

On a possible mechanism of the methane steam reforming in a gliding arc reactor

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Received 20 December 2001; accepted 26 March 2002

Abstract

This work is dedicated to the study of methane steam reforming (SR) using a rotating discharge reactor. The process efficiency is described in terms of methane conversion, SR selectivity, energy input and hydrogen production cost. The experiments clearly demonstrated the ability of glidarc to accelerate chemical reactions at low temperatures and with very low energetic costs. A good approximation model describing the chemical processes on the basis of classical thermodynamics is also proposed. The analysis gives information on reactor design in order to improve its chemical performances.

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Keywords: Plasma reactor; Syngas; Kinetics; Energy cost

1. Introduction

The present paper is a continuation of our studies regarding the hydrogen and syngas production from methane in plasma reactors [1–5]. The analysis of experimental results presented by literature do not recommend, up to this moment, the steam reforming (SR) of the methane by means of plasma technologies as a competitive way to produce synthesis gas [2,3]. Despite this fact, we have performed the above reaction using an improved model of a rotating arc discharge device [3,5], in order to determine the main parameters influencing the chemical process. On the other hand, based on the information gathered by the studies modelling the glidarc behaviour [6–13], we have tried to simulate the kinetics and thermodynamics of the processes occurring in plasma. A compatible mechanism between the physical and the chemical processes is obviously needed, in order to estimate the real perspectives of SR in the plasma field.

2. Experimental

The experiments were conducted at atmospheric pressure, the water and methane being mixed in a heating tube prior to injection in the glidarc reactor. Volume flow rates of methane

and water were adjusted separately and the inlet temperature was fixed at about 400 K in all cases.

The electrical supply of the reactor is a three channels one and is used to power up three cascading discharges. One channel consists of two transformers with rectifiers that allow two running phases: the ignition at high voltage and low current intensity and a complementary energy supply with higher current. The study of various powering regimes was made using an additional resistor that was connected in series with the electric supply device. A detailed description of both the reactor and of the electric scheme is presented in our recent articles [1,3,5].

For each experiment the reactor was functioning about 20 min. The reactor must be thermal isolated in order to avoid the water condensation on the inner electrodes, which can induce undesirable arc ignition and consequently unstable functioning. Due to the electric isolation of the reactor, the discharges do not put any safety problems.

The power input in the gas discharge is determined from voltage and current measurements. A Hall effect probe is used for current determination, and a voltage divider with a ratio of 0.01 is connected to the oscilloscope. The oscilloscope is a Tektronix TDS 460A model and was used with a differential probe voltage. Voltage and current are recorded at the beginning, and at the end of each experiment in order to verify the running stability. Finally, the signal processing is performed on a PC. Each set of data consists of six recordings for voltages and currents,

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corresponding to the power determination of the three phases reactor.

The components of the exhaust gases were analysed on-line and quantified by GC (the hydrogen by means of a TCD detector/HP5890, CO, CO₂ and hydrocarbons with a FID detector/Varian 3400CX). In order to perform this analysis, the unreacted water from the exhaust gases is condensed and the gas sample is passed through a desiccant column. The chromatograms have identified as major components, the unreacted methane, carbon monoxide and hydrogen. Just traces of carbon dioxide were detected in the analysed gas samples, while in some cases, larger amounts of acetylene (up to 1%) were also evidenced. The condensed unreacted water contained a depot of carbon black.

3. Results and discussion

3.1. Characteristics of the discharge

Fig. 1a shows the variation of voltage current and power for one of the three discharges as a function of time for the case when the additional resistor is also connected (R(+ series). Fig. 1b shows the variation of voltage current and power for one of the three discharges as a function of time without the additional resistor (R(-) series). In order to clarify this diagram we have to mention that the voltage is plotted as a negative signal.

A comparison between these two figures indicates that the second arrangement is providing higher voltages and lower currents. The high voltage peaks are corresponding to

