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Experimental Investigation of
Plasma Assisted Reforming of Methane II:
Start-up

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Abstract

This paper is one of a series of papers evaluating the performance of plasmatron methane reformers. An accompanying paper describes the steady state performance of a plasma-assisted reformer operating with methane under partial oxidation conditions. In this paper, the startup performance of plasmatron methane reformers is described.

1. Introduction

Plasma based ignition is used extensively in starting of many combustion processes. These processes operate under near stoichiometric combustion, and the plasma is used only for the ignition stage.

The use of continuous plasma operation has been proposed for processes that operate away from stoichiometric conditions, and in particular to very fuel rich conditions, such as those present in reformers. One such concept is described in an accompanying paper [1]. However, that paper exclusively discusses steady state conditions. That paper also provides the background, the applications for small reformers and different plasma reformers and will not be repeated here. The other papers in this series describe the modeling, using fluid dynamics codes [2], Perfectly Stirred Reactor (PSR) codes [3] and Partially Stirred Reactor (PASR) codes [4].

The purpose of this paper is to briefly describe limited experiments carried out with the same plasmatron methane reformer as in the accompanying paper. Section 2 describes the experimental setup, including the instrumentation utilized and its characteristics. Section 3 describes the result of pulsed ignition. Continuous ignition is described in section 4. Finally, section 5 gives the conclusions.

2. Experimental setup

The experimental setup has been described in the accompanying paper describing the steady state conditions [1]. The main difference between the two papers is in the extensive use of the mass spectrometer to monitor the transient conditions of the plasmatron. Because of its relevance to this paper, a characterization of the temporal resolution of the mass spectrometer is provided prior to showing the experimental results with the plasmatron.

2a. Transient analysis with a mass spectrometer

Typical conditions of the sample gas near the entrance to the capillary are shown in Table 1 for a capillary with an ID of 250 microns. It should be noted that the surface heat transfer coefficient, h, is so high that the gas in the capillary reaches the wall temperature very fast (in distances much smaller than 1 mm). Thus it is a safe assumption that the sample is at the same temperature as the capillary. The temperature of the capillary varies along its length. One section of the capillary is inside reactor, there is a section between the reactor and a heated blanket, and finally is the heating blanket section. At one end of the capillary, the temperature is determined by the gas in the plasmatron, at atmospheric pressure conditions. At the other, the pressure is vacuum, and the temperature is that of the heated capillary. The temperature of the heated capillary is 150 C (423 K).

Table 1. Values for a typical case for the capillary

p	Pa	101000
m dot	kg/s	2.5644E-07
T	K	1300
density	kg/m^3	0.27433337
v	m/s	51.2442538
cp	J/kg K	1196.13342
nu	m^2/s	0.00018873
nuf	viscosity	8.804E-05
k	W/mK	0.08331839
Re		88.7052633
Pr		0.74328058
Nu		169.079181
h	W/m^2 K	92437.0406

Next we calculate the velocity of the sample gas and the pressure along the capillary. It is assumed that the pressure drop is given by the Darcy relationship

$$dp/dx = f \ /D \ u^2/2$$

where f is the friction factor (also known as the fanning factor) and u is the local speed of the gas. The friction factor depends on the Reynolds number. For laminar flows, as in the case of flows in the capillary, the friction factor is given by

