Mass spectra analysis in dry reforming of CH_4 and CO_2 by warm plasma

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Abstract: This paper presents a program to compute theoretical mass spectra of a gas mixture with a desired gas proportions. The program was validated by the experimental data obtained in a mass spectrometer during dry reforming of methane and carbon dioxide by warm plasma tests. Hydrogen and carbon monoxide production is also demonstrated by this technique.

Keywords: mass spectrometry, dry reforming, syngas

1. Introduction

Mass spectrometry is widely used in science. It is a common technique in plasma, vacuum and surface physics and is a powerful tool in active process control in semiconductor and thin film applications [1-2]. Typical low resolution RF quadrupole mass spectrometers (QMS) offer, in principle, the ability to identify the constituents of a gas mixture with high sensitivity. However, due to the high electron impact energy molecules are not only ionized but also split up in a dissociative process which altogether leads to a variety of signals in different mass channels [1] and resulting splice signals and a complicated diagnosis.

On the other hand, plasma discharges are employed in several processes where the dissociation of molecules produces simpler species [3-4]. This is the case of the dry reforming by warm plasma, where methane and carbon dioxide are reformed in hydrogen and carbon monoxide, a mixture better known as *syngas* [5-7].

2. Experimental Set-up and program description

The reactor employed for dry reforming by warm plasma is described in [7]. A controlled mixture of CO_2-CH_4 (1:1) is treated by warm plasma discharge with vortex effect at flow rate of 6-8 LPM and at atmospheric pressure, the power input for a stable discharge is around 420–650 W provided by a high-frequency resonant converter [8]. The exhaust gases were analysed by a quadrupole mass spectrometer (MKS Cirrus) and a gas analyser (Gasboard-3100P). The data obtained by the mass spectrometer were recorded by the software MKS Process Eye Professional v. 5.62.

The program for theoretical mass spectra generator was designed to compute the intensity of each mass channel for all species involved in the gas mixture. This intensity is set according to the proportion of the desired gas mixture. After that, the intensity of all the channels computed are convoluted, normalized and plotted. The normalized intensity for every species considered was taken from the NIST database [9]. The optimal experimental conditions considered in this paper are summarized in table 1.

Table 1. Conditions for gases and power during experimental test

Case	CH_4 -Bal. N_2- [1:1] (LPM)	CO_2 (LPM)	Power (W)	Warm Plasma
1	0	0	0	Off
2	3	3	0	Off
3	3	3	420	On

3. Results

After running the experimental test, the percentage of the exhaust gases was registered on-line in the gas analyser (Gasboard-3100P). The values for each case are shown in table 2.

Table 2. Experimental data from Gasboard-3100P analyzer.

Case	CO %vol	CO_2 %vol	CH_4 %vol	H_2 %vol	O_2 %vol	Other %vol
1	0.01	1.01	1.17	0.58	20.66	76.57
2	0.08	45.72	25	0.8	0.04	28.36
3	24	19	7.7	30	0.04	19.26

The mass spectra were registered during all the experimental tests. The sweep for these results is shown in Fig. 1, indicating the beginning of every case. In Fig. 2 the mass spectra for the case 2 (without plasma) and 3 (with plasma) are shown; the peak intensity of species can be observed in detail.

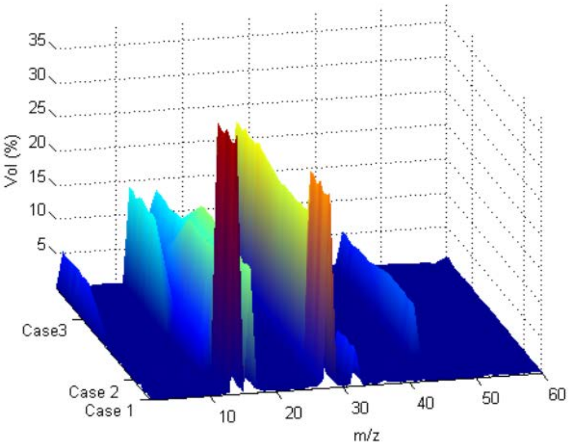

Fig. 1. Mass spectra sweep during experimental test.