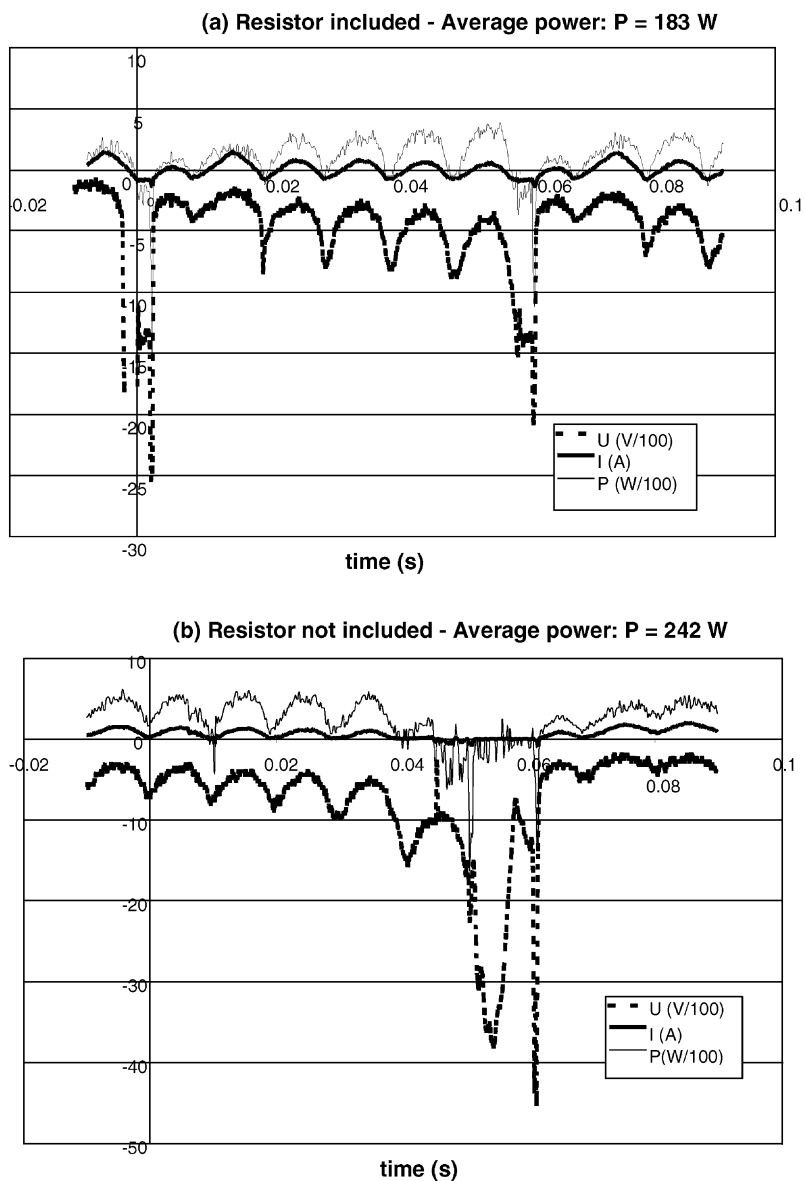


Fig. 1. Voltage and current recordings of a rotating discharge.

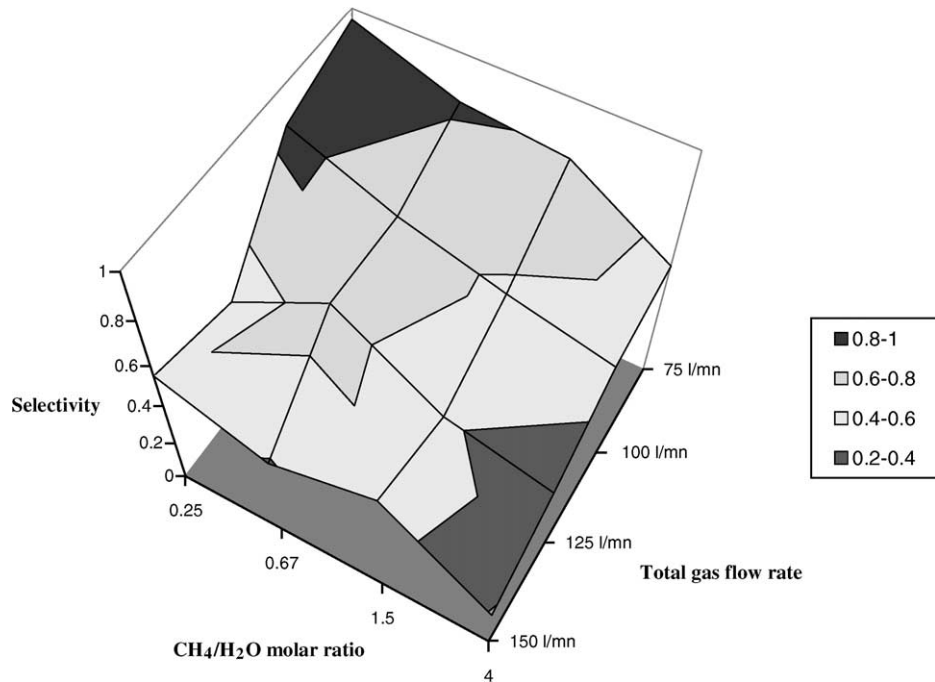


Fig. 2. SR selectivity as a function of reactor's feeding parameters.

a large length (4 cm) of the plasma column and to a non-equilibrium regime. Low voltages are corresponding to a short plasma column and to the greatest values of the current. On the other hand, the equilibrium deviation is greater in the second case (R(-)) than in the first one (R(+)). These observations are in good agreement with literature data [14].