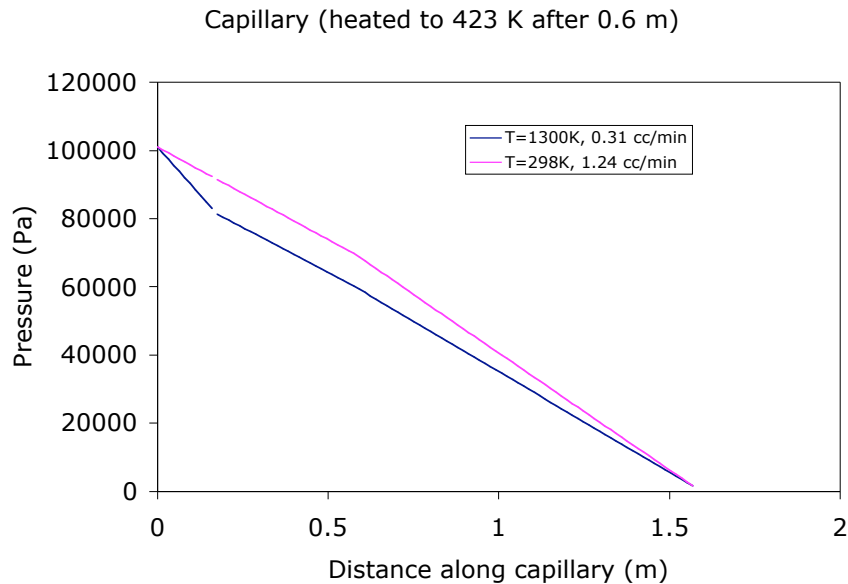$$f = 64/Re$$

Capillary (heated to 423 K after 0.6 m)

Figure 1. Pressure drop as a function of the distance along the capillary

16 cm of the capillary are inside of the plasmatron methane reformer exhaust tube, for direct sampling of the reformate. Two cases are analyzed. During calibration, the temperature of the first 16 cm of capillary is at room temperature (298 K), while during those times when the reformer is operating, the first 16 cm are at approximately1300 K, the temperature of the reformate.. After this region, there are 40 cm of capillary at room temperature, needed to plumb the distance between the reformer and the mass spectrometer. The rest of the capillary, inside a heating blanket and 1 m in length, is heated to 150 C (423 K). It is assumed that a 200 micron capillary is used.

The results are shown in Figures 1 and 2. Figure 1 shows the pressure along the capillary for both cases. The pressure has been calculated by dividing the capillary into small segments and calculating the pressure drop and the fluid properties at each segment. The flow rate is varied until the pressure becomes small and the flow becomes sonic (choke flow) at the capillary end that is in the mass spectrometer. The flow rate for the case of high temperature is 0.31 cc/min, while during calibration the flow rate is 1.24 cc/min (at STP). This result indicates that the pressure at the mass spectrometer should a strong function of the temperature of the gas being sampled. Because of this effect, the operating pressure during the experiments has been in the low 10^{-6} mbar region, somewhat lower than the recommended optimal pressure of the instrument.
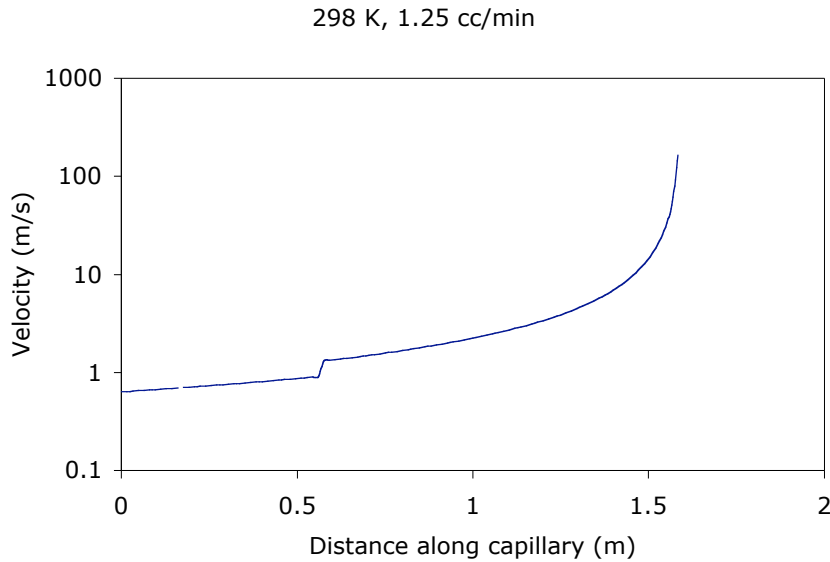

Figure 2. Velocity as a function of the capillary distance for the case at 298 K for the first 10 cm, 423K for the other 90 cm, and for a flow rate of 0.6 cc/min, for a 200 micron capillary.

