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**Plasma Assisted Reforming of Methane II:
Partially Stirred Reactor (PaSR) Simulation**

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Abstract

Plasmatron fuel converters have been investigated for the conversion of a wide range of fuels. This paper is a series of papers describing an experimental and computational study of plasmatron methane reformers. This paper presents a model that uses limited mixing and chemical kinetics to investigate the plasma assisted reforming of natural gas. The Partially Stirred Reactor (PaSR) model from the software package CHEMKIN is used in the analysis. Comparison with plasmatron methane reforming experiments is made.

1 Introduction

In an accompanying paper, the use of two step reforming has been used to model a plasmatron methane reformer [1]. The model assumes that a fraction of the air/fuel mixture combusts stoichiometricly, and then the combustion products mix with the balance air/fuel in a Perfectly Stirred Reactor (PSR). The model did provide quantitative agreement with experiments with a plasmatron methane reformer, in particular on the critical O/C ratio needed for homogeneous reaction, but failed to reproduce the observed concentrations. It was speculated in that paper that the reason was the use of instantaneous combustion (equilibrium conditions) in the first step and instantaneous mixing in the second step that is characteristic of the Perfectly Stirred Reactor, although the model did include finite kinetics in the second step. In this paper, we investigate the possibility of improved agreement by including finite rate of mixing.

The experimental results are described in accompanying papers that describe the steady state experiments with the plasmatron methane reformer [2] and experiments with transients, mainly cold startups [3]. All these experiments and the modeling in this and in the accompanying papers were carried in a reactor without a catalyst to investigate the gas phase chemistry of the plasmatron methane reformer. In an additional accompanying paper [4] a model of fluid dynamics of the plasmatron methane reformer has been investigated. The model in that paper does not include chemistry, and thus can be used to investigate the mixing prior to the region of substantial energy release from the chemistry. However, it provides a framework as for the level of mixing and the distribution of air/fuel mixture through the region of the plasma.

A previous paper attempted to simulate reformers, and in particular plasma reformers, using the Partial Stirred Reactor (PaSR) [5]. That work used the PaSR code [6] available from CHEMKIN 3.7 [7], which did not provide an adequate model because of inadequate input flexibility.

In section 2, a simple model of the plasmatron methane reformer used in the experiments and modeled in the analysis is described. In section 3 the Partially Stirred Reactor (PaSR) model is described, including the assumptions and parameters used in the study. Section 4 described the results of the PaSR code. Section 5 discusses the results and compares them with the experimental results. Finally, Section 6 presents the conclusions.

2 Brief description of the setup

The setup used in the experiments, as well as the experimental results, have been reported in the accompanying papers [2,3], and will only briefly be described here.

The plasmatron used in the experiments [2,3] has two gaseous flows, the wall gas and the swirl gas. The wall gas is injected in the axial direction next to the cylindrical wall of the plasmatron and an axial location similar to the location of the axial nozzle, and is injected without swirl. The swirl gas is injected downstream from the wall air, with a large amount of vorticity (a tangential velocity) in the electrode gap, and serves as the plasma

gas when the plasma is on. The radial component of the swirl gas displaces the discharge towards the axis of the plasmatron, and the tangential component provides the rotation motion that moves the arc roots on the electrodes (to minimize electrode erosion).

The experimental results were carried out with methane premixed with the swirl air, and the balance air injected through the axial gas. This option was used because extensive experiments with propane indicated that it resulted in the best reforming [7].

Downstream from the plasmatron head there is a 5 in long section of the reaction extension cylinder which is also included in the model. The volume of this region is approximately 1000 cm³.

The axisymmetric, steady state fluid dynamic solution has been calculated using a commercially available CFD code, FLUENT, and reported previously [4]. The model was used to determine the effect of initial conditions on the mixing upstream the region where sufficient thermal energy has been released to modify the result, downstream from the plasma region.

3 Partially Stirred Reactor Model

To simulate the limited mixing rates, the PaSR model [5] from CHEMKIN 4.0.2 [7] has been used. The code used was an updated, beta version of the PaSR routine, provided to us by Chou [8]. The code assumes a large number of elements, each individual element being a perfectly stirred reactor. For the present calculations 1000 elements were used. Several initial conditions have been used. The code allows for control of the mixing time and the residence time. The model allows for flexible input of the elements; however, there is a single number of the mixing time, which is assumed constant throughout the reaction volume.