3.2. Chemical diagnosis

In order to be able to compare the actual results with previous ones [1,5], the same characteristic parameters were used: the total flow rate (F), the methane/water molar ratio (M), the conversion, the selectivity of SR reaction (S), the energy input (Wh/Nl incoming gases), the hydrogen

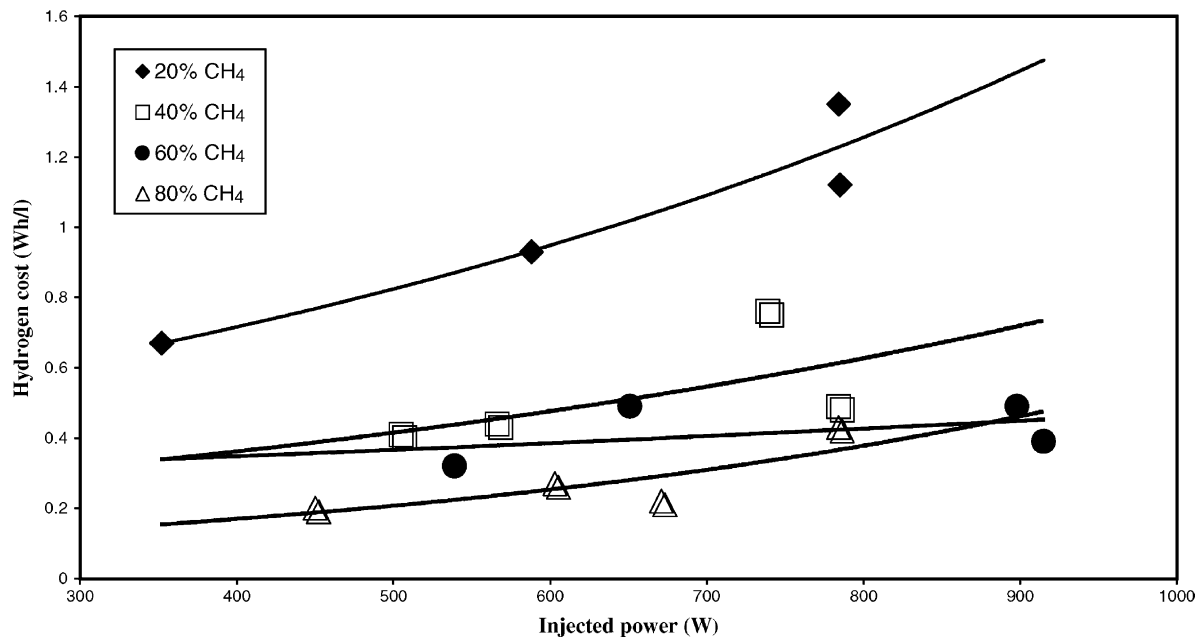
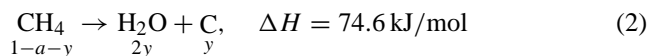
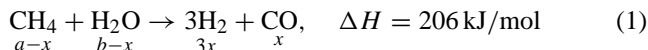


Fig. 3. Dependence of hydrogen cost on the injected power.

production energy cost (Wh/Nl H₂) and an energy equilibrium factor (E_f).

Taking into account that the main reaction products are the hydrogen and the carbon monoxide, we have considered only two main reactions occurring in the reactor:



where a and b are the number of moles of methane and water implied in the SR reaction, x and y the number of moles of methane consumed in the SR reaction, respectively, in the cracking reaction.

Therefore, the selectivity was calculated as the ratio $x/(x+y)$, the theoretical requested power as $[1000 \times (206x + 74.6y) \times \text{methane flow rate (in mol/s)}]$ and E_f as the ratio between the measured injected electric power and the theoretical requested power.

The conversion values were quite low (between 15 and 20%). It was not noticed any dependence between these values and the feeding parameters (i.e. flow rates and CH₄/H₂O molar ratio). However, we have to mention that the R(–) electric arrangement led to higher conversions than the R(+) one.

When we represent the variation of SR selectivity versus feeding parameters of the reactor for the R(–) series (Fig. 2), one can observe two distinct regions separated by an approximate line which is almost the diagonal unifying the minimum M and F values. According to this graphic, on the left side region one finds the highest selectivity values (over 60%). Therefore, we may say that the higher the

methane content in the initial mixture, the lower must be the total flow rate in order to have a better SR selectivity. On the other hand, we also have to mention that not only the conversion but also the selectivity was higher for the R(–) series of experiments comparing with the R(+) series.

3.3. Electric power and energy cost

As shown in Fig. 3, there is a direct dependence between the injected power and the hydrogen cost. We may say that this is an expected dependence but we also have to notice that the costs are increasing for higher water contents in the initial mixture. For example, the energy production cost for 1 l of hydrogen becomes as low as 0.2 Wh, when the initial mixture contains 80 vol.% methane and increases up to 1.4 Wh for 20 vol.% methane in the initial mixture. These costs are about 30% lower than in the R(+) series of experiments [5], and are the lowest values comparing with those we have found in literature [2].

According to the relation defining the equilibrium factor, it results that for $E_f < 1$, the reactor is working out of equilibrium with energetic costs lower than the thermodynamic ones. As shown in Fig. 4, the R(–) series of experiments revealed that there is an entire out of equilibrium exploitation area for $M > 1/2$. The out of equilibrium area is larger than that corresponding to the R(+) series [5], but we have to mention a similitude: the same exploitation zone (i.e. with high water contents in the initial mixture — $M < 2/3$), is requesting more energy than the thermodynamically calculated values. The intriguing aspect regarding the very low energetic costs was also noticed by different authors for other plasma reactions [15,16].