The corresponding velocity of the sample along the capillary is shown in Figure 2, for the case with the room temperature inside the reactor. The discontinuity in the velocity and pressure at 0.6 m is due to the sudden change in gas temperature as the sample enters the section of the capillary that is inside the heating blanket. The velocity is increasing very rapidly towards the end of the capillary, and it should be sonic at the end of the capillary, where the model breaks down. The flow for which this happens is called the critical flow.

For higher flows, the sonic region occurs inside the capillary, while for lower flows the pressure at the end of the capillary is substantially higher, and not consistent to the fact that the capillary ends in a high vacuum system (a few times 10^{-6} Torr). In these calculations it is assumed that the sonic boundary occurs at the end of the capillary. In principle, this is not necessary, as the flow can become molecular in nature (rather than viscous) through a section of the capillary. But in that case the time delay would be shorter than when the sonic boundary is at the end of the capillary, and thus this calculations provides an upper bound to the time delay.

Figure 3 shows the critical flow rate as a function of the capillary size, for the cases of both temperatures. The critical flow rate is proportional to the fourth power of the diameter of the capillary.

The temperature effect on the flow rate is substantial (about a factor of 4), from about 1.2 cc/min for 298 K to 0.3 cc/min for the 1300 K case). As the temperature increases, with viscosity a strong function of temperature, the critical flow through the capillary decreases.
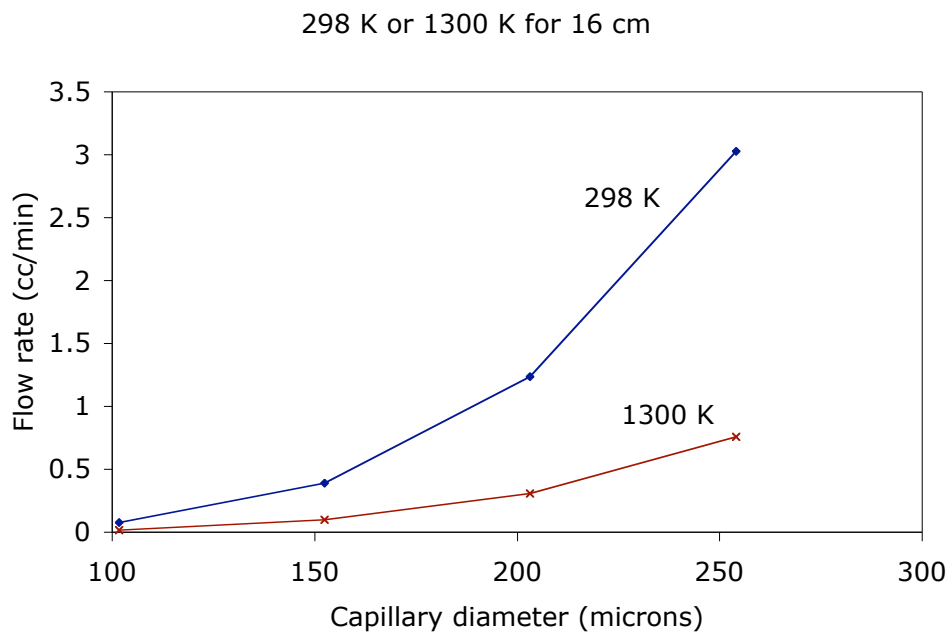
298 K or 1300 K for 16 cm

Figure 3. Flow rate as a function of the capillary size, for the cases of high and low temperatures in the plasmatron methane reformer exhaust..

2.b Calculations vs experiments

The experimental results indicated that there was a 3 s delay at the high temperature, and a 0.5 s broadened rise time. In the experiments it was not possible to determine whether the broadening is due to the time response of the plasmatron methane reformer, or due to the resolution of the MS system (including the sampling).

The volume of the reactor is estimated to be 0.5 l (2in diameter, 10 in long), with a factor of 2 increase due to the volume in the exhaust tube upstream from the sampling point. Then, with 300 liter/min flow rate, it is estimated that the transit time through the reactor is about 0.2 s at room temperature, and that two transit times (for 2 e-foldings, for the case of mixing) is on the order of 0.4 s. For the warm reformate, the2-transit times are on the order of 0.1 s.

