Hydrogen production by aqueous-phase reforming of glycerol over platinum catalysts supported on Al₂O₃: Use of biodiesel by-products

Accepted 19th September, 2017

ABSTRACT

Biodiesel is widely used in the current market in place of fossil fuels. At the end of its production process, 10% of the output stream is comprised of glycerol. The conversion of this glycerol into hydrogen is an alternative that can add economic value to the by-product. This paper presents a study of the aqueous-phase reforming of glycerol, by-product of a biodiesel production process, over platinum catalysts supported on Al₂O₃ for hydrogen production. The mass and energy balances were analyzed and the results showed good productivity, impacting on low energy costs and less polluting waste generation if compared to the others technologies for hydrogen production.

Keywords: Aqueous-phase reforming, biodiesel, glycerol, hydrogen.

INTRODUCTION

Recently, the use of biodiesel to replace fossil fuels has been a subject of interest. Biodiesel is a biodegradable, non-toxic, low-polluting fuel produced from vegetable oils extracted from a variety of raw materials that can be used in diesel engines (Lai, 2014). At the end of its production route, approximately 10% of the output stream which can be reused after a purification process is glycerol (Frozza, 2014).

Due to this significant amount of glycerol formed by the production of biodiesel and to the different possibilities of applications of this by-product in the industry, there are increasing studies about routes of use of this compound (Machado, 2012). One of these routes that have attracted attention is its use as a raw material in obtaining hydrogen (Almeida, 2011).

Currently, 95% of the hydrogen production comes from non-renewable sources (Perez, 2014). The most used process in the industry for the production of hydrogen is the steam reforming of natural gas, reaching half of the world production (Manfro, 2013). The main factor of this wide use is the low cost, which makes the other alternatives little viable. However, it has the disadvantage of the emission of polluting gases and the use of high temperatures in its process (Almeida, 2011).
The Aqueous Phase Reforming (APR) process produces hydrogen gas by catalytic reaction of the liquid reagents (water and glycerol) under conditions of high pressures and low temperatures (Oliveira, 2014).

Operating pressures (generally between 15 and 50 bar) facilitate the use of gas purification processes such as membrane or adsorption (PSA) technologies; low temperatures reduce the incidence of unwanted decomposition reactions; and as the APR is a reasonably simple process, it is unnecessary in the use of multi-reactors (Alvarado, 2011).

The process of aqueous-phase reforming of glycerol has two main steps. Initially, the dehydrogenation of glycerol which is an endothermic process occurs ($\Delta H = 250 \text{ kJ mol}^{-1}$) and corresponds to the decomposition of this compound through the breakdown of the molecule bonds. Cleavage of the C-C bonds may give, in addition to the required products, satisfactory concentrations of carbon monoxide which may react and form unwanted products. Otherwise, the breakage of C-O bonds provides the formation of intermediate alcohol which, upon reacting on the surface of the catalyst produces hydrocarbons (Almeida, 2011).

Equations 1 and 2 show each reaction of the stages of the process and Equation 3 describes the key reaction occurring in APR (Sehested et al., 2004; Shamsi et al., 2005; Manfro et al., 2013) give as:

\[ \text{C}_3\text{H}_5\text{O}_3(\text{l}) \leftrightarrow 4\text{H}_2(\text{g}) + 3\text{CO}(\text{g}) \Delta H^\circ_{298.15 \text{ K}} = 338.02 \text{ kJ mol}^{-1} \]  

\[ \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \Delta H^\circ_{298.15 \text{ K}} = -41.17 \text{ kJ mol}^{-1} \]  

\[ \text{C}_3\text{H}_5\text{O}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g}) \leftrightarrow 7\text{H}_2(\text{g}) + 3\text{CO}_2(\text{g}) \Delta H^\circ_{298.15 \text{ K}} = 214.51 \text{ kJ mol}^{-1} \]

Since this route was pointed out over the years, studies on the catalysts used for the APR of glycerol was carried out and show supported transition metals as the those with the best results (Perez, 2014).

The aim of the present paper is to analyze the aqueous-phase reforming process of glycerol by-product of biodiesel production, over platinum catalyst supported on Al$_2$O$_3$ (Figure 1). In this way, the mass and energy balances were carried out for the process.

**MATERIALS AND METHODS**

The following assumptions were made in the analysis:

- The catalytic reactor, heat exchanger, adsorption columns, pumps and compressors are adiabatic, isothermal and
there is no mass exchange between the system and neighborhood of the equipments;
- The ambient temperature and pressure are constants \( T_0 = 298.15 \text{ K} \) and \( P_0 = 100 \text{ kPa} \).

