SCWG of glycerol were analyzed. For this, we used the Gibbs energy minimization approach in combination with the virial EoS. Comparisons between experimental and simulated data obtained from literature were performed. In addition, the effects of the process variables (temperature, pressure and inlet composition) were evaluated with respect to the product compositions. The coke formation was discussed too.

2. Methodology
2.1. Model formulation
2.1.1. Gibbs energy minimization model

The thermodynamic equilibrium condition for reactive multicomponent closed system, at constant pressure and temperature, with given initial composition, can be obtained by the minimization of Gibbs energy \((G)\) of the system, with respect of the number of moles of each component in each phase, given by:

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

(1)

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

\[
n_i^s, n_i^l, n_i^g \geq 0
\]

(2)

In addition, the restriction of mole balances, given by atom balance for reactive systems (non-stoichiometric formulation):

\[
\sum_{i=1}^{NC} a_{mi} (n_i^s + n_i^l + n_i^g) = \sum_{i=1}^{NC} a_{mi} n_i^0 
\]

(3)

Smith and Missen [24] demonstrated that the stoichiometric formulation is equivalent to the non-stoichiometric one, if all independent reactions are considered. The values of \(\mu_i^0\) can be calculated from the formation values given at some reference conditions, using the following thermodynamic conditions:

\[
\left( \frac{\partial H_i}{\partial T} \right)_p = C_{pi} \quad i = 1, \ldots, NC
\]

(4)

\[
\left( \frac{\partial \mu_i}{\partial T} \right)_p = -\frac{H_i}{RT^2} \quad i = 1, \ldots, NC
\]

(5)

In this work, which considers only a gas phase and a possible solid phase as carbon for coke formation, the Gibbs energy can be expressed as:

\[
G = \sum_{i=1}^{NC} n_i^s \left( \mu_i^0 + RT \left( \ln P + \ln \gamma_i + \ln \phi_i \right) \right) + \sum_{i=1}^{NC} n_i^{c,i} \mu_i^{0_c,i}
\]

(6)

Since, some of the systems analyzed by the present work was at high pressure, the virial equations of state (EoS) truncated at second virial coefficient, were utilized to determine the fugacity coefficient. The second virial coefficient was calculated by the correlation of Pitzer and Curl [25],
which was modified by Tsonopoulos [26]. The following relation determined the fugacity coefficient:

\[
\ln \phi_i = \left[ 2 \sum_j v_j B_{ij} - B_i \right] \frac{P}{RT}
\]

(7)

The Gibbs energy minimization method is widely studied in the literature, being applied in a wide range of systems [27-33]. Some of them related to glycerol reforming processes [19, 27], but none of them presents a complete thermodynamic study about these reactions.

2.2. Model implementation

During the process of optimization, utilizing the Gibbs energy minimization method the number of moles of the gaseous \((n^g)\) and solid \((n^s)\) phase are considered decision variables, while \(T\), \(P\) and the chemical potential of the pure component in the reference state \(\mu_i^0\) are considered parameters. The software GAMS\textsuperscript{®} 23.2.1, (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. [34]. The solid phase formed was considered as solid carbon (pure component). These methodologies and considerations were applied in previous works of our research group with good predictive results for similar systems with methane and biomass [29-33].

A Total of 12 output compounds were selected as representative of the main compounds, which can be found in the output stream of these reactive systems. The thermodynamic data used in the calculations were obtained from literature [35-37]. In almost all the thermodynamic analyses of glycerol reforming processes, the systems were represented considering primary species, such as hydrogen, methane, carbon monoxide, carbon dioxide, water and glycerol, and in some papers the solid carbon \((C_{(s)})\) was considered too. The consideration of the formation of solid carbon is very important because the \(C_{(s)}\) can poison the catalyst in reforming reactions [38].

However, some experimental works in the literature related the presences of secondary components in these reactions, some of the secondary compounds are methanol, ethanol, acetaldehyde, acetone and ethane [39]. In this work, a complete thermodynamic analysis of these reactions was performed and all species mentioned above and some others have been taken into account. The complete list of output compounds, along with their critical parameters, is reported in Table 1.