The transport delay time through the capillary is calculated through the integral

$$\tau_{delay} = \text{integral (dl/v)}$$

where dl is the step length along the capillary and v is the sample velocity along the capillary, calculated above.

The calculated time delays as well as the critical flow rates are shown in Table 2 as a function of the ID of the capillary, for both the lower temperature operation as well as the high temperature..

Table 2. Characteristics of MS capillary using simple model

Capillary ID	microns	102	152	203	254
τdelay (298 K)	s	3.5	1.6	0.9	0.6
Flow rate	cc/min	0.078	0.39	1.24	3.03
τdelay (1300 K)	s	12.35	5.50	3.13	1.99
Flow rate	cc/min	0.02	0.10	0.31	0.76

In order to reduce the response time to less that 5 s, it is necessary to use a 200 micron ID capillary. The flow rates are increased by more than 1 order of magnitude from that using a 100 micron capillary.

The experimentally measured pressure by the internal gauge is on the order of $1.9\ 10^{-6}$ mbar, or about $1.5\ 10^{-6}$ Torr.

In addition to the delay, there is a broadening of the transient, due to diffusion. To estimate the magnitude of the diffusion, assuming that the gas is hydrogen with a diffusion coefficient of about 10 cm^2/s, and assuming a transport time as shown in table 1, the diffusion time that is calculated is small.

It should be noted that there were discrepancies between the observed and measured. For one, when the plasmatron methane reformer was started, and the temperature of the exhaust increased to about 1300 K, there was not a large drop in the pressure of the capillary, as would have been predicted by the results shown in Table 2. However, the

calculations have been useful in guiding the choice of the capillary, and in understanding the nature of the delay and the loss of resolution due to diffusion.

Using the experimental results it is possible to determined the e-folding of the concentration. The easiest and fastest method to change the concentration in for determining the time response of the mass spectrometer is by turning down the plasma during reforming, and looking at the changes in the ion currents. This is faster in our setup than changing the inputs (due to long piping). Using the results determined in the accompanying paper for propane [5] the e-folding of the concentration is found to be about 0.5 s, or 1 s for a 90% change. Thus it is not possible with the present setup to determine responses faster than this. As will be seen below and in the accompanying paper [5], this is about the time constant of the changes.

2.c Calibration with CFD code.

The simple model was tested using a commercially available CFD code, FLUENT. The calculations for a 1 m long capillary, 250 micron diameter, at 298 K, indicated a mass flow rate of 3.3 10^{-7} kg/s (needs double precision to converge). Using the simple model described above, the calculated mass flow rate is 1.15 10^{-7} kg/s, or about a factor of 3 lower. In order to make the two agree, the Reynolds model for the friction factor f was decreased until the two agreed. They did agree for a multiplier of 0.35.

3. Start-up experiments – pulse ignition

The experiments were carried out by establishing the flows, and the turning on the plasma. Two sets of experiments were carried out. In this section, experiments with short operation of the plasmatron will be described.

The power supply was turned on and then off, such that the on time was less than 1 s. The process was done manually, and thus the on-time differs from experiment to experiment, but the resulting performance of the plasmatron does not seem to be sensitive to the length of the on-time of the plasmatron.

The value of the instantaneous power in the plasma was varied in these experiments. The process involved adjusting the power without the presence of the methane. Then the power was turned off, the methane turned on, and the plasma pulsed in the manner described above.

The mass spectrometer was calibrated for hydrogen, oxygen and methane. Hydrogen was calibrated using measurements of the reformate with the GC, while oxygen was calibrated using air as the sample gas and methane by measuring the composition of the air/methane mixture and calculating the methane concentration from the known flow rates.

