

PSFC/JA-05-10

**Experimental Investigation of
Plasma Assisted Reforming of Methane I:
Steady State Operation**

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August 22, 2005

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Supported by Chevron Texaco, ArvinMeritor and Department of Energy, Office of
FreedomCar and Vehicle Technologies

Abstract

Plasmatron fuel converters have been investigated for the conversion of a wide range of fuels. This paper is one of a series of paper investigating the performance of plasmatron methane reformers. In this paper a systematic experimental investigation is carried out of the reformation of methane in a plasmatron fuel reformer at steady state conditions. The effect upon reformation of flow rate distribution and electrical power level are investigated for a given geometry that has been thoroughly studied with a similar gaseous fuel, propane. Startup issues are investigated in an accompanying paper.

1. Introduction

There is a need for a compact, efficient hydrogen generator for onboard applications [1-16]. In addition, the manufacturing of synthetic fuels starts with the generation of synthesis gas [see, for example, 17]. The development of a homogeneous (without the use of a catalyst) process would be attractive, as the cost of the catalyst and the reactor is a major component of plants used to generate hydrogen rich gas for natural gas upgrading. It may be particularly useful for smaller scale plants.

Homogeneous reactors have been studied in the past [18-20]. The performance has been lacking, and thus industrial generators of synthesis gas use catalytic processes.

The plasma assisted fuel converters [21-30] use continuously generated plasma as means of facilitating the reformation of hydrocarbon fuels. The process used in plasmatron fuel converters [21-23] is partial oxidation, where there are as many atoms of oxygen as there are atoms of carbon. Under ideal circumstances, the oxygen carbon atoms would combine and form carbon monoxide molecules, releasing all the hydrogen atoms as hydrogen molecules. In practice it is necessary to have more atoms of oxygen than atoms of carbon, and thus the carbon to oxygen atom ratio (O/C ratio), is larger than 1. The process of partial oxidation is exothermic, but with relatively slow kinetics. The use of plasma enhanced partial oxidation process has been proposed and investigated in the past. [21-31]

The purpose of this and accompanying papers is to explore the performance of a homogeneous methane reformer that uses a continuous plasma source, without the use of thermal recuperators. This paper describes the steady state experimental results. The plasmatron fuel converter is described in section 2. Section 3 describes the results of reforming methane, and studies the composition of the reformat as well as the major system parameters of the reformer. The effect of turning off the plasma once the reactor reaches steady state is discussed in section 3, to determine the advantages of using the plasma continuously. In section 4, the dependence upon plasma power is discussed. Finally, section 5 provides the conclusions.

The accompanying papers describe the startup testing [32], and modeling using Perfectly Stirred Reactor code [33], Partially Stirred Reactor code (PASR) [34] and fluid dynamics with the use of a CFD code [35],

2. Plasmatron fuel converter system

Figure 1 shows a diagram of the plasmatron fuel converter used in the present experimental and modeling effort. It consists of an axially symmetric set of concentric electrodes with an axial gap. There is a gaseous input across the gap, and since it has a large swirl flow associated with it, it is referred as the swirl gas. The purpose of this flow is to push the discharge, which originates across the gap, to the volume of the plasmatron. This flow has both a radial component that pushes the discharge towards the axis of the device, as well as a swirl component that rotates it.

The discharge is created by a constant current power supply. The power supply thus produces very high voltages (on the order of 10-20 kV) under conditions where the plasma is not present, as well as relatively low voltage to maintain the discharge. During the current maintaining phase, the voltage is on the order of 500-2000 V, and it is time varying. As the discharge lifetime increases, its length increases, with an associated increase in the discharge voltage. The electric field away from the sheaths is on the order of 400 V/cm, the gas temperature is on the order of 2400 K and the electron energy is on the order of 1 eV [35]

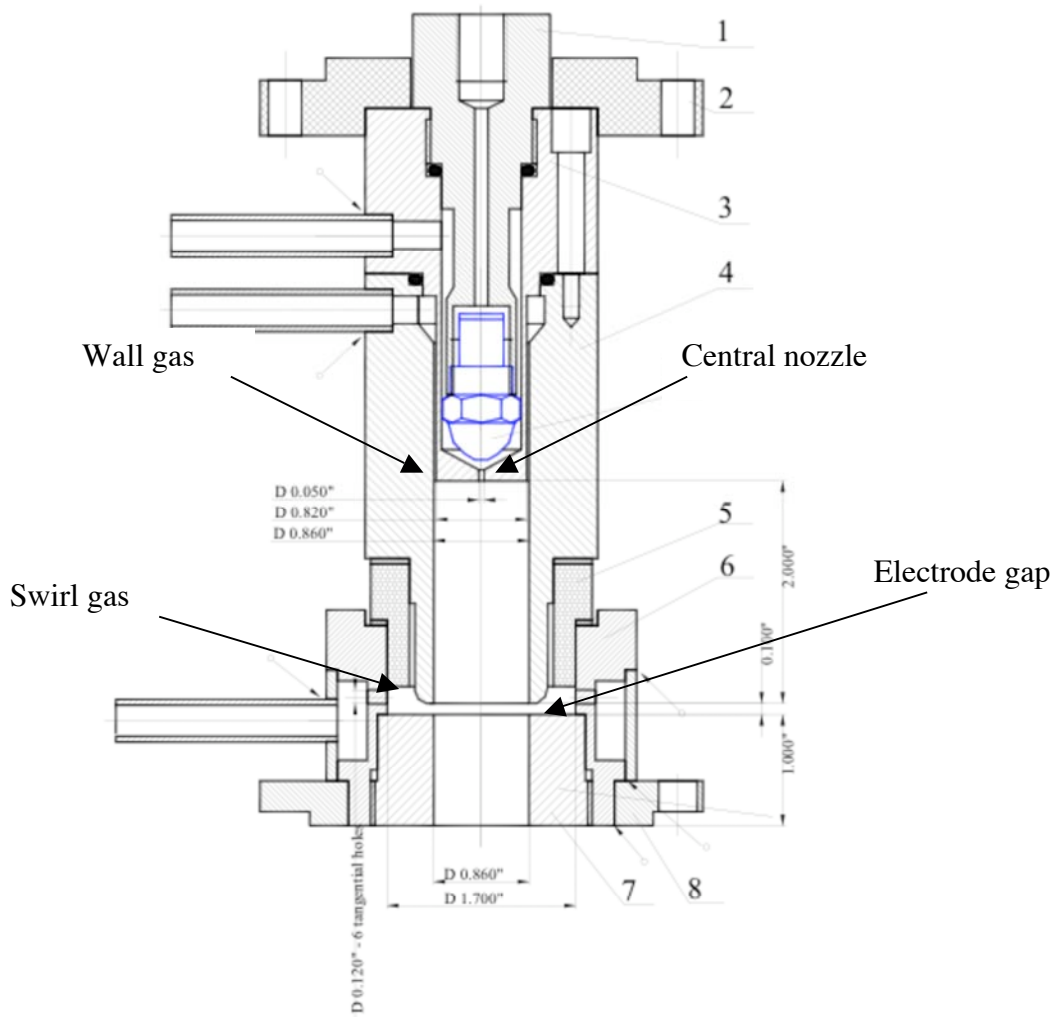


Figure 1. Diagram of the plasmatron methane converter used in the present experiments

There are several other inputs to the plasmatron. There is an axially directed centered input that is commonly used for liquid fuels. The liquid nozzle is surrounded by a fast gas flow, making up an air-assisted injector. The nozzle and axial injection has not been used in the present experiments, as previous experiments with propane indicated that best performance is obtained when the hydrocarbon fuel is mixed with the swirl gas.

There is a third input of gases, an axial gas that is injected at the same axial location of the air assist injector, but at large radii. The wall air is injected mainly in the axial direction. In the cases of the experiments described in this paper, and the modeling to analyze them, the axial gas is composed exclusively of air.

The methane flow is measured using a calibrated rotameter, while the air flows are measured and controlled with mass flow controllers. It was difficult to use a mass flow controller with methane because the low flow rates of methane made very difficult to maintain proper calibration. Two rotameters in parallel were used to provide the required methane flow, with both operating near the middle of their range. Under these conditions, the methane flow was accurate within 10-20%. The rotameters are compensated for pressure variations that occurs as the swirl air is varied. There is no variation in pressure at the rotameters when the wall air is varied.

