Acid gas degradation by non-thermal plasma and energy estimation

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Abstract. This paper describes a method to estimate the energy efficiency in the system performed to treat acid gases by plasma discharges. The electrical energy consumed by the plasma is evaluated by an electrical diagnosis, taking into account the experimental voltage and current applied to the power source. The estimation of the electrical energy generated by solid oxide fuel cells is based on the method of modeling the energy produced by the species generated by the plasma discharge and taking also into account the temperature of the gases.

1. Introduction

Actually, the necessity to treat the mixture of gases like carbon dioxide (CO₂) and hydrogen sulfide (H₂S) has a great interest and some conventional techniques which are employed for this purpose are based on the incineration process and pyrolysis or gasification processes [1-5]. The hybrid plasma offers at least three fundamental properties that make it attractive for this application: The temperature and energy density far exceeds that of conventional techniques, Ability to produce active species with much lower reaction times than those achieved by conventional techniques, The active species have high concentrations of energy, even when the temperature of the plasma remains varied [6]. Consequently, high energy density and the low inertia of plasma are used to break the molecular bonds of the gases in question, obtaining as a final product constituent particles and gases with high value-added energy.

The main strategies for the waste management are the increase of material recovery, which can reduce the landfill disposal and the improvement of energy recovery from waste. In the plasma process the organic compounds are thermally decomposed in their constituent elements and converted into a synthesis gas (syngas), which mainly consist of hydrogen and carbon monoxide, while the inorganic material are melted and converted into a dense, inert, non-leachable vitrified slag [7-10]. This syngas is cleaner than that produced by conventional gasification processes [7] due to the high temperatures involved, which allow breaking down all the tars, char and dioxins.

In [11] Galeno et. al. proposed the integration between plasma gasification unit and a solid oxide fuel cell (SOFC) and established the energy suitable by using a numerical model based on the combination of a thermochemical model and a electrochemical model for the SOFC, and they found...
that the syngas has a lower heating value of 9.20 MJ/kg and it is composed by the species shown in table 1.

**Table 1. Syngas composition.**

| Specie | Composition (vol %) |
|--------|---------------------|
| H₂     | 28.65               |
| CO     | 37.37               |
| CO₂    | 1.41                |
| H₂O    | 14.19               |
| N₂     | 17.12               |
| H₂S    | 0.22                |
| others | 1.04                |

Considering a previous plasma model presented by Hirsch et. al. [12], in this paper the specific energy consumption is computed and the main species generated by the plasma discharge are estimated by mass balance. It is worth mentioning that the output species represent only an estimate of the main products generated during the treatment of acid gases by plasma discharge.

2. Model
The method to estimate the energy efficiency in the system performed to treat acid gases by plasma discharges is performed in two steps. The first step is to estimate the efficiency of degradation depending on the plasma temperature as it is described in figure 1.

![Figure 1. Structure of the method.](image)

In figure 1, the applied energy $E_{applied}$ to the plasma is used to compute the distribution of temperature in the plasma $T_{plasma}$ by using some transport coefficients depending on the temperature $T$ of the gases (thermal conductivity $\kappa$, heat source density $Q$, mass density $\rho$, thermal capacity $C_p$ and $U$ is the vector of velocity) [12]. The term source $Q$ is calculated from

$$Q = \sigma E^2 - q$$

(1)

by considering the electrical field $E = |\nabla V|$ and the electrical conductivity $\sigma$ depending on the temperature $T$. The temperature dependent quantity $q$ is defined by an interpolation function and
introduced to account for radiation losses [13, 14]. The mass density is calculated from the ideal gas law

\[ \rho = \frac{pM}{RT} \]  

(2)

where \( p \) is the static pressure of the gas, \( M \) the molar mass of the gas and \( R = 8.32 \text{JK}^{-1}\text{mol}^{-1} \) the perfect gas constant.

The plasma modeling described in this paragraph is quite simple and approximate. Considering the plasma at LTE, without any sheath, does not describe the fine mechanisms involved, as arc discharge plasma. However, it provides a satisfactory temperature profile in a relatively short computing time and with reasonable memory requirement for a desktop computer. This temperature profile as well as the mol number \( N \) of the species \( x \), the molar formation enthalpy \( \Delta H_f \), and the degradation fraction of the species \( x \% \), are then used as the input parameter for the computing of the specific energy consumption \( E_{\text{min}} \) [15].

3. Mass balance

Having estimated the value of the percentage of degradation according to the total power applied to the plasma reactor, the temperature and the inward species, the mass balance is proposed as shown in figure 2.

![Figure 2. Schema of the mass balance.](image)

The concentration of the output species depends on the species in the inward flow and power applied, since the latter determines the percentage of degradation for the waste gases (CO\(_2\) and H\(_2\)S). To estimate the concentration of output species, we performed a mass balance as follows. If the concentration of each input atom is equal to every output atom, we have:

\[ C^E_x = C^S_x \]  

(3)

Where \( C^E_x \) is the concentration of the inward species \( x \) and \( C^S_x \) is the concentration of the output species \( x \). In the case of argon, being neutral species, the equivalent balance is:
\[ C_{Ar}^S = C_{Ar}^E \]  

Relating the degradation percentages for input species \( H_2S, \ CO_2 \) and \( H_2O \), we have the following outlet concentrations corresponding to the portion not degraded by plasma:

\[ C_{H_2S}^S = \left( 1 - \frac{\% H_2S}{100} \right) C_{H_2S}^E \]  

\[ C_{CO_2}^S = \left( 1 - \frac{\% CO_2}{100} \right) C_{CO_2}^E \]  

\[ C_{H_2O}^S = \left( 1 - \frac{\% H_2O}{100} \right) C_{H_2O}^E \]  