The experiments were carried out at various ratios of O/C. As in the accompanying paper [1], the O/C ratio was varied by changing the wall air, with constant swirl air (60 lpm) and methane (40 lpm). The O/C ratio was varied from 1.63 to 2.24.
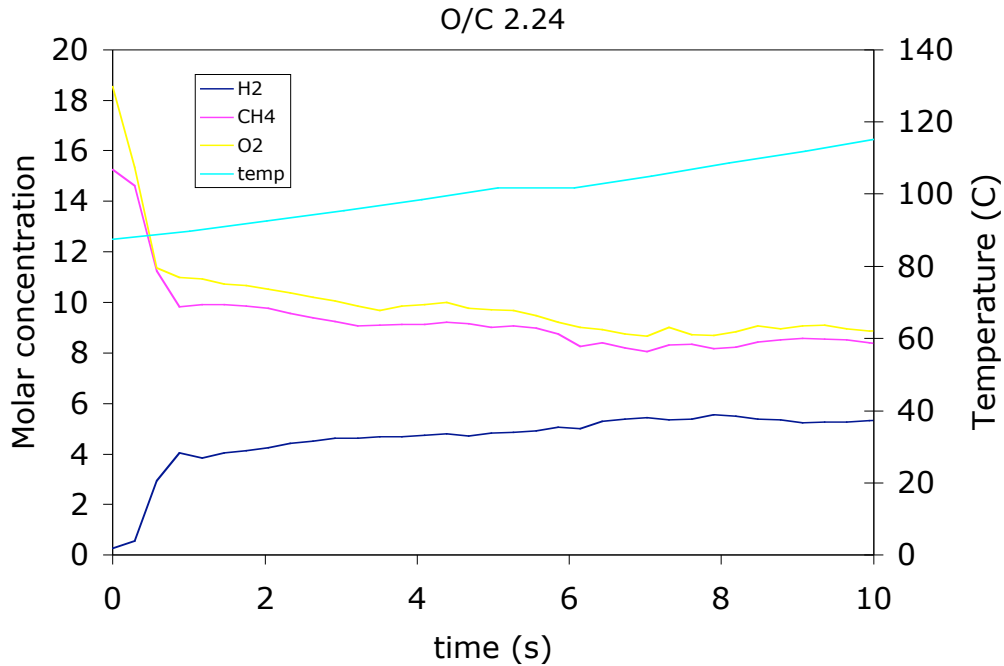

Figure 4. Time response of H_2, O_2 and CH_4 for O/C = 2.24 and 160 W.

Results of the hydrogen, oxygen and methane concentrations are show in Figure 4 as a function of time for conditions of O/C = 2.24 and 160 W of plasma power. Because of the ~ 3 s time delay, it is not clear where the start up occurs in the mass spectrometer. The second measured point by the MS shows increase of H_2 and decrease of both methane and oxygen. The transient lasts about 0.8 s, where the transient is defined as the time it takes for the 10%-90% change. It is not possible to determine whether the width of the transient is due to instrumental limitations of the MS system or time response implications of the plasmatron methane reformer. However, it can be said that the response of the plasmatron methane reformer cannot be longer than about 0.8 s, and could in fact be smaller.

The hydrogen concentration reaches more than about 4% in less than 1 s, and then slowly increases. The methane conversion is about 30% at times of about 2 s, increasing to about 50% at 10 s. The oxygen concentration follows the methane concentration.