The composition of the gas is determined using both a gas chromatograph and a mass spectrometer.

The mass spectrometer is a Pfeiffer OmniScan 200. The device has a 200 micron ID capillary sampling line that is directly introduced into the reactor, at a location close to the exit of the reactor. The volume of the reactor upstream from the sampling point, including the plasmatron head volume, is about 1000 cm³. The reactor volume is used in the calculations in the accompanying papers. The capillary is heated in order to prevent condensation in the column. The length of the capillary is about 1.5 m, and results in a time delay of about 3 s. This is a pure time delay. The device can take samples at a rate of 3 Hz, and the length of the capillary does result in small but measurable diffusion. Real time concentration of oxygen, methane, water and hydrogen can be obtained. Unfortunately, because of interference between N₂ and CO (with both masses of 28), it is not possible to reliably monitor either. The accompanying paper describing the startup of the plasmatron methane converter further described the MS system. The mass spectrometer is calibrated by placing gas standards through the plasmatron, and then measuring the signal. The signal is compensated by the pressure in the mass spectrometer.

The GC is an Agilent MTI-2000 model with two columns, one for permanent gases and the second one for hydrocarbons. The GC is calibrated using gas standards from BOC gases in the range approximately similar to those that are being measured. The GC sampling point is near the mass spectrometer location.

Special attention was given to measure the composition of the gas as accurate as possible. The results indicated that the GC has a reproducibility of about 8%. The mass flow controllers are calibrated at the manufacturer (Omega), and are supposed to have an accuracy of 1% through the middle of the range. The rotameters used in the experiments have an accuracy of about 5%. It was determined that the key parameter for the reforming, the O/C ratio, could vary by about 15%, and it differed from the measurements of the composition of mixed reagents, and that calculated from the inputs. However, during a given set of runs the deviation remained relatively constant, as some

of the parameters were being slightly varied while the other remained constant. Thus, although comparison between experiments carried out in different days have the uncertainty in the O/C ratio of ~15%, results from a given set of results during the same set of experiments have decreased relative uncertainty.

There is a temperature sensor (a thermocouple) located near the axis, 12.5 cm below the plasmatron head.

Tests were carried for a single flow rate of methane, which is injected in the swirl gas. The methane flow rate was 0.45 g/s, about 25 kW heating power.

3 Steady state reforming

3.1 Reforming with plasma on

In this section the steady state plasma reforming characteristics are described. We have carried out a series of experiments with a systematic variation of the air in the swirl gas and the axial air. The experiment is carried out at well-determined conditions (flows, electrical power), and the composition is monitored with the mass spectrometer. The temperature is monitored by a thermocouple in the reactor. Gas samples for analysis with the GC are taken when the temperature and composition have stabilized.

Results of these experiments are shown in Figure 2. Shown are contours of constant hydrogen, carbon monoxide, carbon dioxide and methane concentrations in the dry gas, as a function of the air flow rates in the axial gas and the swirl gas. The value of the contour is shown in the bar to right of each graph.

The experimental protocol held the swirl air at a given flow rate, while changing the wall air. This process was repeated for 3 different swirl airs. In this manner, the required adjustment of the methane rotameters was minimized. We have followed this method as it is experimentally easier, and more reproducible, to vary one air or the other, instead of varying both in order to keep constant the overall O/C ratio.

The results indicate that the hydrogen concentration has a broad, saddle-like peak, with the maximum along the diagonal. The variation of the hydrogen concentration does not vary much, from about 10 to 14%. The variations of the concentration of CO show the same characteristics as hydrogen, following the maximum for hydrogen, across the diagonal. In contrast, the concentration of CO₂ and the methane conversion increase monotonically towards conditions of higher O/C ratios.

Figure 3 shows some of the overall parameters of the conditions analyzed in Figure 2. The O-to-C ratio is shown. The constant O/C lines are aligned along the diagonal, just as the H₂ and CO concentrations in Figure 2. This indicates the importance of the parameter O/C for hydrogen generation. The CO₂ concentration and the methane conversion are also functions of the O/C ratio.

Figure 3 also shows the temperature in the reactor, which increases, in the general direction of increased O/C (as more of the fuel is fully combusted, as indicated by the increased CO₂ concentration).

The efficiency shown in Figure 3 refers to the heating value of the reformat divided by the heating value of the fuel. A substantial fraction of the fuel, about 1/3- 1/2 is spent in driving the gas phase partial oxidation. Thus, it seems that without heat recuperation, the process is rather inefficient.

Finally, the hydrogen yield shows the same saddle-type behavior than the hydrogen concentration, with a maximum along the diagonal (with an O/C of about 1.7).

The results indicate that the performance of the plasmatron fuel reformer is dependent on the overall O/C ratio, and rather independent of the distribution of the air (in either swirl air or wall air). The swirl air needs to be sufficiently high to result in the generation of a plasma in the volume of the plasmatron. For swirl air flow rates less than about 40 lpm, the plasma remained in the electrode gap, not being pushed out into the volume of the reactor.

The results in Figures 2 and 3 will be used in the Partially Stirred Reactor (PaSR) analysis discussed in an accompanying paper.

The experiments were repeated for lower O/C ratios, in order to determine the dependence of the process parameters in this regime, even though it results in non-optimal reforming. As in the experiments described above, the methane flow is 0.45 g/s. and the axial air flow was changed. However, the swirl air flow was held constant. The methane was premixed with the swirl air, as in the previous experiments. The results are shown in Figure 4, as a function of the O/C ratio.

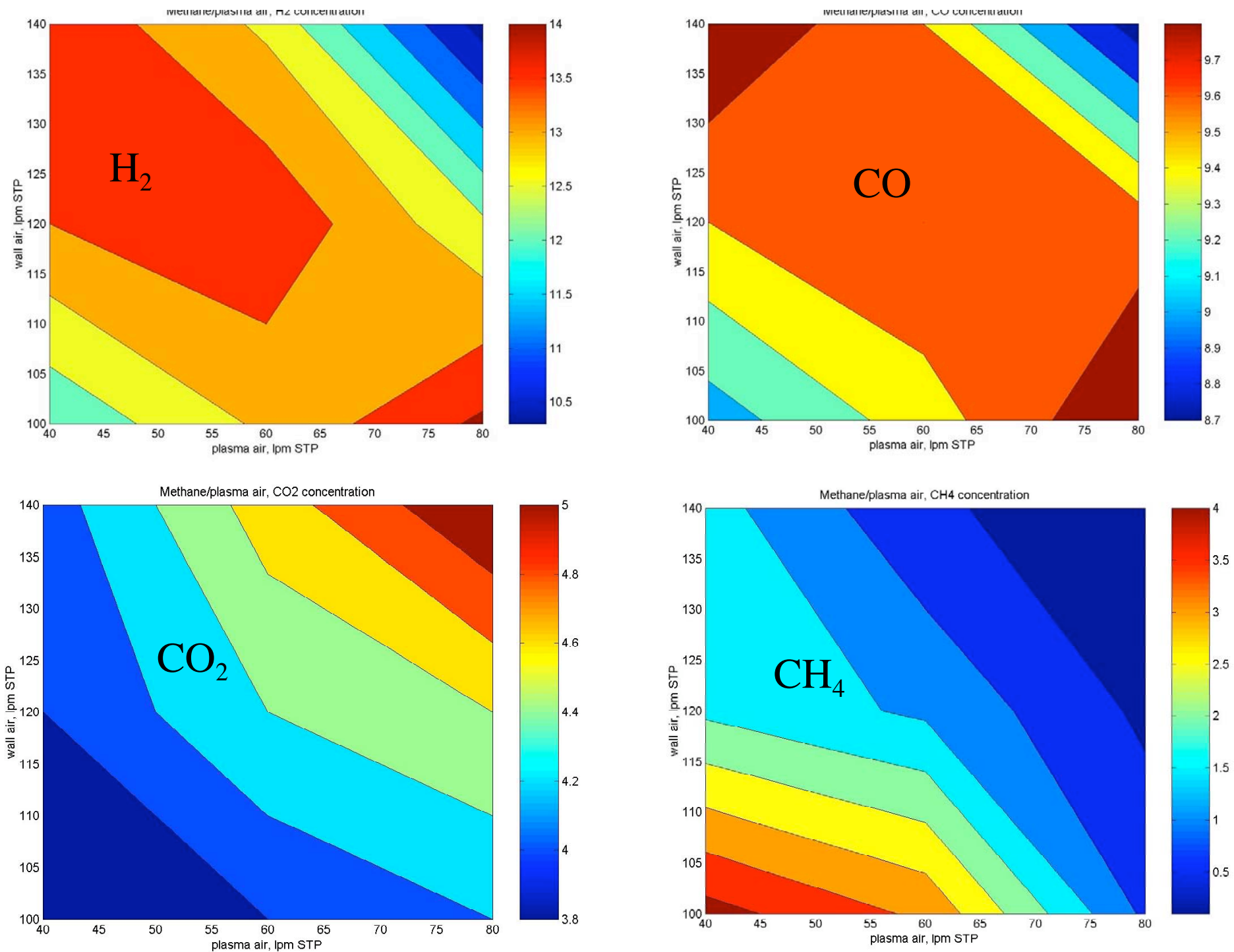


Figure 2. Contours of constant H₂, CO, CO₂ and CH₄ as a function of swirl air (plasma air) and axial air (wall air)