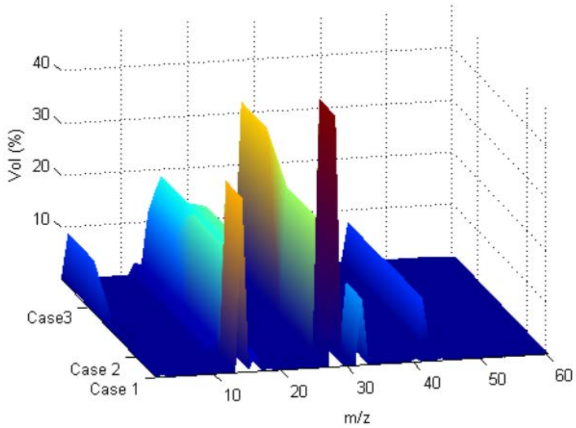

Fig. 3. Theoretical mass spectra.

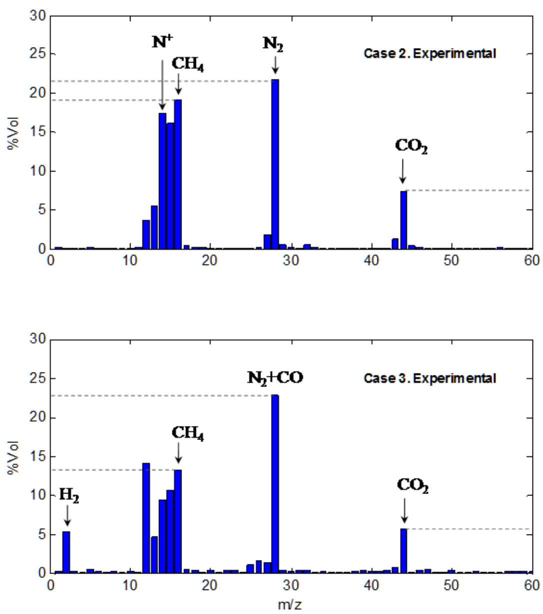

Fig. 2. Experimental mass spectra for the cases 2 and 3.

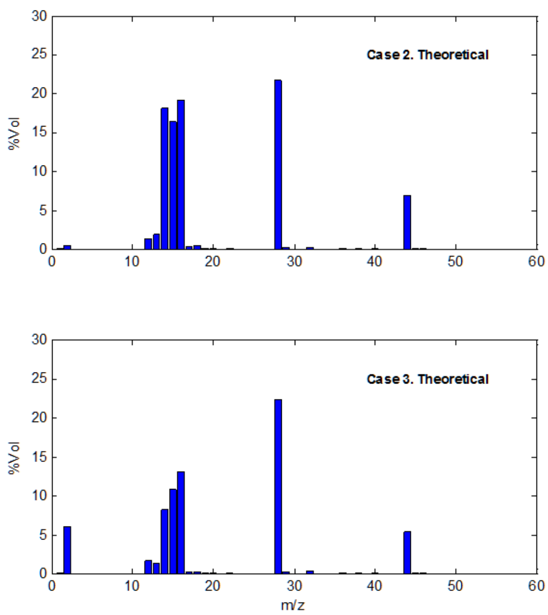

Fig. 4. Theoretical mass spectra for the cases 2 and 3.

From experimental results it is demonstrated the reforming of CH_4 and CO_2. The destruction and removal efficiency (DRE) was calculated according to [10]. For CH_4, DRE = 69.2%; for CO_2, DRE = 58.44%. There is also a notable increment of the H_2 and CO peaks, so the *syngas* production by warm plasma is demonstrated. The experimental mass spectra shows the grow up of peak 2, from case 2 to 3, corresponding to the hydrogen production under plasma action. The increment of the peak 28 corresponds to the CO production.

Reproducing the percentages of the gas mixtures according to table 1, and considering the case 2 and 3, the program was run and the theoretical results are shown in Fig. 3.

These theoretical results show a great approach to the experimental values, making from the program a tool to predict mass spectra for a desired gas mixture. Some additional peaks appear in experimental spectra that do not appear in theoretical one (see peak 12, for example). The reason for this difference is due to impurities in the gases used for the experimental tests and erosion of electrodes.

4. Conclusion

Preliminary experimental results obtained, indicate that warm plasma discharge could be considered as a promissory technique to dry reforming , in a continuous way, of CH_4 and CO_2 at considerably energetic input (420W) and to produce *syngas* (H_2 and CO).

The quantification of conversion efficiency in plasma processes by mass spectroscopy is difficult due to the peaks overlapping. Therefore, the simulation program to predict mass spectra results an adequate tool to this purpose.

A future improvement in this simulation is to achieve the deconvolution of an experimental mass spectrum according to the theoretical database, in order to obtain the volumetric proportion of every gas in the mixture.

5. References

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