The temperature, as measured by the thermocouple, is also shown in Figure 4. The temperature is increasing at a rate of more than 2 K/s. The temperature measured by the thermocouple is not a measurement of the gas temperature and it may be more an indication of the temperature of the walls.
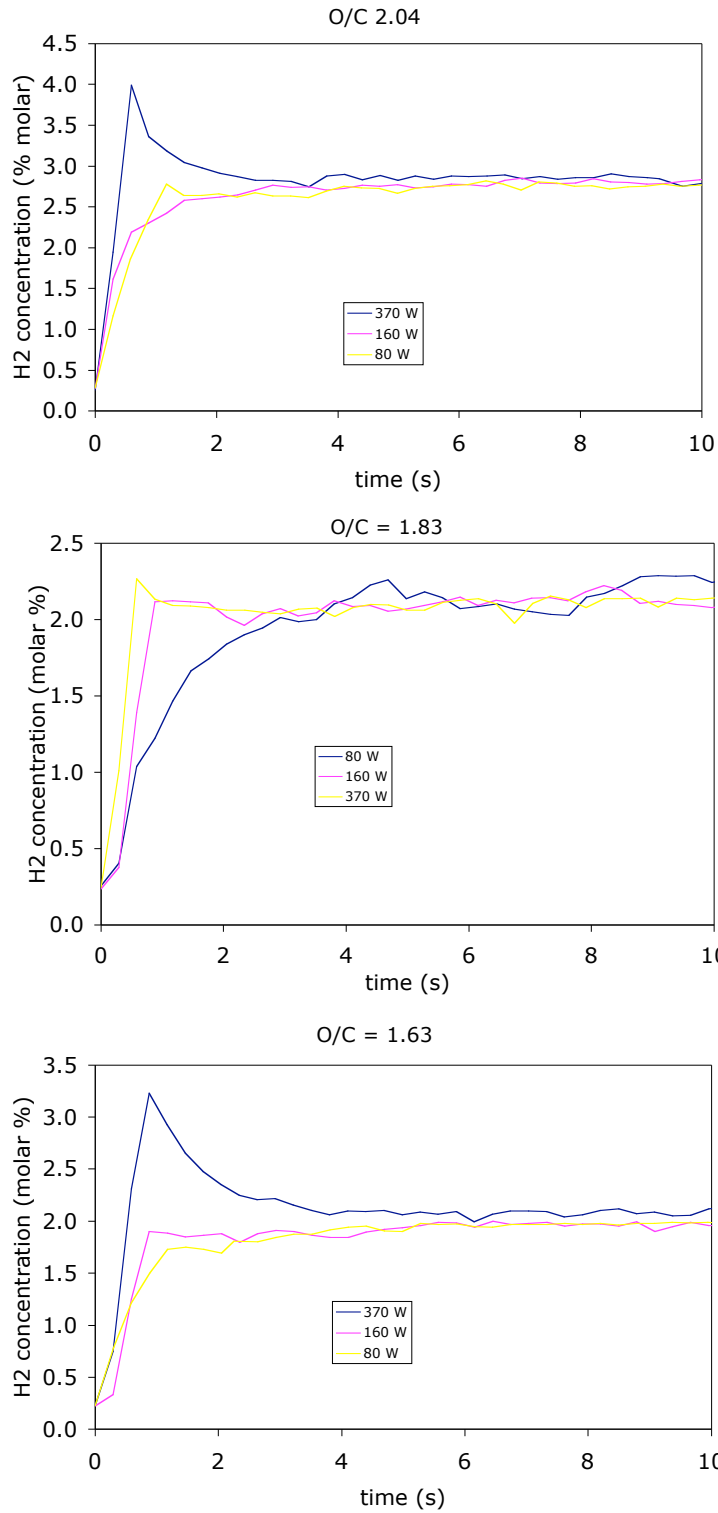
Figure 5. H_2 concentration as a function of time for (a) O/C = 2.04, (b) O/C = 1.83 and (c) O/C = 1.63 for several value of electrical plasmatron power

The transients in the hydrogen concentration for O/C = 2.04, 1.83 and 1.63 for several values of plasmatron electrical power are shown in Figure 5. It is clear from the figures that increased hydrogen yield occurs for those conditions with higher power right during turn-on and immediately after shut down of the plasma. However, for all these cases, following the turning of the plasma, the hydrogen concentration reaches the same value. The oxygen and methane plots, not shown, follow the same behavior, with concentrations after the transients that are independent of the instantaneous plasma power during the pulsed turn-on.