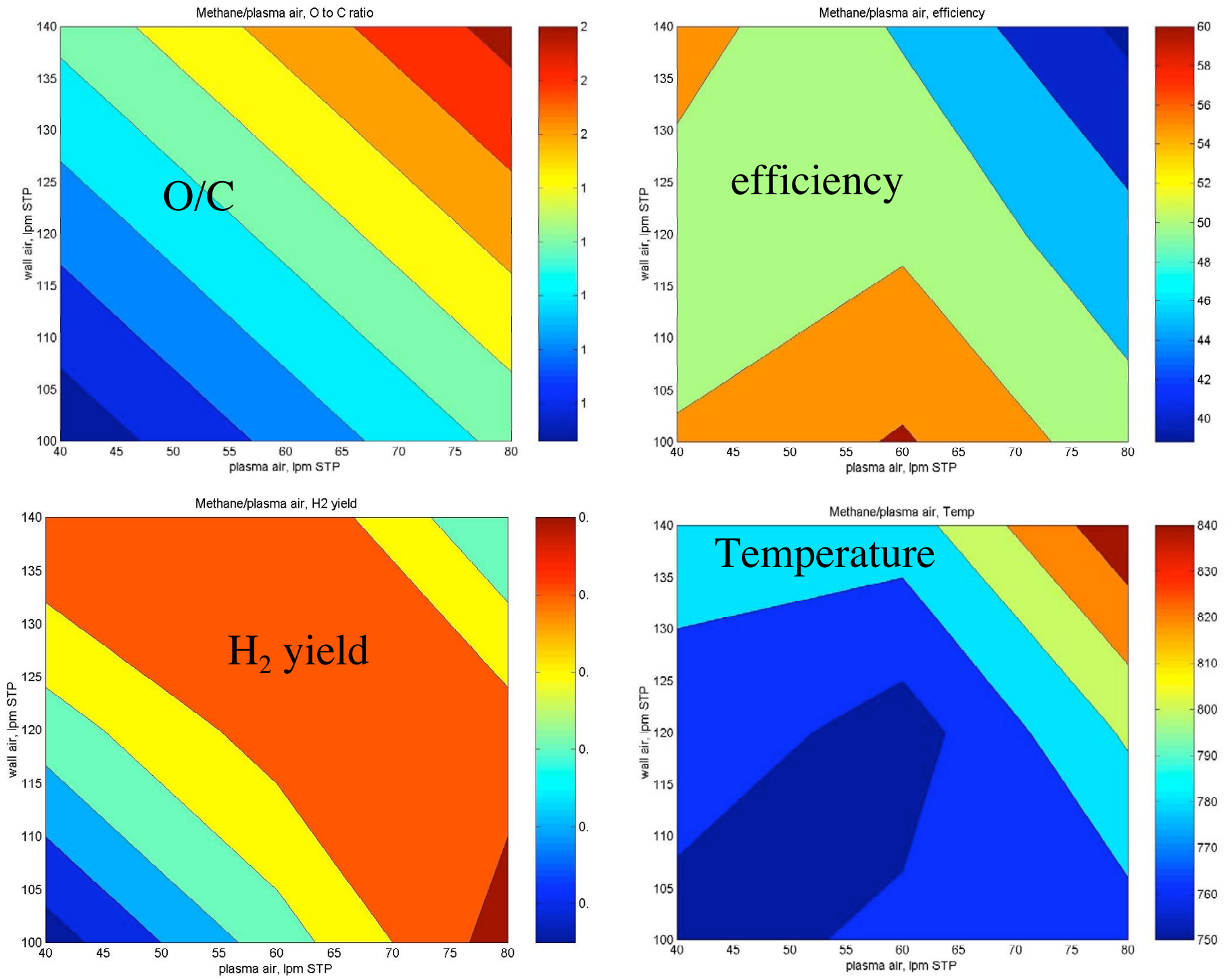


Figure 3. System parameters for the same conditions as Figure 2; (a) O/C (b) efficiency (c) H₂ yield and (d) Reactor temperature

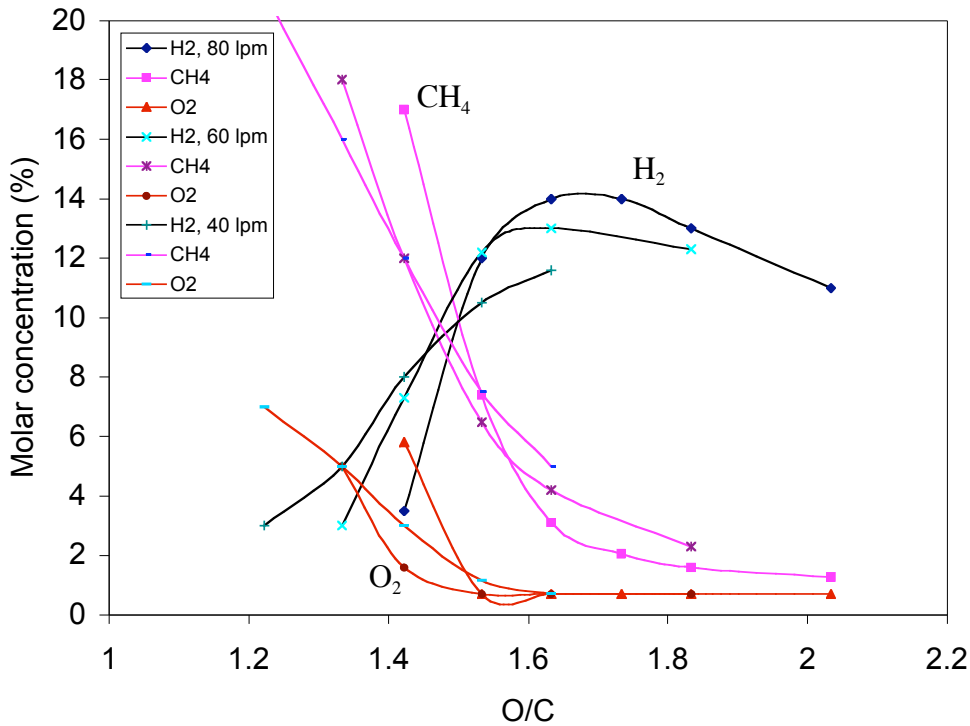


Figure 4. Molar concentration of hydrogen, methane and oxygen as a function of O/C for air flows in the swirl gas of 40, 60 and 80 lpm.

Figure 4 shows a larger dependence on the hydrogen concentration on the O/C ratios, for ratios lower than those from Figures 2 and 3. The threshold for good reforming is $O/C \sim 1.6$, which agrees with the results in an accompanying paper [33]. The methane conversion also increases relatively fast (and the methane conversion drops) at O/C ratios lower than 1.6. The oxygen concentration follows the methane concentration.

It can be seen that the results of Figure 4 do not quite agree with those shown in Figures 2 and 3. The reforming “cliff” that is clearly seen in Figure 4 is not noticed in Figures 2 and 3, although there is only one point in Figures 2 and 3 that operate at O/C less than 1.6, and even then it operates at $O/C \sim 1.43$ for the swirl flow rate where the hydrogen concentration is the least sensitive to O/C in Figure 4. This inconsistency is thought to be due to the uncertainty in the measurement of the O/C, as mentioned in the previous section.