**Problem formulation**

**Streams 01, 02 and 03**

According to the study by Liu et al. (2006) and Shabaker et al. (2004), 10% glycerol and 90% water in the feed stream of the reactor of catalytic reforming provide a better production rate for the process. Using lower water flow leads to higher energy consumption in heating the aqueous mixture.

According to Fonseca et al. (2015) in this paper, a glycerol flow of 1.77 kmol h\(^{-1}\), which corresponding to stream 02 was used. This result implies the use of a water flow of 81.54 kmol h\(^{-1}\) for stream 01 (Figure 1).

Stream 03 is the sum of streams 01 and 02 after leaving the mixer, which means that stream 03 is 83.31 kmol h\(^{-1}\).

**Stream 04**

The reaction occurring in the batch reactor of catalytic reforming is a first-order reaction (Figure 1) and the mass balance for the components is given by Equation 4:

\[
(F_G + F_w) = (F_{CO} + F_{CO2} + F_{H2} + F_{CH4}) - \sum (r_{H2}dw)
\]  

Lehnert and Claus (2008) obtained that a higher catalytic activity for APR of glycerol is given by the use of Pt-catalyst supported in \( \text{Al}_2\text{O}_3 \), with a rate of generation for hydrogen production of \( r_{H2} = 7.6.10^{-3} \text{ mol} \text{min}^{-1} \text{g}^{-1} \text{cat} \), 45% glycerol conversion and 85% hydrogen selectivity. Also there are in the outflow stream, in addition to hydrogen, \( \text{CO} \) (0.2 mol%), \( \text{CO}_2 \) (32 mol%) and \( \text{CH}_4 \) (3.3 mol%). These data were obtained under operating conditions of 523.15 K and 2 MPa, which were later used for the analysis in this paper. As the concentration of \( \text{CO} \) is minimal compared to the concentration of the other compounds, it was disregarded.

**Stream 05**

Equation 5 gives the mass balance for the heat exchanger. The cold fluid used for the thermal exchange was water (Figure 1), cooling the stream 04 to ambient temperature.

\[
(F_{CO2} + F_{H2} + F_{CH4}) = (F_{CO2} + F_{H2} + F_{CH4})
\]  

**Stream 06**

The molar flow rate of methane is very low when compared to the flow of hydrogen and carbon dioxide. Therefore, according to studies by Sant et al. (2014) that used silicalite zeolites as adsorbents in an adsorption column at ambient temperature and pressure of 0.1 MPa, 100% adsorption rate for methane was considered in this paper. Equation 6 shows the mass balance for stream 06 given as:

\[
\frac{dF_{CH4}}{dt} = (F_{CO2} + F_{H2} + F_{CH4}) - (F_{CO2} + F_{H2})
\]  

**Stream 07**

Cavenati (2005) obtained at the ambient temperature and pressure of 0.5 MPa, approximately 90% of \( \text{CO}_2 \) removal with 13X zeolites adsorbents in an adsorption column. Accordingly, the mass balance for the stream 07 is calculated by Equation 7:

\[
(F_{CO2} + F_{H2}) - \frac{dF_{CO2}}{dt} = F_{H2}
\]  

**Energy balance**

The values of \( C_p \) for the compounds involved in each stream can be determined using data by CHERIC (2016) through Equation 8. Equation 9 was used to calculate the heat transfer rate for each compound of the APR process.

\[
C_p = \int_0^T (A + BT + CT^2 + DT^3 + ET^4) dt = w, G, CH_4, CO_2, H_2
\]  

\[
Q = \dot{n}C_p(T - T_0)
\]  

**Reactor of catalytic reforming**

The energy balance for the batch reactor is given by Equation 10. In this case, \( T = 523.15 \text{ K} \) and \( T_0 = \text{ambient temperature} \).

\[
\Delta H = (Q_{CO} + Q_{CO2} + Q_{H2} + Q_{CH4}) - (Q_G + Q_w)
\]  

**Heat exchanger**

For the counter current shell and tube heat exchanger, the
Table 1: Flow rates of the streams for the process of hydrogen production by aqueous-phase reforming of glycerol over platinum catalysts supported on Al₂O₃.