The GRI 3.0 mechanism was used in the calculations [10]. This mechanism has been developed to model methane combustion over a very wide range of conditions. It has 53 species and about 350 equations. The temperature of the combustion products in the first step is about 2200 K, at which temperature substantial levels of NO and nitrogen-carbon compounds are made. Nitrogen chemistry is followed.

Figure 1 shows schematically the reactor network. Since it is in steady state, the input flow rates are balanced by output flow rates, not show in Figure 1. The parameter of the inputs will be described below. The PaSR reactor is described by identifying the number of elements (1000), the residence and the mixing times, the pressure and the initial conditions. The results are dependent on the initial conditions, but it has also been experimentally determined that certain parameters are more conducive to ignition and good conversion.

The experimental setup had two independent flows, the swirl flow and the axial flow. The experimental results evaluated in this paper have swirl gas that is composed of all the methane and ***** some of the air. The methane flow in the experiment was 0.45 g/s,

corresponding to a heat of combustion of about 25 kW. The O/C ratio of the experimental points investigated in this paper is varied by changing the axial air.

The model used three independent input flows. The first flow represents the arc discharge, which is modeled using a high temperature gas, with the composition of the swirl gas. The assumed temperature of the plasma gas is 2400 K. There is some indirect evidence that this is the temperature of the arc, through high temperature chemistry (formation of nitrogen oxides in the absence of fuel, formation of acetylene in the absence of air), and power balance from fast frame images of the discharge [11].

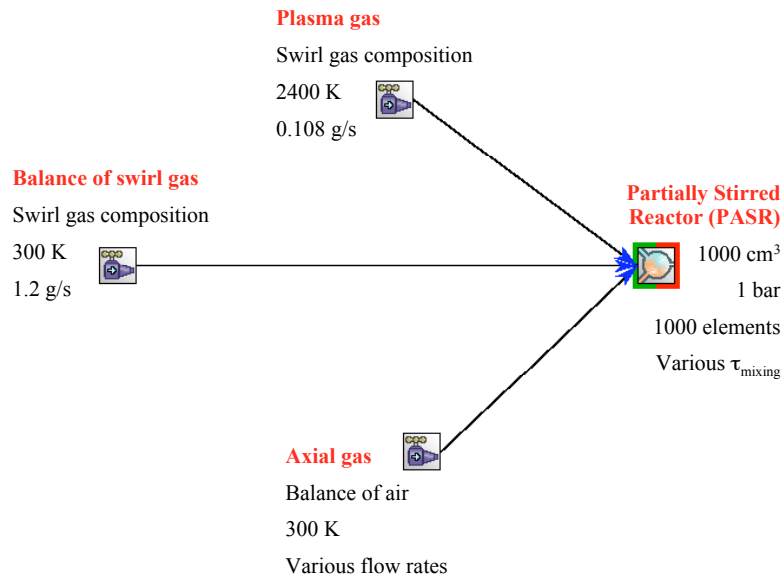


Figure 1. Schematic diagram of the PASR model showing the different flow inputs

Table 1
Flow rates of axial air for the overall O/C ratios considered

O/C	Axial air (g/s)
1.43	2.16
1.63	2.59
1.83	3.02

The total flow rate of the swirl air is 1.2 g/s. The swirl air is premixed with the methane, 0.45 g/s, thus the flow of swirl air of 0.86 g/s, or 40 lpm (STP). The plasma gas is just a fraction of the swirl gas that goes through the plasma region and gets heated to the plasma temperature, 2400 K. The flow rate of this hot gas corresponds to the power delivered by the power supply. In the experiments the plasma power during most of the steady state experiments is ~ 375 W. For this power, this temperature and gas composition, the flow rate of the high temperature gas is 0.108 g/s. The impact of the turning off the plasma is investigated by changing the temperature of the plasma gas from

2400 K to 300 K. The balance of the swirl flow that is not plasma is at room temperature (300 K).

The third input flow is the wall air, adding up to the overall air flow rate. The temperature of the third input flow is 300 K. The flow rate of this gas varies, to model the experimental results and to change the O/C ratio. The axial air flow rate varies as shown in Table 1.