3.2 Reforming without plasma

In order to determine the effects due to the plasma, we have investigated the reforming in the absence of plasma. Once the reactor achieves steady state with the plasma on, it is shut off and then allowed to reach a new equilibrium.

It has been found that the reforming in the absence of the plasma is very sensitive to the flow rates. The results from the effect of the plasma were obtained in a different run than those in the previous section, where the effect of the plasma was explicitly investigated as a function of the flow rates of swirl air and wall air, for constant methane flow. Because the pressure varied during the experiments, it was necessary to adjust the rotameters. Even then it is hard to control the methane flow to better than about 10-20%. Some of the reproducibility issues in this paper may be due to this issue. By contrast, we think that the air mass flow controllers are relatively accurate.

We have tried to eliminate the problem by using the GC and MS gas analysis to determine the gas composition prior to start up of the reformer, to determine the ratio of O/C, and comparing it with the calculated O/C ratio from the known input flow rates. Using this method shows a disagreement with the O/C calculated from the flow rates of the reagents of about 25%.

Results of reforming without the plasma are shown in Figures 5 and 6. The hydrogen and CO concentrations are slightly lower than in the case with the plasma on, by about 30%. But the flow rate is about 20% higher, and thus the hydrogen yields are comparable in both cases, about 35-40%. Methane concentration is lower in the case of no plasma by about a factor of 2, while the CO₂ concentration is slightly higher. Thus, more of the methane is being converted but it is going into combustion products rather than hydrogen or CO.

The efficiency is not shown in Figure 6, as it is misleading, with best efficiency when there is no conversion.

The effect of plasma vs no plasma is dramatically shown in Figure 7. After achieving steady state conditions without plasma, the plasma was turned on. The transients are measured with the mass spectrometer, and steady state concentrations of hydrogen, water, oxygen and methane following the plasma turn-on were measured. It should be noted that the temperature, as indicated by the thermocouple in the middle of the reactor, did not reach steady state conditions.

Figure 7 shows the concentration of hydrogen with and without plasma, as a function of O/C, for several values of the swirl air flow. This figure shows that at the high O/C (> 2) the plasma plays a minor role. However, it plays a major role for lower O/C. The critical O/C ratio for the case of no plasma is around 2, as compared in Figure 4 in the case of plasma, of about 1.6.

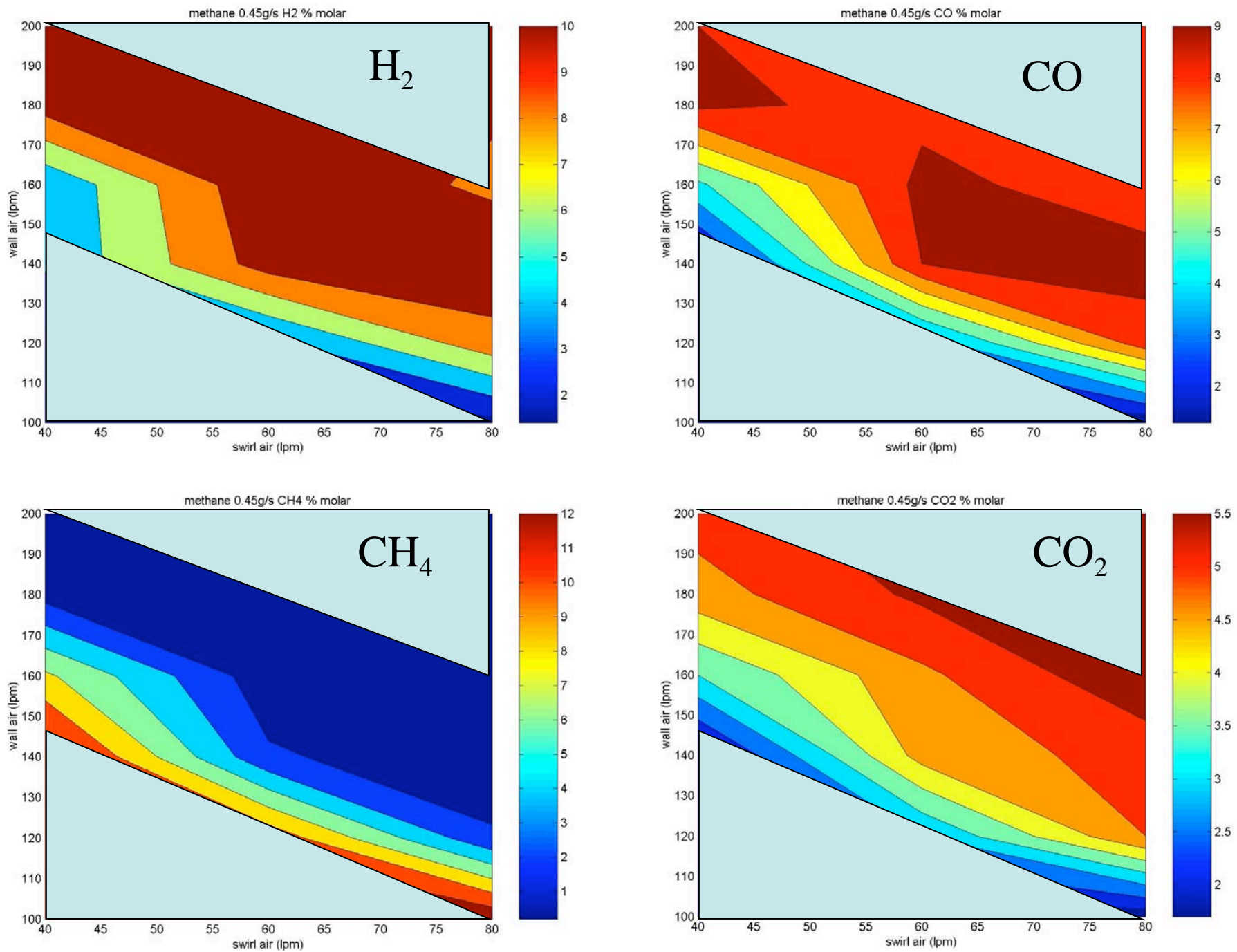


Figure 5. Same as Figure 2 but in the absence of plasma.