It is clear from Figure 5 that the hydrogen concentration increases with O/C ratio, especially at the higher values of O/C. Figure 6 shows the H_2 concentration 10 s after startup, for the cases in Figures 4-5, as a function of the O/C ratio.
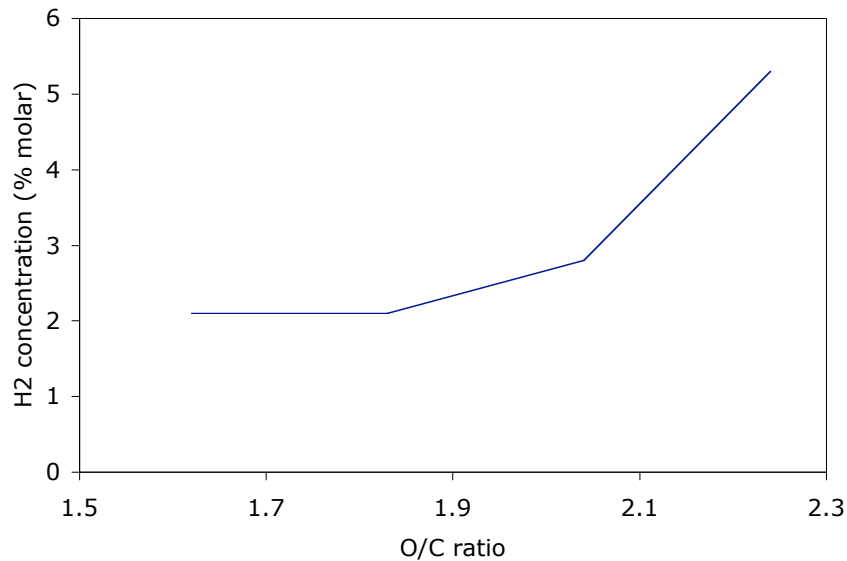

Figure 6. H_2 concentration at 10 s for different values of O/C.

H_2 concentrations as high as 5% can be obtained with methane using the plasma device as a short time igniter. It may be possible to obtain even higher concentrations at higher O/C ratios. There should be an optimum value beyond which the hydrogen in the fuel is consumed and turned into water. We have yet to explore these conditions of higher O/C ratio.

It is not clear how the device operates with 2% hydrogen conversion. The modeling that we have performed, and presented in accompanying papers, fails to reproduce the conversion. We also have yet to model the start-up phase.

4. Start-up – continuous ignition.

In this section, results of varying the power at a constant value of O/C are presented.

The experiments were nominally carried out at 60 lpm swirl air, 120 lpm wall air and 40 lpm methane, premixed with the swirl air. This flow rates would correspond to an O/C of about 1.83. Comparing the results in this section with those of the previous section indicate a discrepancy, and the O/C could be as high as 2.2 (see the discussion on the monitoring of the O/C ratio in the accompanying paper [1]).

Figure 7 shows the results for the conditions described above. The power was varied for several startups, and then the power was shut down, allowing the reaction to continue. After a few seconds, the methane was shut off.
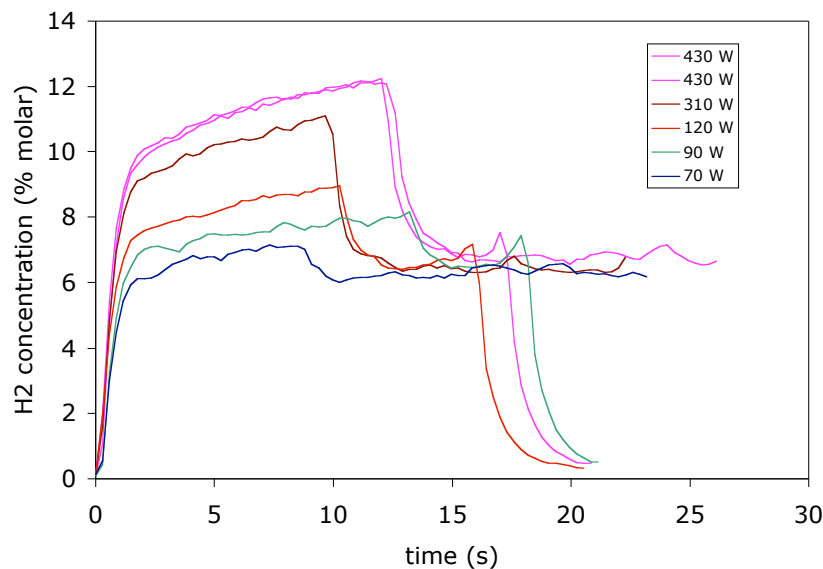

Figure 7. H_2 concentration for O/C ~ 2.2 for several values of power.