The residence time in the reactor is variable, as the volume of the reactor is constant (1000 cm³). The residence time is determined by the volume of the reactor, the average density of the gases in the reactor, and the mass flow rate.

The simulation is a statistical simulation using the MonteCarlo method. Each element of the simulation is modeled as a Perfectly Stirred Reactor. Every MonteCarlo time step random cells are mixed (with both mass and heat transfer), some are removed and new ones are introduced. The overall response of the system is such to reproduce the mixing time, the average residence time in the reactor and the characteristics of the input (mass flow rates, input composition and temperatures of the gases [6]).

The MonteCarlo step is an input that has been varied through the calculations, but it is on the order of 150 μ s. The time has to be long enough to insure that some elements in the reactor are changed, but small enough to make sure that the number of the introduced elements do not significantly change the instantaneous composition or temperature in the reactor.

Several mixing models have been used. The IEM (Interchange by Exchange with Mean), as well as the CURL methods were used. There was no difference in the results using both methods, and thus only the results from the CURL method will be presented.

4 Partial Stirred Reactor (PaSR) Results

It is necessary to provide adequate initial conditions for the system to evolve to a steady state condition with good reforming. The results are dependent on initial conditions (initial composition and temperature). If these initial conditions are not provided, such as if the reactor is filled with room temperature reagents, the solution reached a low average temperature state, with little chemistry. Mathematically, there are two stable equilibrium states for a given set of inputs, and the one that is reached is dependent on the initial conditions. In this paper we are interested in the high temperature, steady state solution. It has been determined that if the initial temperature is > 1000 K, chemistry takes place and reaches steady state condition with adequate reforming.

The model provided in this paper deals only with steady state conditions, not with the startup conditions, which still need to be understood.

Once the reactor is started in a mode that results in a good conditions for reforming (high temperature), the inputs are modified and the run restarted to investigate the effect of the new conditions. The run is continued until steady state is obtained.

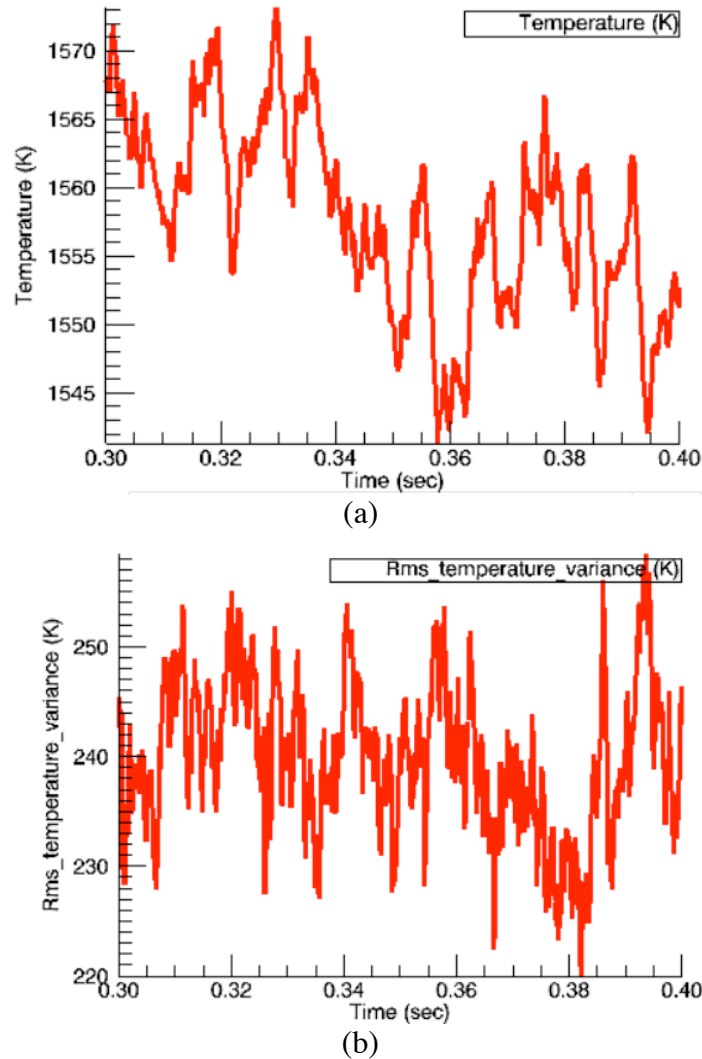


Figure 2. Typical transient (a) average reactor temperature and (b) reactor temperature variance for the case of $O/C \sim 1.63$ and $\tau_{\text{mix}} = 1$ ms.