<table>
<thead>
<tr>
<th>Streams</th>
<th>Flow rates (kmol/h⁻¹)</th>
<th>Fg</th>
<th>Fw</th>
<th>FCH₄</th>
<th>FCO₂</th>
<th>FH₂</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>1.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.77</td>
</tr>
<tr>
<td>02</td>
<td>-</td>
<td>81.54</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>81.54</td>
</tr>
<tr>
<td>03</td>
<td>1.77</td>
<td>81.54</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>83.31</td>
</tr>
<tr>
<td>04</td>
<td>-</td>
<td>-</td>
<td>2.62</td>
<td>26.23</td>
<td>53.66</td>
<td>82.51</td>
<td></td>
</tr>
<tr>
<td>05</td>
<td>-</td>
<td>-</td>
<td>2.62</td>
<td>26.23</td>
<td>53.66</td>
<td>82.51</td>
<td></td>
</tr>
<tr>
<td>06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>26.23</td>
<td>53.66</td>
<td>79.89</td>
<td></td>
</tr>
<tr>
<td>07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.63</td>
<td>53.66</td>
<td>56.29</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Enthalpy changes of the equipments for the process of hydrogen production by aqueous-phase reforming of glycerol over platinum catalysts supported on Al₂O₃.

<table>
<thead>
<tr>
<th>Equipments</th>
<th>ΔH (kJ/kmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor of catalytic reforming</td>
<td>767231109.0</td>
</tr>
<tr>
<td>Heat exchanger</td>
<td>468640703.2</td>
</tr>
<tr>
<td>Adsorption columns</td>
<td>0</td>
</tr>
</tbody>
</table>

Gas is considered the hot stream at the temperature of 523.15 K and the water is the cold stream at the ambient temperature. As it is an adiabatic process, the energy balance can be defined by Equation 11 given as:

\[
\Delta H = Q_{H₂O} = (Q_{H₂} + Q_{CO₂} + Q_{CH₄})
\]  

Adsorption columns

The two adsorption columns for the APR process have better operating results at temperature of 298.15 K. The temperature outside the columns is considered as ambient temperature and also in the value of 298.15 K. According to Incropera et al. (2008), Equation 12 describes the heat transfer rate for the neighborhood-system of the adsorption columns:

\[
Q = \frac{T_{∞,1} - T_{∞,4}}{\frac{1}{2\pi h_1 r_1} + \frac{ln(r_2/r_1)}{2\pi L_1 K_A} + \frac{ln(r_2/r_2)}{2\pi L_2 K_B} + \frac{ln(r_2/r_2)}{2\pi L_3 K_C} + \frac{1}{2\pi h_4 r_4}}
\]  

RESULTS AND DISCUSSION

Thermodynamically, the use of low temperatures and high pressures so that the water is kept in its liquid phase, favoring the WGS reaction, allows hydrogen generation with low amounts of CO in the product stream (Ozgur and Uysal, 2011). Tables 1 and 2 show the results for mass and energy balances of the process. At the end of the process we have an outflow stream of 56.29 kmol h⁻¹. As in this paper it was considered an efficiency of 90% for the second adsorption column, we still have 4.66% of CO₂ in stream 07.

In Equation 12, \( T_{∞,1} \) and \( T_{∞,4} \) are temperature of the system and temperature of the neighborhood, respectively, for the adsorption columns. As in this paper the columns are considered adiabatic, we have that the values for \( T_{∞,1} \) and \( T_{∞,4} \) are the same, implying \( Q = 0 \).

Conclusions

In this study, a glycerol aqueous-phase reforming over platinum catalysts supported on Al₂O₃ was analyzed through mass and energy balances. The methodology implemented in this paper was satisfactory as regards the low energy consumption and emissions of environmental contaminants. At the end of the process the outflow stream is of 56.29 kmol h⁻¹, which still contains 4.66% of CO₂ due to the 90% of efficiency considered. The APR process offers a greater possibility for directly using crude glycerol as the feedstock.

ACKNOWLEDGMENTS

The authors would like to appreciate ICT/UFVJM, CNPq, FAPEMIG and CAPES for assistance rendered in the course of the research.
REFERENCES


Machado BAS, Figueiredo TVB (2012). Prospeção tecnológica sobre processo de transesterificação com ênfase na produção de biodiesel [Technological prospecting on transesterification process with emphasis on biodiesel production]. ProspeCT&I - Congresso brasileiro de prospecção tecnológica. 5: 14-22


Submit your manuscript at http://www.academiapublishing.org/ajb