As in the previous experiments, the hydrogen concentration rises in about 1second after the plasma is started, and similarly decays in about 1 s after the plasma is shut down. The hydrogen concentration is a strong function of power when the plasma is on. Once the plasma is shut down, the reformer continues to operate, as described in the previous section. The transient, again, takes on the order of 1 s. As in the previous section with plasma ignition, the hydrogen concentration after the plasma is shut down is insensitive to the value of the power during the time when the plasma is on. The hydrogen concentration is on the order of 6%, which indicates that the O/C ratio may have been larger than 2.2.

Figure 8 shows the hydrogen concentration as a function of power at 2 s after start-up. The concentration at 0 power is that corresponding to the concentration after the plasma has been shut off, and does not correspond to 2 s after start-up. At the highest power, above 400 W, the hydrogen concentration rises to above 10%, indicating the advantages of the plasma at conditions of fixed O/C ratio.

The experiments need to be extended to other values of O/C, and to compare the maximum hydrogen concentration and methane conversion for the cases of pulsed ignition and continuous ignition.

5. Conclusions

In this paper, a brief experimental campaign to investigate the start-up of plasmatron methane reformers has been described. The experiments indicate that when the plasmatron is used as an igniter, the hydrogen concentration is a function of O/C. Furthermore, the tests indicate that it is possible to increase the hydrogen concentration and the methane conversion by increasing the O/C to about 2.2. As the O/C for stoichiometric combustion of methane is O/C ~ 4, the reformer is still operating at very fuel rich conditions.
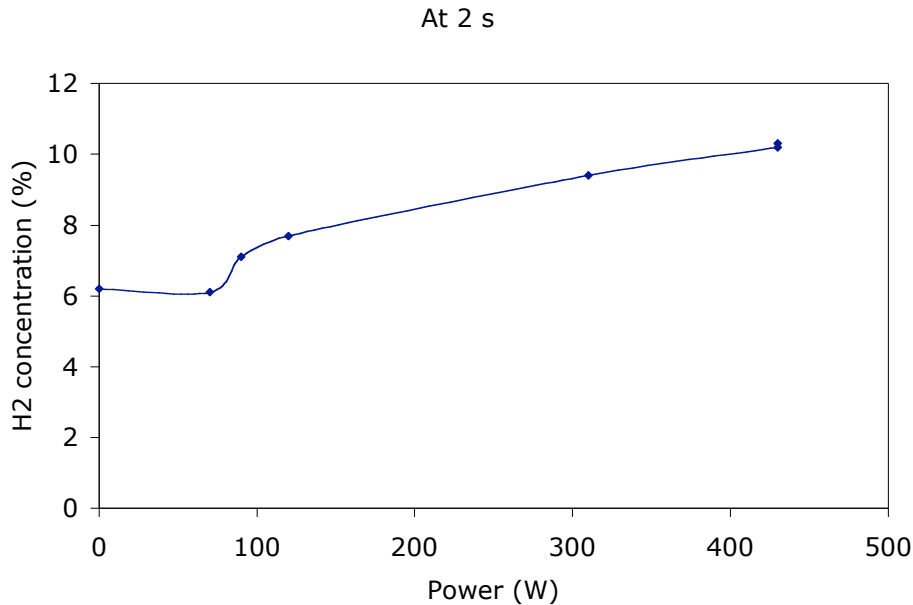
At 2 s

Figure 8. H_2 concentration at 2 s as a function of plasma power at fixed O/C.

When the plasmatron is used in continuous ignition mode, the use of the plasma at a given O/C ratio increases the hydrogen concentration and the methane conversion. Increasing the power increases the hydrogen concentration. High hydrogen concentration, as high as 10-12%, can be obtained in ~ 1 s with O/C on the order of 2.2 with 300-400 W.

References

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