Figure 2 shows the results for the transient to steady state in the case of $O/C \sim 1.63$ and $\tau_{\text{mix}} = 1$ ms. The average temperature is shown in Figure 2 (a), while the temperature variance is shown in Figure 2(b). There is a relatively short-lived transient at the start of the simulation (from 0.3 s through about 0.35 s), as the conditions of the simulation have changed. The transients after this short initial period are from fluctuations due to the statistical nature of the MonteCarlo simulation.

Figure 2 follows the transient for 0.1 s, starting from conditions obtained in the previous 0.3 s. The mixing time in Figure 2 is 1 ms, and thus there are plenty of mixing times for

reaching steady state. The residence time, on the other hand is about 0.02 s, and thus there are only about 5 residence times in the transient analyzed.

The mixing time although initially estimated from the fluid dynamic calculations, is not known once chemistry takes place. CFD calculations [4] indicate that inside the plasmatron head mixing is strong, with mixing times on the order of 100 μ s but with short residence times (the plasmatron volume is small), with longer residence times in the reaction extension cylinder (about 20 ms) and longer mixing times (about 1 ms). We have used the mixing time as a parameter, calculating the results for mixing times from 0.5 ms to 10 ms.

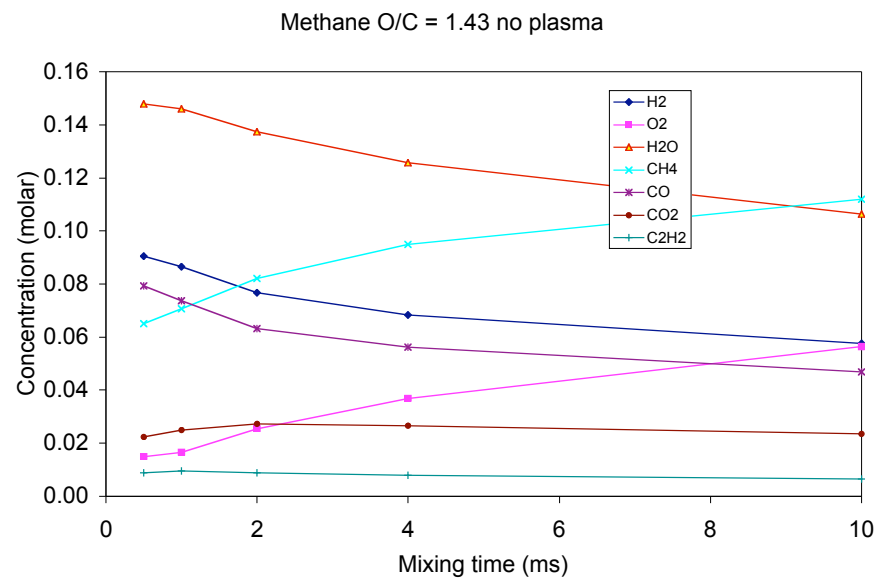
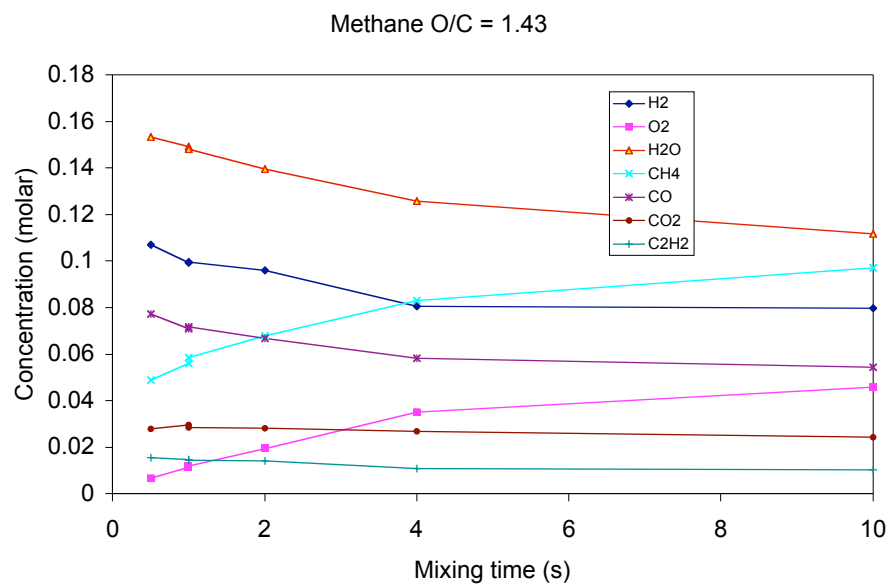
The results for O/C \sim 1.43 are shown in Figure 3. Figure 3a shows the concentrations (molar) of the reformat at the end of the simulation period, for different values of the mixing time, τ_{mix} . The balance is mostly nitrogen, with $< 1\%$ of other species.