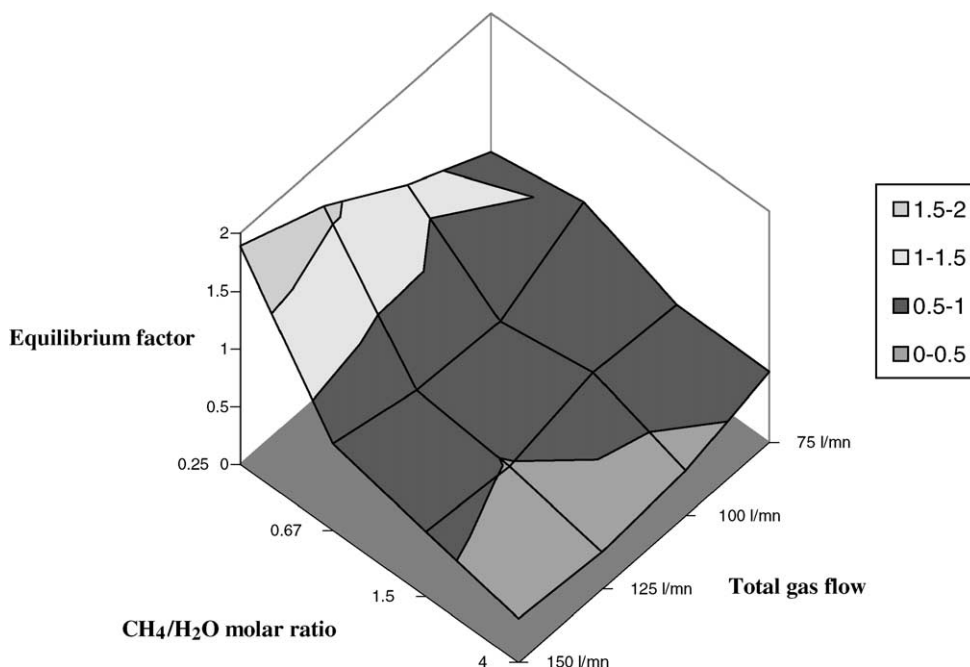


Fig. 4. Equilibrium/non-equilibrium exploitation zones for the glidarc reactor/R(–) series.

3.4. Thermodynamic calculations

The plasma chemical processes were simulated by means of Chemical Workbench code, version 2.5 (Kinetic Technologies, Russia). The thermodynamically equilibrium reactor model (TER) was used for all calculations. This kind of model reactor is regarding the system under investigation as a heterogeneous one that may consist of several uniform phases. The state of thermodynamic equilibrium is achieved by internal chemical and phase transformations. The TER code uses the common principle of entropy maximum for the calculation of chemical and phase composition. According to this principle, the chemical composition corresponds to the probability maximum of energetic levels distribution for macro particles. The method is considering 268 atomic and ionic species that could appear in the system $a\text{CH}_4 + b\text{H}_2\text{O}$ and was applied for two situations: at constant pressure and temperature and at constant pressure and energy input.

Fig. 5 presents the as calculated concentration variation of the main species appearing in the above system for different molar ratios (M). As can be seen from these graphics, the CO_2 production has a maximum at about 800 K but its concentration is higher for lower M values. On the other hand, the acetylene formation is noticed for temperatures higher than 2400 K and only for the cases when the methane concentration in the initial mixture is over 50%. The CO and H_2 concentrations remain almost constant in the temperature range 1400–2400 K.

3.4.1. Preliminary model

We have tried to model the chemical processes occurring in the glidarc reactor starting from conclusions drawn in our previous studies. The gliding arc is a plasma string with a diameter of about 1 mm, surrounded by a weak ionised zone [7,13]. Therefore, we have considered that the reactions occur mainly in the discharge. As is already known,