On the other hand, the \( H_2S \) portion degraded is converted to species that determines the following reaction:

\[ 1H_2S \rightarrow 1H_2 + 1S \]  

The probability of formation of \( H_2 \) and \( S \) is proposed to be 50%. In the case of \( CO_2 \), the reaction that determines the species generated from its degradation is:

\[ CO_2 \rightarrow CO + \frac{1}{2} O_2 \]  

where the probability of generation of \( CO \) is 75% and \( O_2 \) is 25%. For \( H_2O \), the reaction that determines the degradation is:

\[ H_2O \rightarrow H_2 + \frac{1}{2} O_2 \]  

where the probability of generation of \( O_2 \) is proposed 25% and 75% for \( H_2 \). In the case of air, it is known that its general composition is 79% \( N_2 \) y 21% \( O_2 \). In that case, the concentrations of these output species are:

\[ C_{N_2}^S = (0.79) C_{Air}^E \]  

\[ C_{O_2}^S = (0.21) C_{Air}^E \]  

In the same way to the case of Argon, the balance for each atom is realized. The addition of each output concentration for every species gives their total output concentration (see figure 2).

4. Results

Figure 3 presents the image of the hybrid plasma discharge [16]. The plasma model was implemented in the free software Saturne with the approximated geometry of the discharge and 2 kW of applied power; the result of the temperature profile is shown in figure 4.
The temperature profile presents high temperature values, more than 10000 K in the arc region. This temperature is sufficient to crack the hydrogen sulfide and carbon dioxide molecules; the non-thermal plasma at the end on the electrodes does not permit the recombination process of these molecules. Figure 5 presents the estimation of the minimum power to degrade the CO₂ and H₂S molecules.

According to this, the degradation percentage values are estimated as follow. The %H₂S value is estimated to be 95%; the molecule of carbon dioxide is stronger than H₂S, then the %CO₂ value is estimated to be 50%; in the case of H₂O, the value %H₂O is 30% due to the recombination in the steam phase. A numerical test of the mass balance was run taking into account the % values of degradation, supposing 10 minutes of the duration of the experiment, and 20 l.p.m. inward gas flow with the composition described in table 2.

In the case of the species N₂ and O₂, their concentration is the equivalent value to introducing 8.46% of air. In this mixture of inward species, the total concentration is 31.7899 g/min. The mass balance was computed according to the schema presented in figure 2 and the equations (4) to (12). The result is presented in table 3.
Table 2. Composition of the inward gas flow.

| Specie | Concentration (g/min) | Composition (vol %) |
|--------|-----------------------|---------------------|
| Ar     | 13.7842               | 41.27               |
| N₂     | 1.5839                | 6.68                |
| O₂     | 0.4811                | 1.78                |
| H₂O    | 1.9900                | 9.95                |
| H₂S    | 3.8976                | 13.44               |
| CO₂    | 10.0531               | 26.88               |

Table 3. Result of the mass balance. The final mass accumulation is after 10 minutes of treatment duration.

| Specie | Concentration (g/min) | Composition (vol %) | Final mass (g) |
|--------|-----------------------|---------------------|----------------|
| Ar     | 13.7842               | 43.36               | 137.842        |
| N₂     | 1.5839                | 4.98                | 15.839         |
| O₂     | 1.8869                | 5.94                | 18.869         |
| H₂     | 2.2991                | 7.23                | 22.991         |
| H₂O    | 1.3930                | 4.38                | 13.930         |
| S      | 1.8514                | 5.82                | 18.513         |
| H₂S    | 0.1949                | 0.61                | 1.948          |
| CO     | 3.7699                | 11.86               | 37.699         |
| CO₂    | 5.0266                | 15.81               | 50.265         |

The total concentration of the output species is 31.7899 g/min, the same value of the total concentration of the inward species; as a result the mass balance presents a correct agreement. The mixture gas of the output species H₂, CO, H₂O and N₂ represents mainly the composition of syngas. Table 4 presents the composition of syngas in the output gas flow, having a good agreement with the composition reported in [11] (see table 1). In this case, to total mass of syngas is 0.09046 kg; If the lower heating value of syngas in a fuel cell is 9.20 MJ/kg, then the total energy produced is estimated to be 0.8322 MJ.

In the total output gas flow there are also species like CO₂ and H₂S that are not totally degraded. In this case, these gases can be extracted and feed backed to the inward flow. Otherwise, it is recommended to increase the applied power to reach higher degradation values for these molecules and reduce their concentration in the output.

The energy consumption to degrade the mixture of gases for 10 minutes and 2kW of applied power is calculated to be 1.2 MJ. Relating the energy consumption and production of electrical energy, the resultant efficiency of the system is 69.35%.

5. Conclusions

From gases like CO₂ and H₂S, the plasma process produces syngas and it can be applied to fuel cells to generate electrical energy. The efficiency estimated can reach 69.35%, making the plasma process a quasi-self sustained system.

The remaining gas species can be separated from the total flow and feed backed the system, especially in the case of Ar, CO₂ and H₂S.

The plasma model and the mass balance are quite simple and approximate. In the mass balance only the main species are considered but it is well known that plasma discharges produces a great
quantity of free radical that can interact with other species creating chain reactions. However, the model here depicted presents a good approximation to the results mentioned in section 1.

**Table 4. Output syngas composition.**

| Specie | Composition (vol %) |
|--------|---------------------|
| H₂     | 25.41               |
| CO     | 41.68               |
| H₂O    | 15.40               |
| N₂     | 17.51               |

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