Figure 3 show that the conversion of methane decreases (and so does the hydrogen concentration) as the mixing time is increased. The composition is relatively sensitive with mixing times for short mixing times, but then becomes relatively independent of mixing time. Similarly, the temperature decreases with increasing mixing time, and because of constant reactor volume, the residence time increases. The temperature variance also increases, as a direct result of reduced mixing.

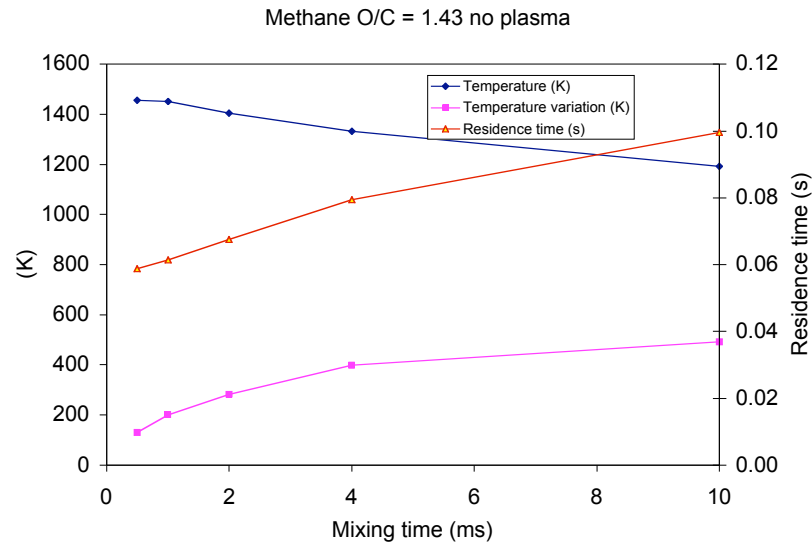
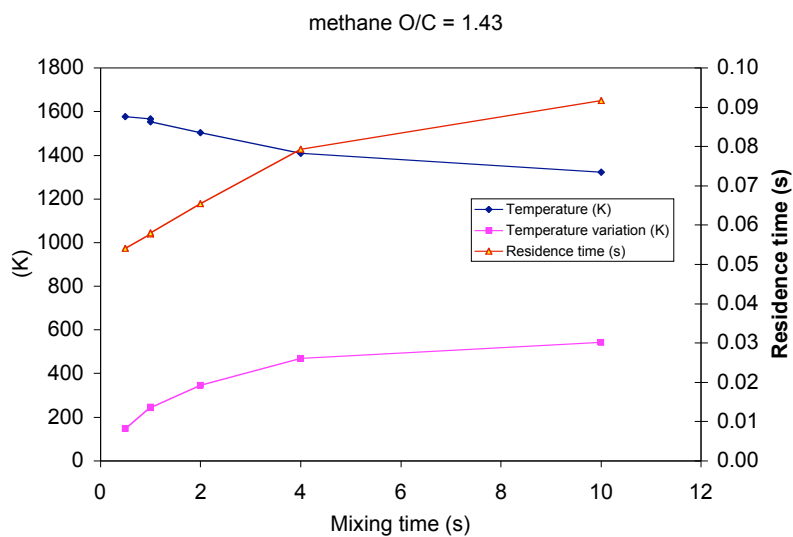
To investigate the effect of statistics, two points were calculated for the residence time of 1 ms. Both points are plotted in Figure 3 for the case with plasma. Although not thorough measurement of the statistics, it indicates the amount of spread in the curves, demonstrating that the error bars in Figure 3 are small.