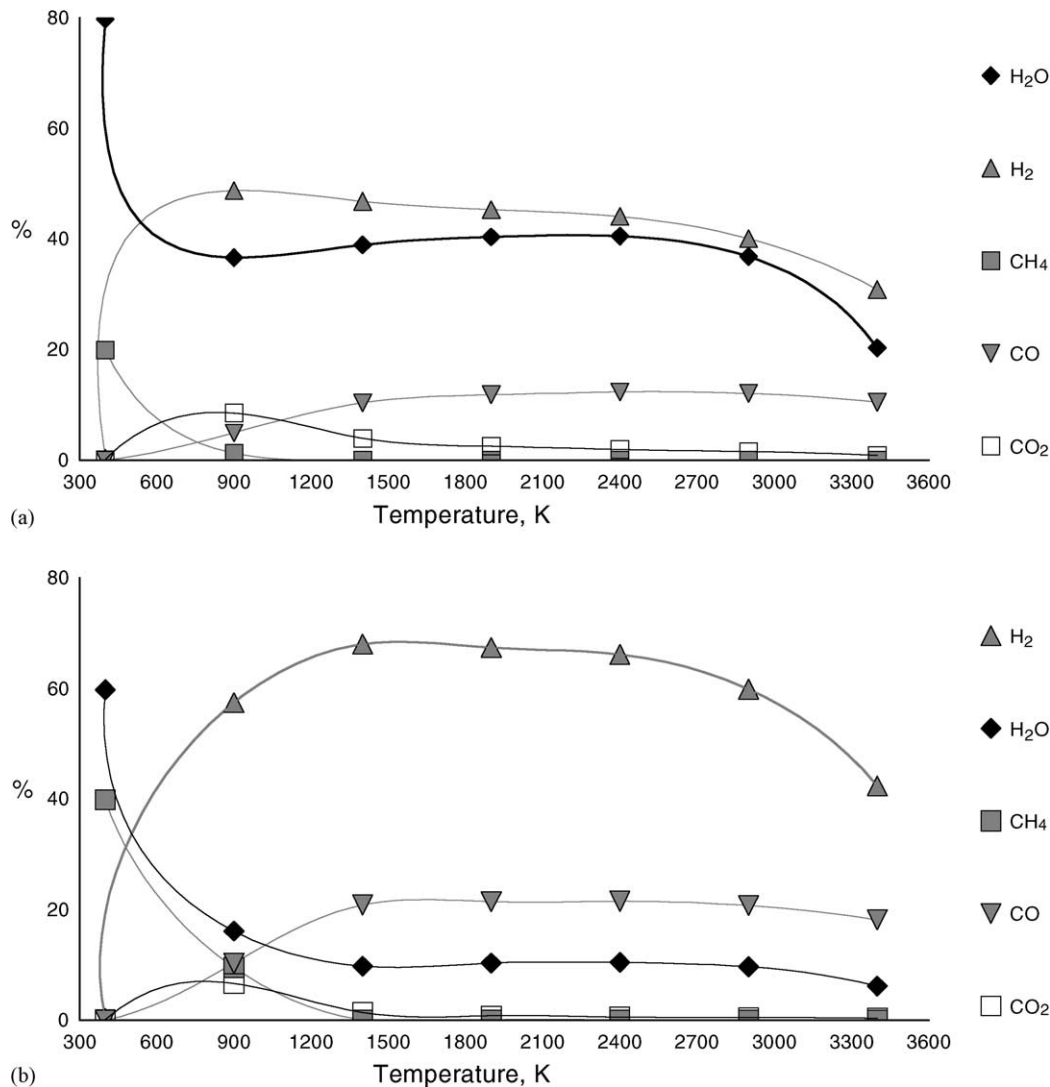


Fig. 5. Calculated variation of the chemical composition as a function of temperature for the system $\text{CH}_4 + \text{H}_2\text{O}$: (a) $M = 0.25$; (b) $M = 0.67$; (c) $M = 1.5$; (d) $M = 4$.