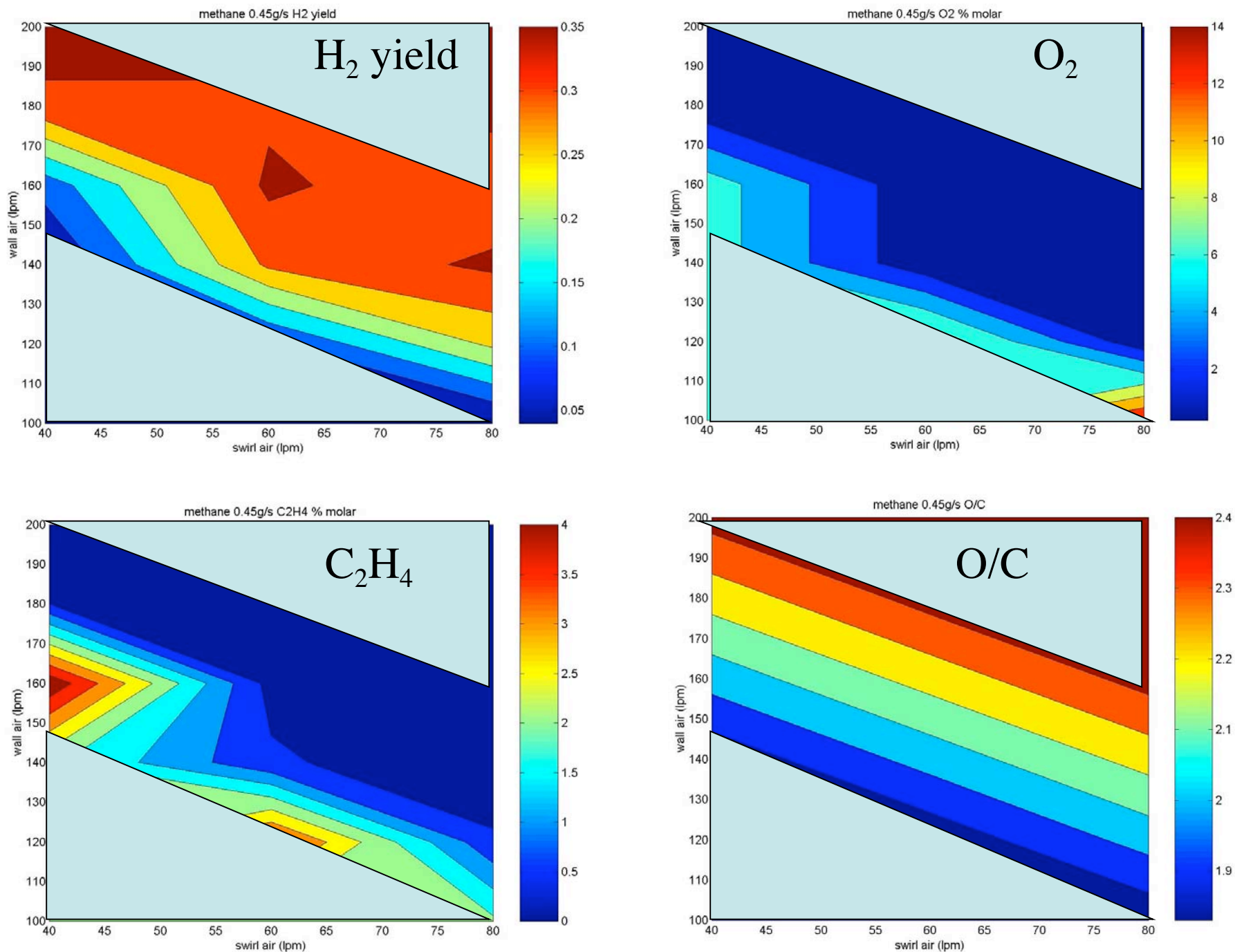


Figure 6. Hydrogen yield, oxygen and C₂'s concentration in reformat, as well as O/C for the cases also shown in Figure 5

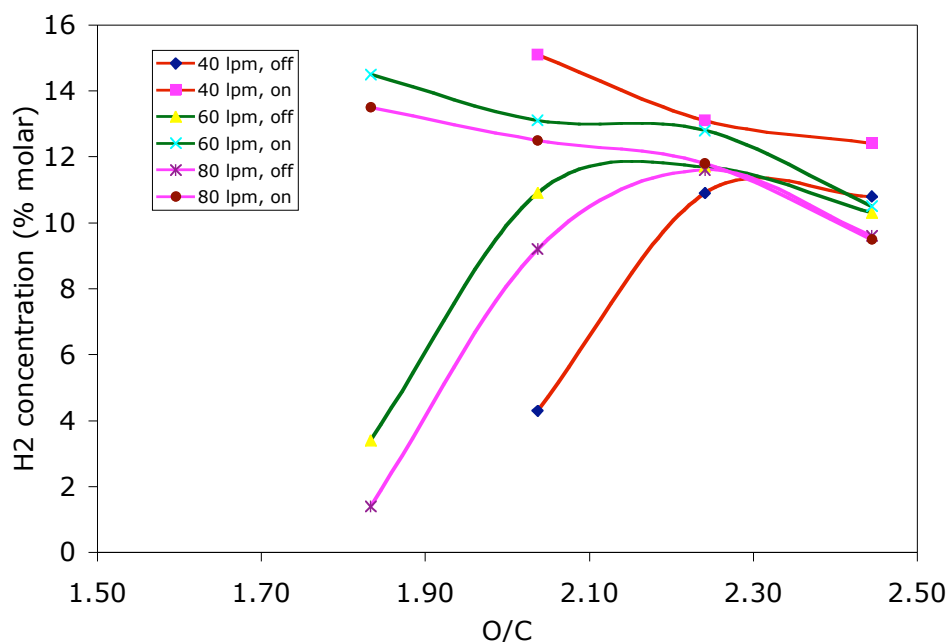


Figure 7. Hydrogen concentration as a function of the O/C ratio for several values of the swirl air flow rate, with and without the plasma.

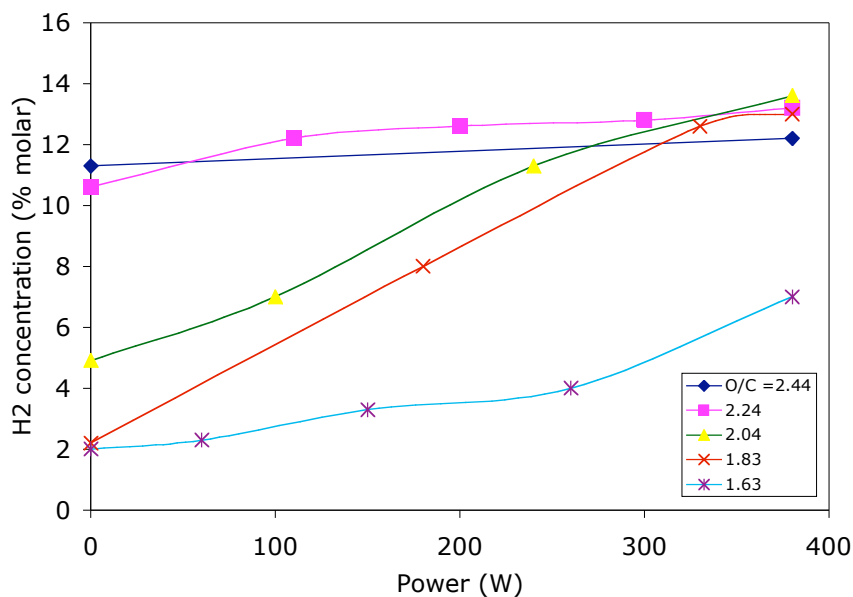


Figure 8. Dependence of H₂ concentration as a function of power for various values of O/C, for a swirl air of 60 lpm and 0.45 g/s methane flow.

4 Power effect

The effect of the plasma power on the methane reforming was also investigated. The experiments were performed at various O/C ratios, with the reactor already warmed up. The gas composition with high power (~380 W) and no plasma power were measured

using the GC and the MS, while at other power levels they were measured only with the MS. The swirl air is held constant at 60 lpm, and the O/C is varied by changes in the wall air.

Figure 8 gives the results of these experiments. At high values of O/C, the effect of the plasma power is relatively small, with a ~20% drop in hydrogen concentration. It should be noted that the maximum hydrogen concentration occurs with plasma, at an O/C ~ 2. However, when the hydrogen concentration was optimized at this O/C ratio, there was substantial sensitivity to the plasma power, with large drop in methane conversion at powers less than about 300 W. The carbon balance is within 5%, but as with the previous sections, there is a difference of 7-15% between the O/C calculated from the flows and that measured from the GC. The O/C measured is higher than that calculated from the flows.

6 Conclusions

In this paper the effect of the distribution of the air was investigated, at fixed methane flow rate. Only conditions of steady state have been investigated, with an accompanying paper describing the start up. It was determined that the hydrogen concentration and yields depended on the overall O/C ratio, and that the distribution of the air between swirl and wall had only a small effect.

The effect of the plasma power was investigated. It was determined that the need of the plasma depends on the O/C ratio. At high O/C ratios (O/C ~ 2.2) the dependence on plasma power is small, with a ~20% decrease in hydrogen concentration without the plasma. However, at O/C ~ 2, the plasma is needed, and higher power is better. At even lower O/C ratios (O/C < 1.6), the reforming even in the presence of plasma, is poor.

The results are compared with modeling in accompanying papers.

Acknowledgements

This work was performed under auspices of ArvinMeritor, ChevronTexaco and Department of Energy, Office of FreedomCar and Vehicle Technologies. The support and interest from Dr. S. Diamond from DoE, R. Smaling and N. Khadya, from ArvinMeritor, and T. Rufael, from ChevronTexaco, are appreciated.