Figure 3 shows also the case when the plasma is turned off. It is interesting to note that the reaction continues, at reduced temperature (by about 150 K), decreased temperature variance, and slightly reduced methane conversion (methane concentration up by about 30%, with hydrogen concentration decreasing by about 20%).

Figure 4 shows the results for the O/C ratio of 1.63. The trends are similar, with slightly higher methane conversion. The hydrogen concentration has remained relatively constant with respect to the previous case of O/C \sim 1.43, but the methane conversion is higher by about 25%. The hydrogen yield is up because although the concentration remained constant, the total flow rate has gone up. The test for spread was also performed in this Figure, but for the case with no plasma and 1 ms mixing time.

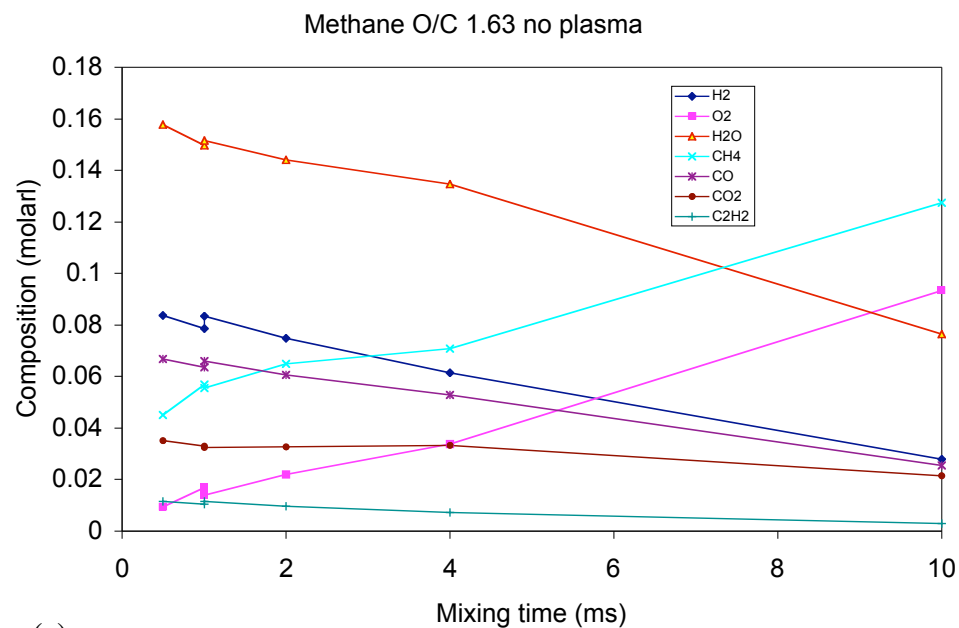
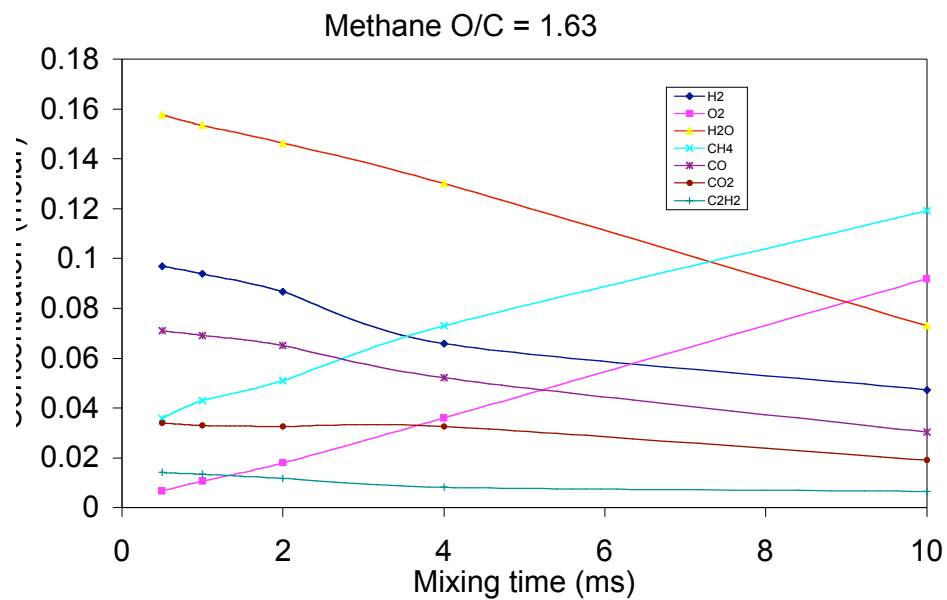