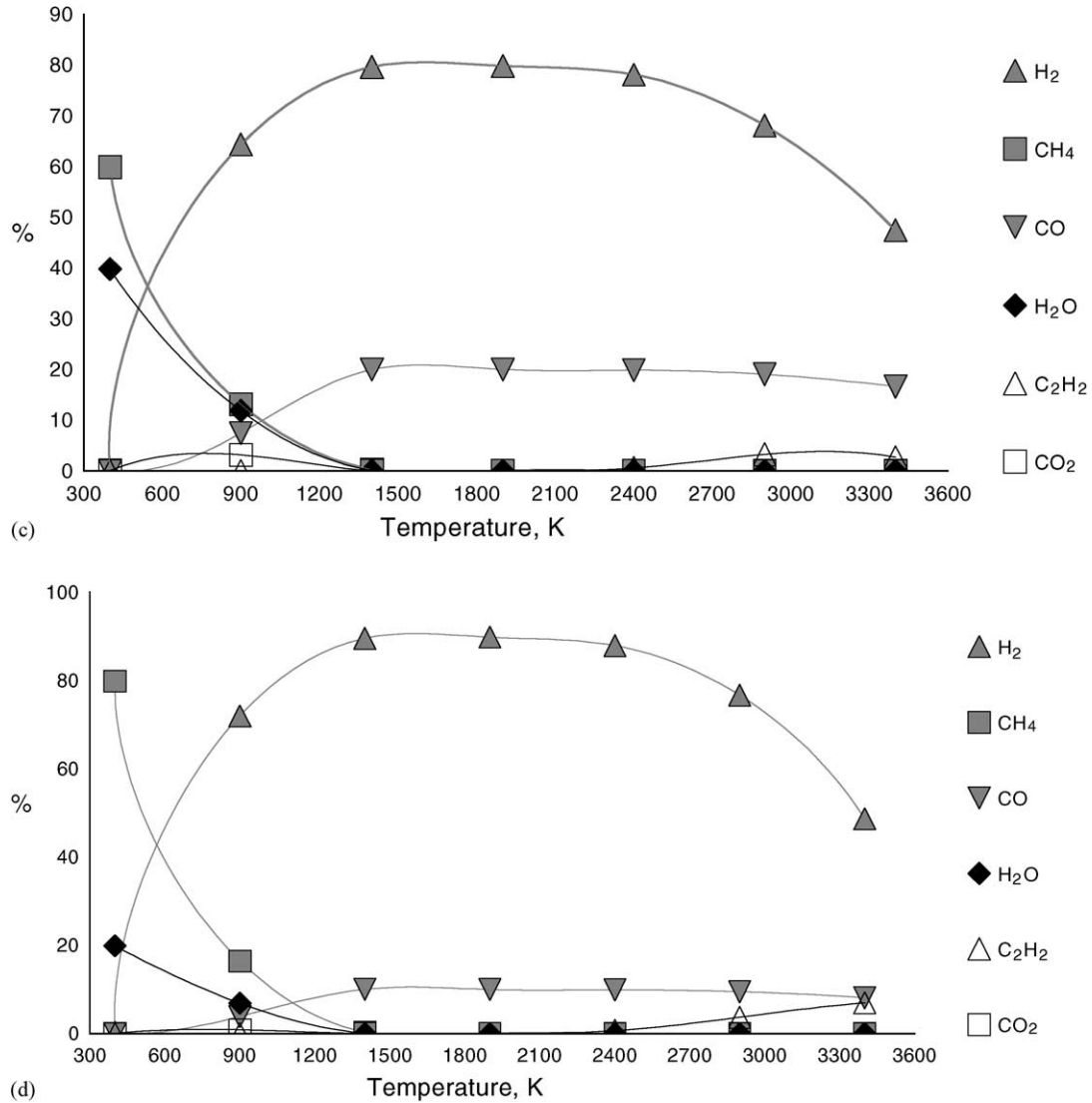


Fig. 5. (Continued).

only a small fraction (10–15%) of the inlet gases penetrates the discharge [17]. Consequently, in our model we have divided the inlet gas stream in two parts: 90% that remains at 400 K and 10% that are heated in the discharge. We also have considered that both streams arrive at thermodynamic equilibrium. According to previous measurements, the temperature on the outer surface of the discharge string ranges between 2000 and 3000 K [6,13]. Finally, we have considered, in this initial model, that the two resulting streams are perfectly mixed and arrive at thermodynamic equilibrium.

Performing the calculations we noticed that the model predicted the appearance of carbon dioxide in the outlet gases instead of carbon monoxide (Table 1). This result is due to the fact that the as calculated temperature of the outlet gas stream is of 700–800 K, where the CO₂ concentration has its maximum (see Fig. 5). However, this prediction is not true because according to our analyses there was almost no CO₂ in the resulted gases and the mean temperature in the reactor increased from one end to another with maximum 100 K [13]. On the other hand, this model is not able to

Table 1
Example of comparative results for the preliminary thermodynamic model

<i>M</i>	CH ₄ (%)		H ₂ (%)		CO (%)		CO ₂ (%)	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
0.67	63	69	29.6	26	0.1	5	7.3	–
4.00	70	71	29	26	–	3	1	–

explain the low energetic costs experimentally recorded. The results clearly indicated that the model is not correct and has to be improved in order to fit with the experiment

3.4.2. Model depending on glidarc temperature profile

Taking into account the above conclusions we decided that thermodynamic equilibrium could not be applied for the final mixture. Therefore, the glidarc zone has to be treated as an almost adiabatic zone. This means that in this

kind of model, the gas penetrating the discharge is initially almost instantaneous heated up to more than 2000 K. Afterwards, its temperature follows the temperature profile of the arc and when it leaves the string, sharply cools down to ambient temperature without any heat exchange. Therefore, this model implies mass transfer but no heat transfer between the arc and the rest of the gas stream. The gas composition would be, in this case, the result of the two flows mixing downstream of the discharge, the obtained final