Table 1. Chemical compounds considered in the simulations and your thermodynamic properties.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>(T_C) (K)\textsuperscript{4}</th>
<th>(P_C) (bar)\textsuperscript{4}</th>
<th>(V_C) (m\textsuperscript{3}/kmol)\textsuperscript{4}</th>
<th>(\omega) (-)\textsuperscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H\textsubscript{2}O</td>
<td>647.3</td>
<td>220.0</td>
<td>0.056</td>
<td>0.348</td>
</tr>
<tr>
<td>Glycerol</td>
<td>C\textsubscript{3}H\textsubscript{8}O\textsubscript{3}</td>
<td>850.0</td>
<td>75.0</td>
<td>0.260</td>
<td>0.513</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H\textsubscript{2}</td>
<td>33.0</td>
<td>13.0</td>
<td>0.064</td>
<td>0.000</td>
</tr>
<tr>
<td>Methane</td>
<td>CH\textsubscript{4}</td>
<td>191.1</td>
<td>45.8</td>
<td>0.099</td>
<td>0.013</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO\textsubscript{2}</td>
<td>304.2</td>
<td>73.9</td>
<td>0.094</td>
<td>0.420</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>133.0</td>
<td>35.0</td>
<td>0.093</td>
<td>0.041</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O\textsubscript{2}</td>
<td>154.6</td>
<td>50.4</td>
<td>0.073</td>
<td>0.022</td>
</tr>
<tr>
<td>Ethane</td>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>305.4</td>
<td>48.2</td>
<td>0.148</td>
<td>0.105</td>
</tr>
<tr>
<td>Propane</td>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>369.9</td>
<td>42.0</td>
<td>0.200</td>
<td>0.152</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C\textsubscript{2}H\textsubscript{4}</td>
<td>283.1</td>
<td>50.5</td>
<td>0.124</td>
<td>0.073</td>
</tr>
<tr>
<td>Propylene</td>
<td>C\textsubscript{3}H\textsubscript{6}</td>
<td>369.9</td>
<td>45.4</td>
<td>0.182</td>
<td>0.143</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH\textsubscript{2}OH</td>
<td>512.6</td>
<td>80.13</td>
<td>0.116</td>
<td>0.559</td>
</tr>
</tbody>
</table>

\textsuperscript{4}Source:[35-37].
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-ideality’s of the studied systems.

In order to compare the results calculated using the proposed approach with the values found in literature, the mean relative error (MRE) was used, according to equation 8.

\[
MRE = \frac{1}{NPE \cdot NCE} \sum_{j} \sum_{i} \frac{x_{j,i}^{\text{lit}} - x_{j,i}^{\text{sim}}}{x_{j,i}^{\text{lit}}} \tag{8}
\]

where \(NPE\) is the number of experimental points, \(NCE\) is the number of components for each experimental point, \(x_{j,i}^{\text{sim}}\) is the value calculated by the present work using the proposed virial model and \(x_{j,i}^{\text{lit}}\) is the experimental or simulated value obtained in the literature.

Figure 1 shows the validation of the virial proposed model in comparison with the experimental results of Byrd et al. [15] and the simulated results from the work of Castello and Fiori [27]. The experiments of Byrd et al. [15] were performed at the following conditions: temperature of 800 °C (1073.15 K), pressure of 241 bar and with feed concentration in the range of 5 to 40 wt%.

The simulations of the present work and that obtained in the work of Castello and Fiori [27] were performed under the same above mentioned conditions. However, Castello and Fiori [27] used the Peng-Robinson EoS in the Gibbs energy minimization model.

![Figure 1. Virial model validation with the experimental data from Byrd et al. [15] and the simulated data from Castello and Fiori [27] for the SCWG of glycerol. Symbols: solid line: virial proposed model predictions; black symbols: experimental data from Byrd et al. [15]; dashed line + white symbols: simulated data from Castello and Fiori [27].](image)

Analyzing the Figure 1 it is possible to verify that the virial proposed model predictions are in good agreement with the experimental behavior reported by Byrd et al. [15]. The highest deviations were observed in the higher initial feed concentration region (above 25 wt%). It can also be seen that the model predictions for \(H_2\) production is better than that observed for the other compounds (\(CO_2\), \(CH_4\) and \(CO\)). The MRE between the experimental and simulated data was 0.692.