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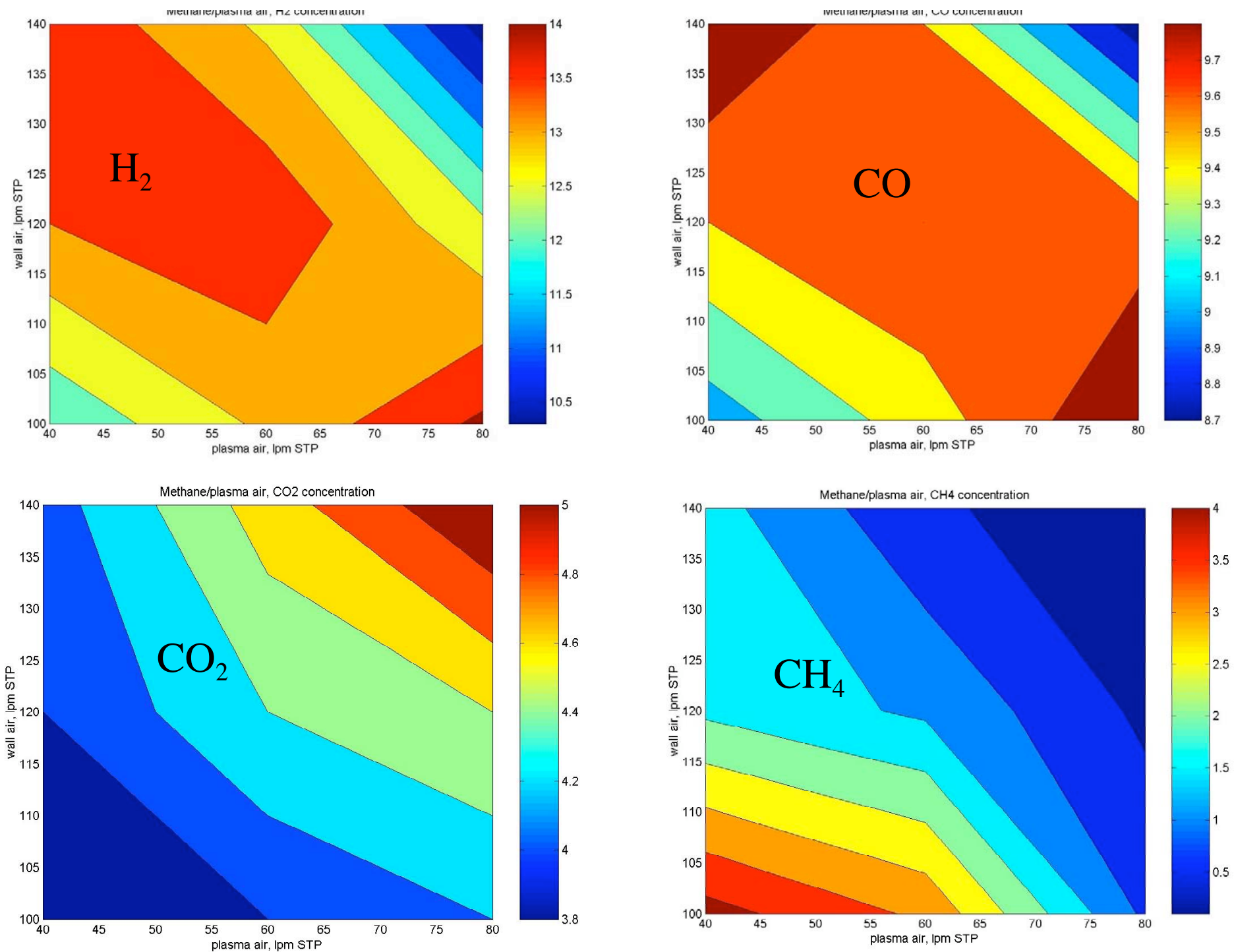


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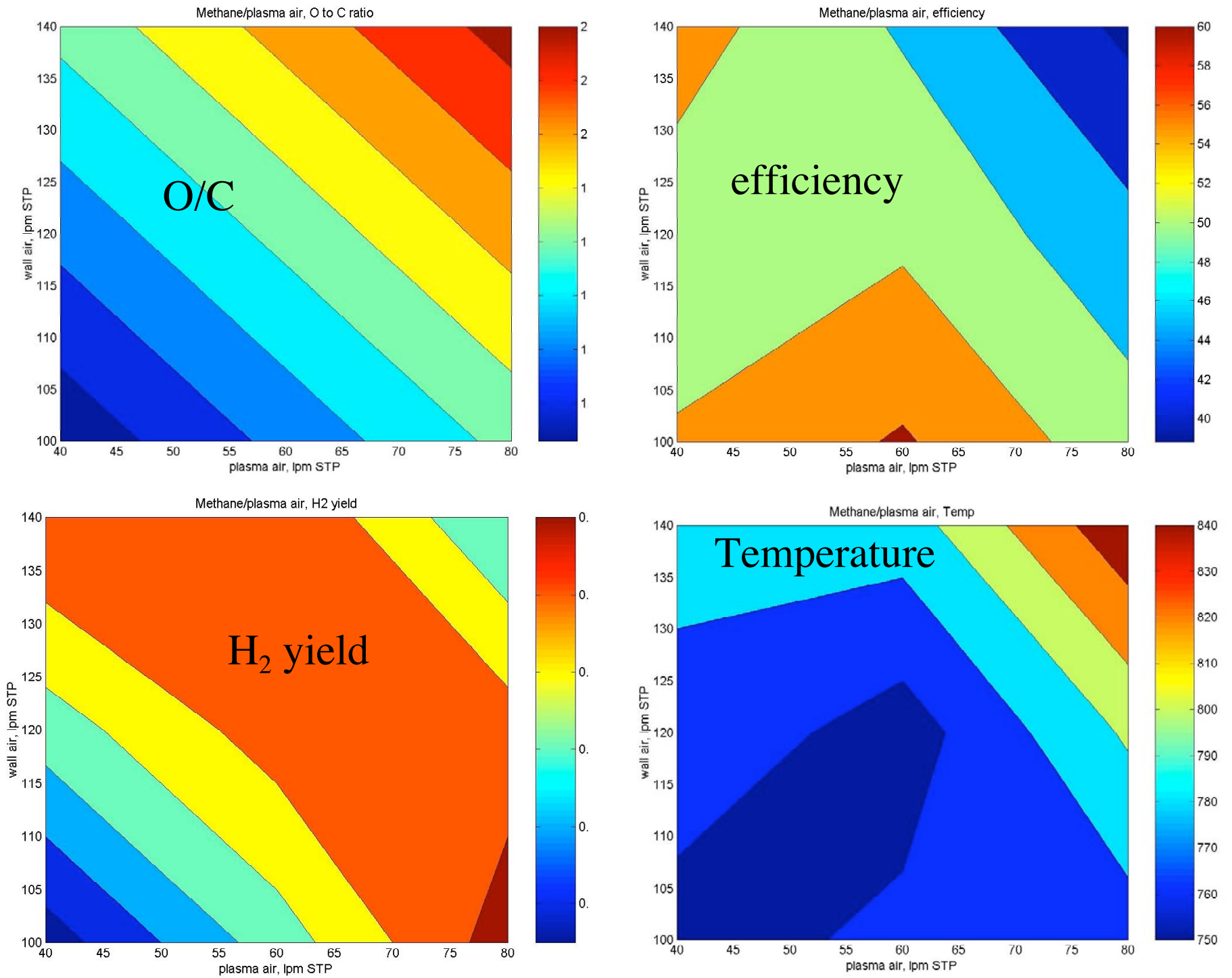


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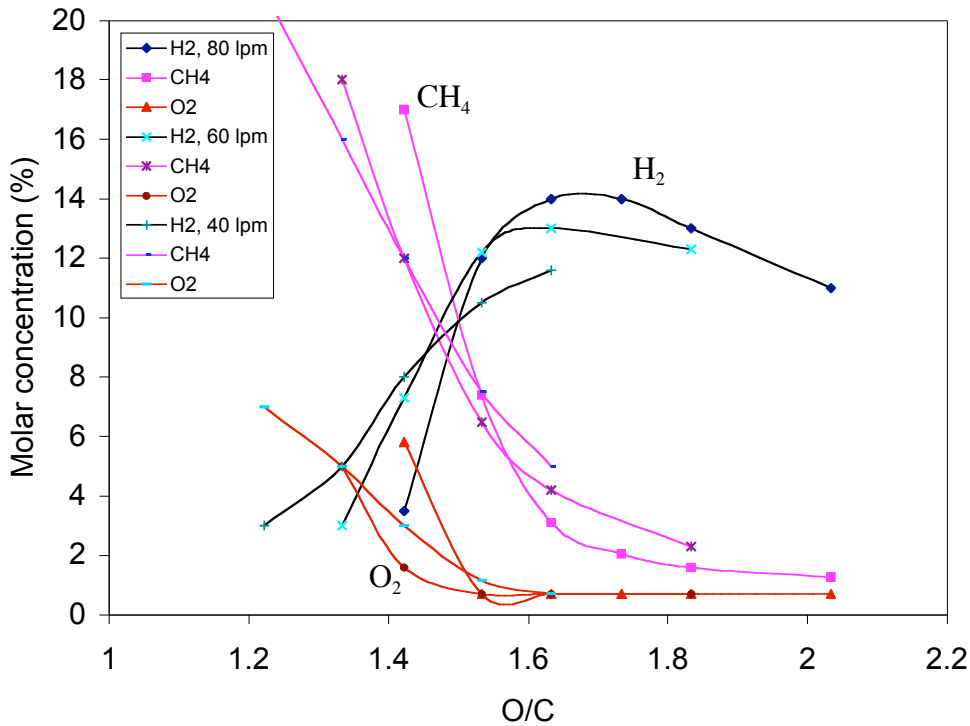