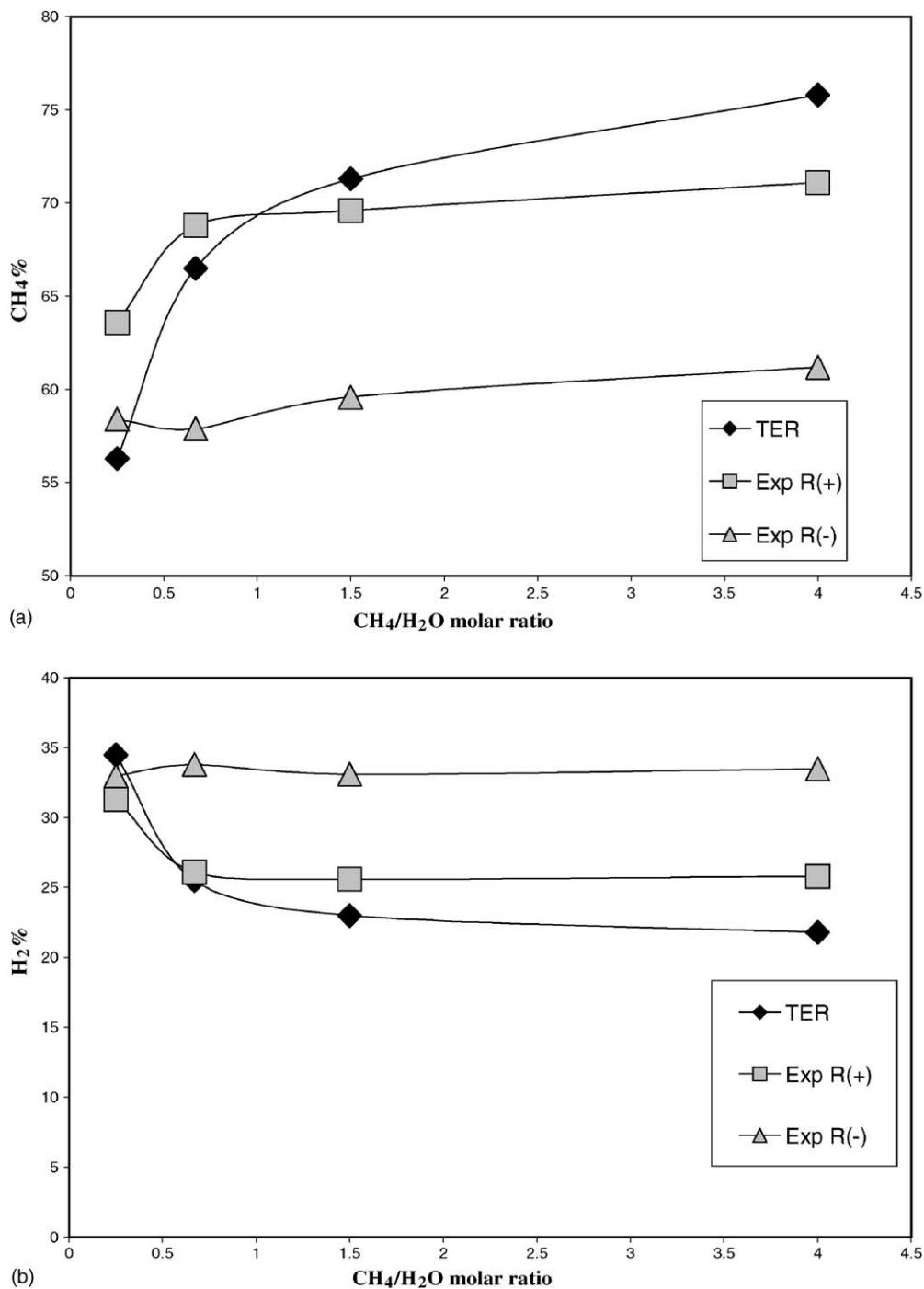


Fig. 6. Variation of methane (a) and hydrogen (b) concentration at the reactor's outlet (TER: thermodynamically calculated, Exp: experimentally determined).

chemical composition being far from thermodynamic equilibrium.

Taking into account that the temperature on the discharge surface is usually around 2500 K, one can expect to find only CO and no CO₂ among the reaction products. On the other hand, the possibility of having higher temperatures (up to 3000 K) on the outer surface of the arc could explain the presence of acetylene in some of the samples with $M > 1.5$ (see Fig. 5).

The thermodynamic results, obtained by means of this improved model, were expressed as methane and hydrogen concentrations at the reactor's outlet (Fig. 6). The calculation has also taken into account the volume variation due to the change of mole number for the gas passing through the discharge. The plotted experimental data are mean calculated values of the methane and hydrogen concentrations, at the reactor's outlet, for series of experiments with the same CH₄/H₂O molar ratio.