Still in the Figure 1, it is also interesting to note that the use of the Virial equation instead of Peng-Robinson EoS does not result in changes in the predictive ability of the Gibbs energy model,
although it leads to a significant mathematical simplification of the Gibbs energy minimization problem.

3.2. Comparison between the technologies

Table 1 shows the better conditions for H$_2$ production observed in all reaction analyzed with the operational temperature fixed at 1073.15 K. The SR, PO, ATR and DR were analyzed at 1 bar and the SCWG was analyzed at 250 bar.

Table 1. Better conditions for H$_2$ production for the different reforming technologies analyzed.

<table>
<thead>
<tr>
<th>Process</th>
<th>Pressure (bar)</th>
<th>Temperature (K)</th>
<th>Molar ratio</th>
<th>Molar fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H$_2$</td>
</tr>
<tr>
<td>SR</td>
<td>1</td>
<td>1073.15</td>
<td>1/3 (Gly/H$_2$O)</td>
<td>61.9</td>
</tr>
<tr>
<td>PO</td>
<td>1</td>
<td>1073.15</td>
<td>1/0.5 (Gly/O$_2$)</td>
<td>52.9</td>
</tr>
<tr>
<td>ATR</td>
<td>1</td>
<td>1073.15</td>
<td>1/1/1 (Gly/H$_2$O/O$_2$)</td>
<td>51.0</td>
</tr>
<tr>
<td>DR</td>
<td>1</td>
<td>1073.15</td>
<td>1/1 (Gly/CO$_2$)</td>
<td>46.2</td>
</tr>
<tr>
<td>SCWG</td>
<td>250</td>
<td>1073.15</td>
<td>1/9 (Gly/H$_2$O)</td>
<td>40.5</td>
</tr>
</tbody>
</table>

Analyzing the Table 1 it’s interesting to emphasize that higher molar fraction of H$_2$ was observed in the SR reaction (with a molar ratio glycerol/water = 1.0/3.0 in the feed stream). The lower molar fraction of H$_2$ was observed for the SCWG reaction. However this process presented the lowest production of CO between all processes analyzed, with that, the subsequent purification processes of H$_2$ become simpler for the SCWG.

The better conditions observed for syngas production (with a molar ratio more close to 2.0 as possible) was presented in the Table 2. The SR, PO, ATR and DR were analyzed at 1 bar and the SCWG was analyzed at 250 bar again. Each case presented a different temperature of reaction to the better condition for syngas production.

Analyzing the Table 2 it is interesting to emphasize that the highest molar fraction of H$_2$ was observed to the SR reaction (91.4% of the dry gas), with 1273.15 K of operational temperature and with a glycerol/water molar ratio of 1.0/3.0, in that conditions the H$_2$/CO molar ratio was 1.99.

The SCWG of glycerol presented the highest H$_2$/CO molar ratio between all analyzed processes, 3.21 at 1273.15 K and with a glycerol/H$_2$O molar ratio of 1.0/9.0.

Table 2. Better conditions for syngas production for the different reforming technologies analyzed.

<table>
<thead>
<tr>
<th>Process</th>
<th>Pressure (bar)</th>
<th>Temperature (K)</th>
<th>molar ratio</th>
<th>molar fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H$_2$</td>
</tr>
<tr>
<td>SR</td>
<td>1</td>
<td>1273.15</td>
<td>1/3 (Gly/H$_2$O)</td>
<td>60.8</td>
</tr>
<tr>
<td>PO</td>
<td>1</td>
<td>873.15</td>
<td>1/0.5 (Gly/O$_2$)</td>
<td>46.5</td>
</tr>
<tr>
<td>ATR</td>
<td>1</td>
<td>973.15</td>
<td>1/1/1 (Gly/H$_2$O/O$_2$)</td>
<td>51.6</td>
</tr>
<tr>
<td>DR</td>
<td>1</td>
<td>873.15</td>
<td>1/1 (Gly/CO$_2$)</td>
<td>41.7</td>
</tr>
<tr>
<td>SCWG</td>
<td>250</td>
<td>1273.15</td>
<td>1/9 (Gly/H$_2$O)</td>
<td>57.7</td>
</tr>
</tbody>
</table>

The lower molar fraction of syngas was observed for the dry reforming of glycerol (62.5%) at 873.15 K and with a glycerol/CO$_2$ molar ratio of 1.0/1.0, in that conditions the H$_2$/CO molar ratio was 1.99, however was observed solid carbon formation (1.16 moles of C$_{(s)}$). Solid carbon formation was observed in the PO too (0.65 moles of C$_{(s)}$ at 873.15 K and with a glycerol/O$_2$ molar ratio of 1.0/0.5).