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It has been found that the reforming in the absence of the plasma is very sensitive to the flow rates. The results from the effect of the plasma were obtained in a different run than those in the previous section, where the effect of the plasma was explicitly investigated as a function of the flow rates of swirl air and wall air, for constant methane flow. Because the pressure varied during the experiments, it was necessary to adjust the rotameters. Even then it is hard to control the methane flow to better than about 10-20%. Some of the reproducibility issues in this paper may be due to this issue. By contrast, we think that the air mass flow controllers are relatively accurate.

We have tried to eliminate the problem by using the GC and MS gas analysis to determine the gas composition prior to start up of the reformer, to determine the ratio of O/C, and comparing it with the calculated O/C ratio from the known input flow rates. Using this method shows a disagreement with the O/C calculated from the flow rates of the reagents of about 25%.

Results of reforming without the plasma are shown in Figures 5 and 6. The hydrogen and CO concentrations are slightly lower than in the case with the plasma on, by about 30%. But the flow rate is about 20% higher, and thus the hydrogen yields are comparable in both cases, about 35-40%. Methane concentration is lower in the case of no plasma by about a factor of 2, while the CO₂ concentration is slightly higher. Thus, more of the methane is being converted but it is going into combustion products rather than hydrogen or CO.

The efficiency is not shown in Figure 6, as it is misleading, with best efficiency when there is no conversion.

The effect of plasma vs no plasma is dramatically shown in Figure 7. After achieving steady state conditions without plasma, the plasma was turned on. The transients are measured with the mass spectrometer, and steady state concentrations of hydrogen, water, oxygen and methane following the plasma turn-on were measured. It should be noted that the temperature, as indicated by the thermocouple in the middle of the reactor, did not reach steady state conditions.

Figure 7 shows the concentration of hydrogen with and without plasma, as a function of O/C, for several values of the swirl air flow. This figure shows that at the high O/C (> 2) the plasma plays a minor role. However, it plays a major role for lower O/C. The critical O/C ratio for the case of no plasma is around 2, as compared in Figure 4 in the case of plasma, of about 1.6.

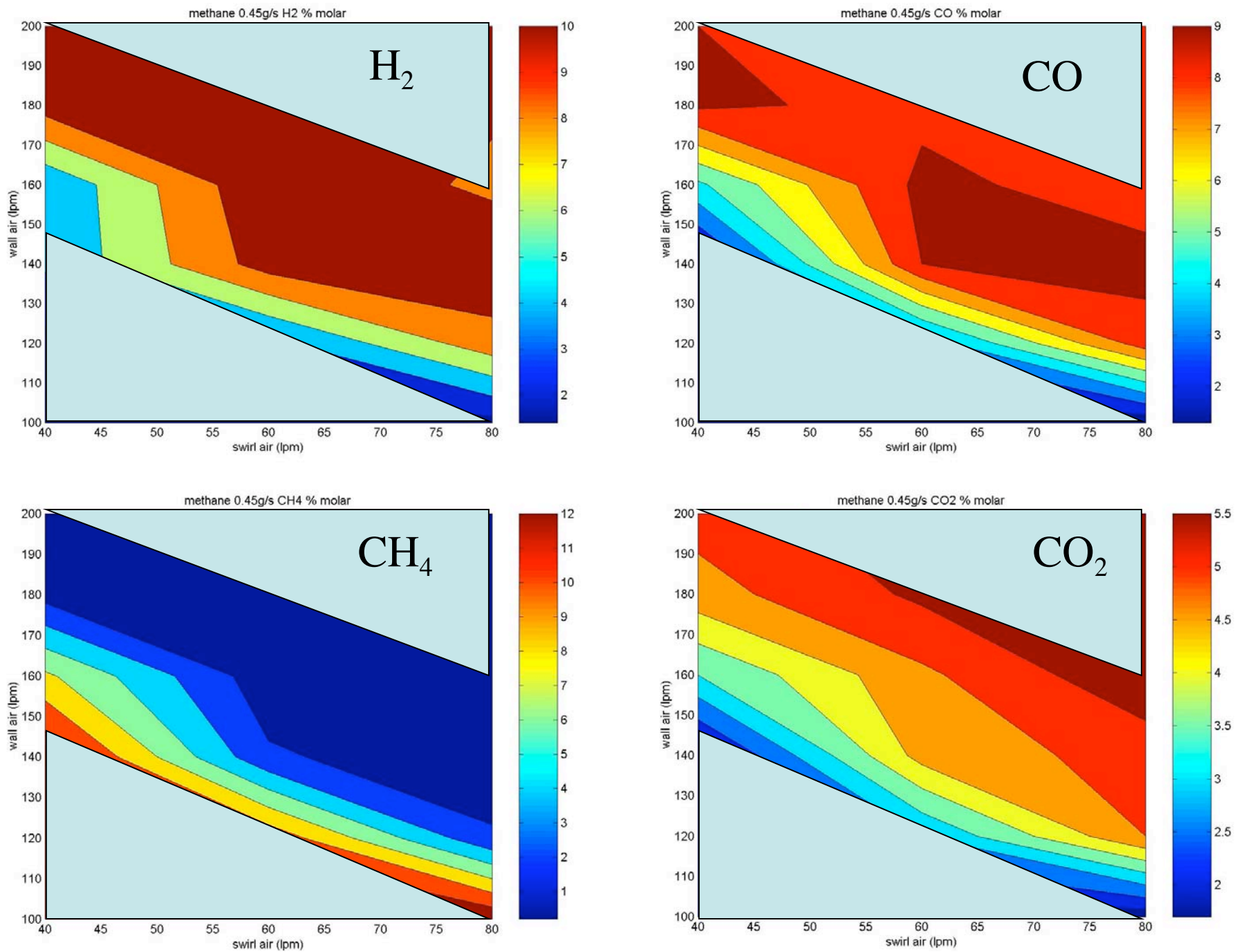


Figure 5. Same as Figure 2 but in the absence of plasma.