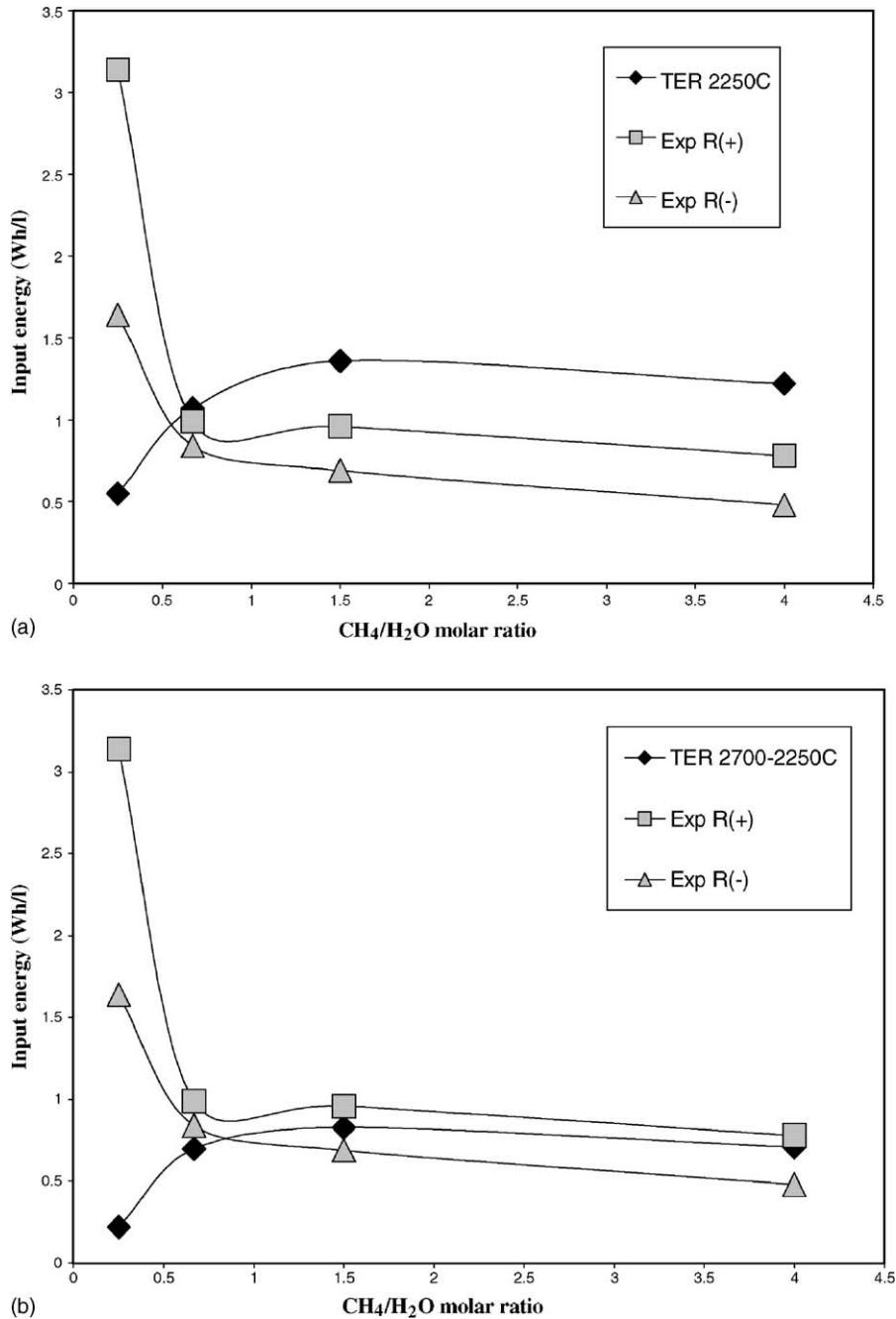


Fig. 7. Variation of input energy vs. M for the symmetric (a) and asymmetric (b) temperature profile of discharge (TER: thermodynamic model, Exp: experiments).

As shown in Fig. 6, the values of R(+) series present a good fit with the model. Nevertheless, the differences between the calculated values and the R(–) series are not large but the tendency is somehow different. Taking into account that the plasma column was longer for the R(–) series (see Fig. 1), this has implied a larger gas fraction passing through the discharge (more than 10%). On the other hand, the corresponding non-equilibrium plasma regime may had as a result, a more significant concentration of radical and ionic species in the surrounding zone of the discharge and therefore, an increased reactivity comparing with the R(+) experiments.

As we said before, a very intriguing aspect for some of the plasma reactions is the very low energetic cost. The mechanism based on a symmetric temperature profile of the plasma string can also describe relatively well the evolution of energy cost as a function of input chemical composition (see Fig. 7). The model can be improved if we consider an asymmetric temperature profile where the inlet temperature in the discharge is higher than the outlet temperature (Fig. 7b). In fact, at this temperature asymmetry of the gliding arc discharge was practically observed in our previous studies [7].

The largest differences between the theoretical and experimental values appear for the low M values (i.e. high water concentrations). In this case, thermodynamic calculations for the temperature corresponding to the arc outlet, indicated that the hydrogen concentration resulted from the exceeding water dissociation is <2%. Therefore, most of the injected energy is used to heat up the water vapours passing through the discharge. This might be considered as a turning of non-equilibrium plasma into thermal plasma, which is overheating the reaction media, and the reagents in all degrees of freedom uniformly consume energy.

4. Conclusions

Glidarc discharges allow high specific throughputs in the reaction zone, which generally largely exceed other chemical methods, including electrochemical and thermal ones.

The experimental results indicate as best exploitation parameters for syngas production, in this type of plasma reactor, $M > 0.5$, $F < 130$ l/min. On the other hand, an inverse dependence between M and F values must be maintained in order to obtain good results (i.e. a quite high selectivity (60–80%) and low energy costs). We also have to mention that if one is interested in hydrogen production, $M > 1.5$ and $F > 100$ l/min are requested in order to obtain energy costs ranging between 0.4 and 0.2 Wh/Nl H₂.

The proposed mechanism gives a good image on the SR chemical processes occurring in the glidarc. Evidencing the weak point of this technical approach (i.e. the low chemical conversion), it suggests the improvement of reactor design in order to cover with the arcs as much as possible from the reaction volume. Taking into account the obtained specific energy consumption, there are hopes that the final cost of the produced hydrogen could be lowered to about 0.1 €/m³ which would become competitive with the classic technologies [2–4,18].

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