Table 3 shows the comparison between all reforming processes with respect to H$_2$ and CO production and the results obtained for the H$_2$/CO molar ratio. The same glycerol/X (where X are
H₂O, O₂, CO₂ or combinations between them) molar ratio of 1.0/3.0, was used in all simulations performed.

The SR, PO, ATR and DR were simulated at 1 bar and the SCWG was simulated at 250 bar and three operational temperatures (873.15, 973.15 and 1073.15 K) were evaluated.

Analyzing the Table 3 it is possible to verify that the highest concentrations of H₂ are observed in the steam reforming reaction. Still in the Table 3 it’s possible to verify that the SR and ATR presented H₂/CO molar ratio close to 2.0 in the conditions in which the reactions were analyzed. The SCWG presented the highest H₂/CO molar ratio between all reforming processes analyzed.

Another interesting effect is that the elevation of operational temperature results in reductions of the H₂/CO molar ratio in the product, basically by inducing the production of CO in the system. This behavior was observed in all reforming processes analyzed.

Table 3. Comparison between all reforming technologies of glycerol.

<table>
<thead>
<tr>
<th>Reforming technology</th>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
<th>Molar fraction (mol%)</th>
<th>Molar ratio H₂/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂</td>
<td>CO</td>
</tr>
<tr>
<td>SCWG</td>
<td>873.15</td>
<td>250</td>
<td>8.5</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>973.15</td>
<td>250</td>
<td>15.8</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>1073.15</td>
<td>250</td>
<td>25.3</td>
<td>10.5</td>
</tr>
<tr>
<td>SR</td>
<td>873.15</td>
<td>1</td>
<td>55.0</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>973.15</td>
<td>1</td>
<td>61.7</td>
<td>23.0</td>
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<td></td>
<td>1073.15</td>
<td>1</td>
<td>61.9</td>
<td>26.5</td>
</tr>
<tr>
<td>ATR</td>
<td>873.15</td>
<td>1</td>
<td>46.1</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>973.15</td>
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<td>47.8</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>1073.15</td>
<td>1</td>
<td>46.3</td>
<td>25.3</td>
</tr>
<tr>
<td>OR</td>
<td>873.15</td>
<td>1</td>
<td>19.8</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>973.15</td>
<td>1</td>
<td>17.9</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>1073.15</td>
<td>1</td>
<td>16.0</td>
<td>12.0</td>
</tr>
<tr>
<td>DR</td>
<td>873.15</td>
<td>1</td>
<td>29.0</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>973.15</td>
<td>1</td>
<td>32.1</td>
<td>43.7</td>
</tr>
<tr>
<td></td>
<td>1073.15</td>
<td>1</td>
<td>31.8</td>
<td>47.7</td>
</tr>
</tbody>
</table>

4. Conclusion

A thermodynamic analysis for hydrogen and syngas production from glycerol using different reforming technologies has been performed. The SR, PO, ATR, DR and SCWG were evaluated. The composition of the products was calculated using the Gibbs energy minimization approach in combination with the virial equation of state.

The model was validated with simulated and experimental data obtained in literature with good agreement between then.

Hydrogen yields were found to increase directly with temperature in all reforming processes analyzed. The increase of the operating pressure results in large amounts of solid carbon in the product stream in the partial oxidation and dry reforming processes. In the other processes the formation of solid carbon was not observed. The syngas production with H₂/CO molar ratio close to 2.0 was found without solid carbon formation only in the steam reforming of glycerol.

The proposed model implemented in the GAMS software and solved with the CONOPT solver show to be robust, fast and reliable to perform the thermodynamic analysis of the different glycerol reforming technologies analyzed.
References