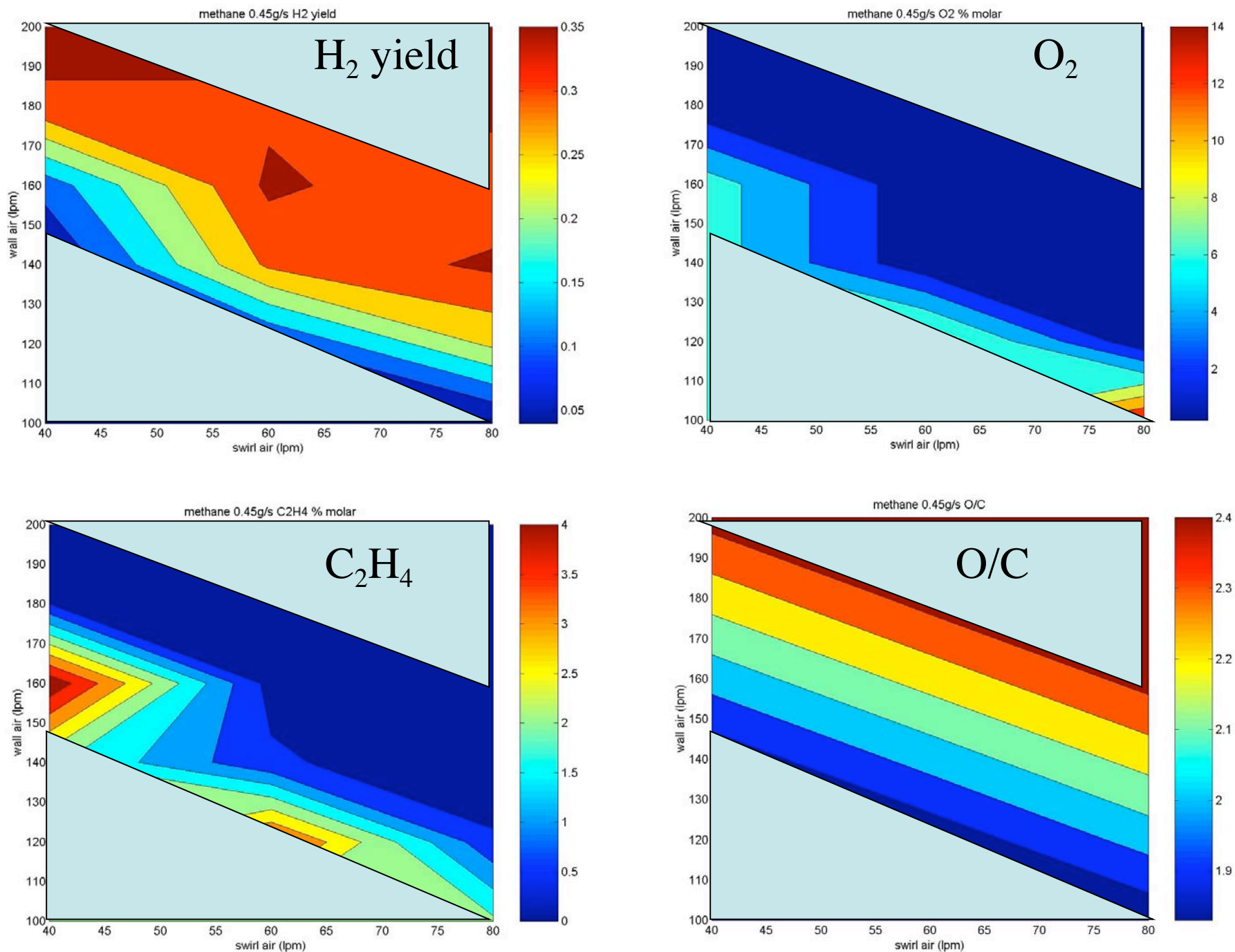


Figure 6. Hydrogen yield, oxygen and C₂'s concentration in reformat, as well as O/C for the cases also shown in Figure 5

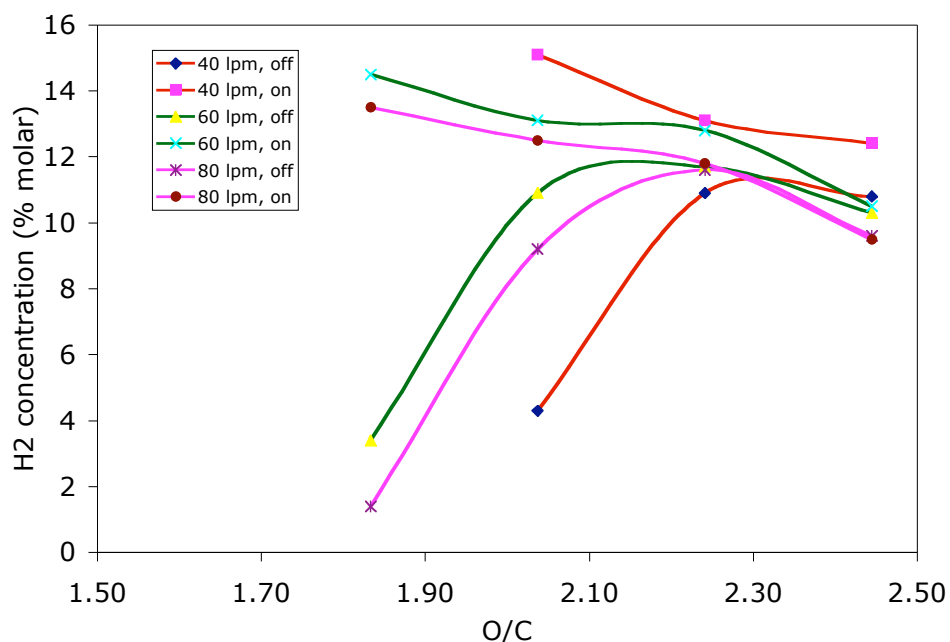


Figure 7. Hydrogen concentration as a function of the O/C ratio for several values of the swirl air flow rate, with and without the plasma.

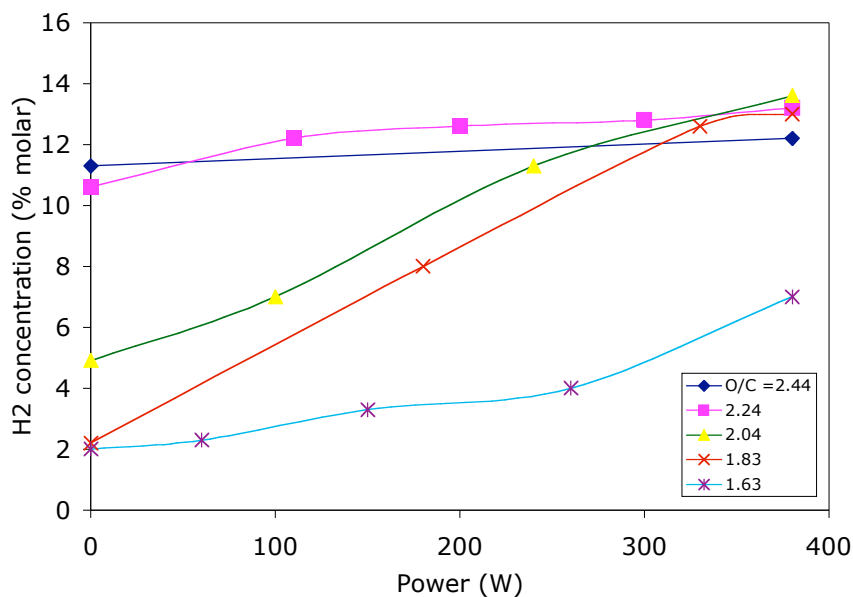


Figure 8. Dependence of H₂ concentration as a function of power for various values of O/C, for a swirl air of 60 lpm and 0.45 g/s methane flow.

4 Power effect

The effect of the plasma power on the methane reforming was also investigated. The experiments were performed at various O/C ratios, with the reactor already warmed up. The gas composition with high power (~380 W) and no plasma power were measured

using the GC and the MS, while at other power levels they were measured only with the MS. The swirl air is held constant at 60 lpm, and the O/C is varied by changes in the wall air.

Figure 8 gives the results of these experiments. At high values of O/C, the effect of the plasma power is relatively small, with a ~20% drop in hydrogen concentration. It should be noted that the maximum hydrogen concentration occurs with plasma, at an O/C ~ 2. However, when the hydrogen concentration was optimized at this O/C ratio, there was substantial sensitivity to the plasma power, with large drop in methane conversion at powers less than about 300 W. The carbon balance is within 5%, but as with the previous sections, there is a difference of 7-15% between the O/C calculated from the flows and that measured from the GC. The O/C measured is higher than that calculated from the flows.

6 Conclusions

In this paper the effect of the distribution of the air was investigated, at fixed methane flow rate. Only conditions of steady state have been investigated, with an accompanying paper describing the start up. It was determined that the hydrogen concentration and yields depended on the overall O/C ratio, and that the distribution of the air between swirl and wall had only a small effect.

The effect of the plasma power was investigated. It was determined that the need of the plasma depends on the O/C ratio. At high O/C ratios (O/C ~ 2.2) the dependence on plasma power is small, with a ~20% decrease in hydrogen concentration without the plasma. However, at O/C ~ 2, the plasma is needed, and higher power is better. At even lower O/C ratios (O/C < 1.6), the reforming even in the presence of plasma, is poor.

The results are compared with modeling in accompanying papers.

Acknowledgements

This work was performed under auspices of ArvinMeritor, ChevronTexaco and Department of Energy, Office of FreedomCar and Vehicle Technologies. The support and interest from Dr. S. Diamond from DoE, R. Smaling and N. Khadya, from ArvinMeritor, and T. Rufael, from ChevronTexaco, are appreciated.

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