(a)

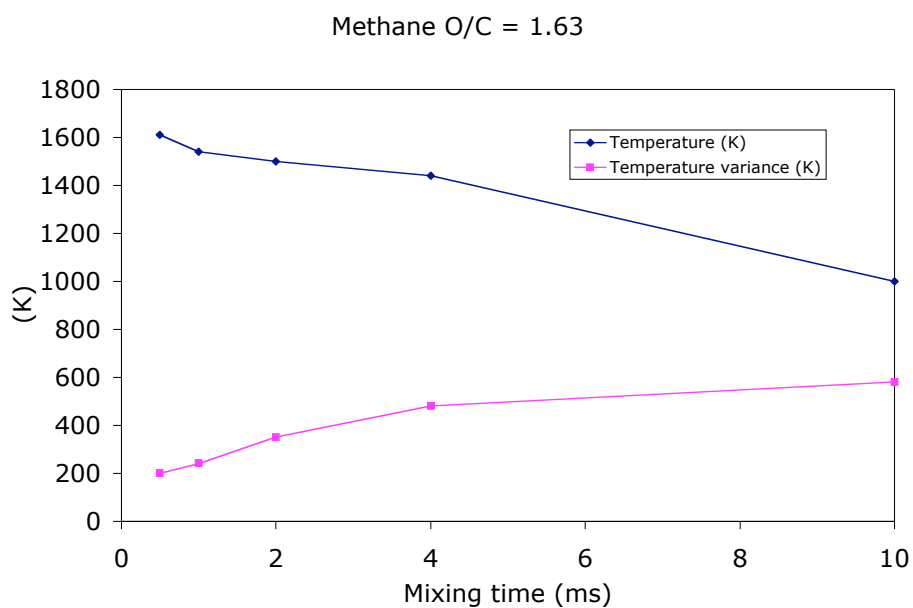


(b)

Figure 3. (a) Composition and (b) average temperature, temperature variance and residence time as a function of time for a mixing time. Figures on left are for plasma on while those on right are for plasma off.



(a)



(b)

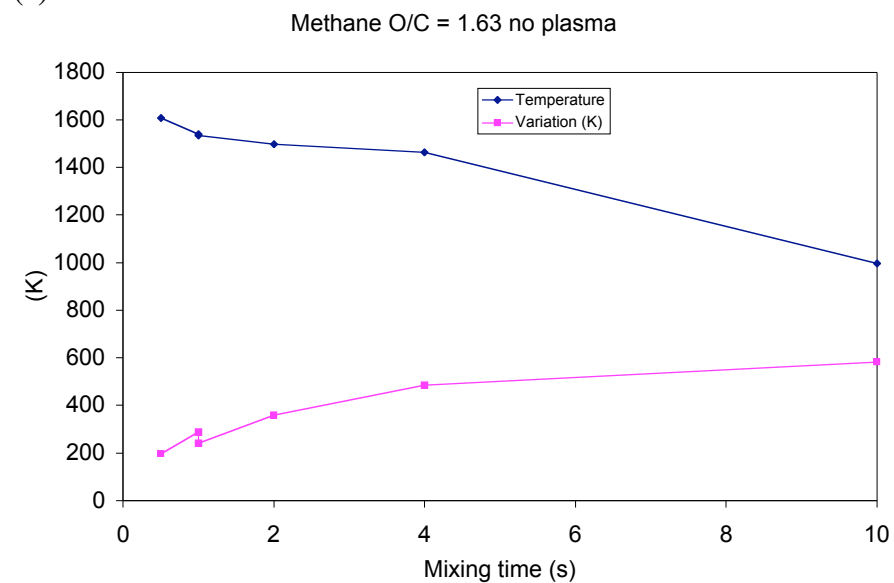
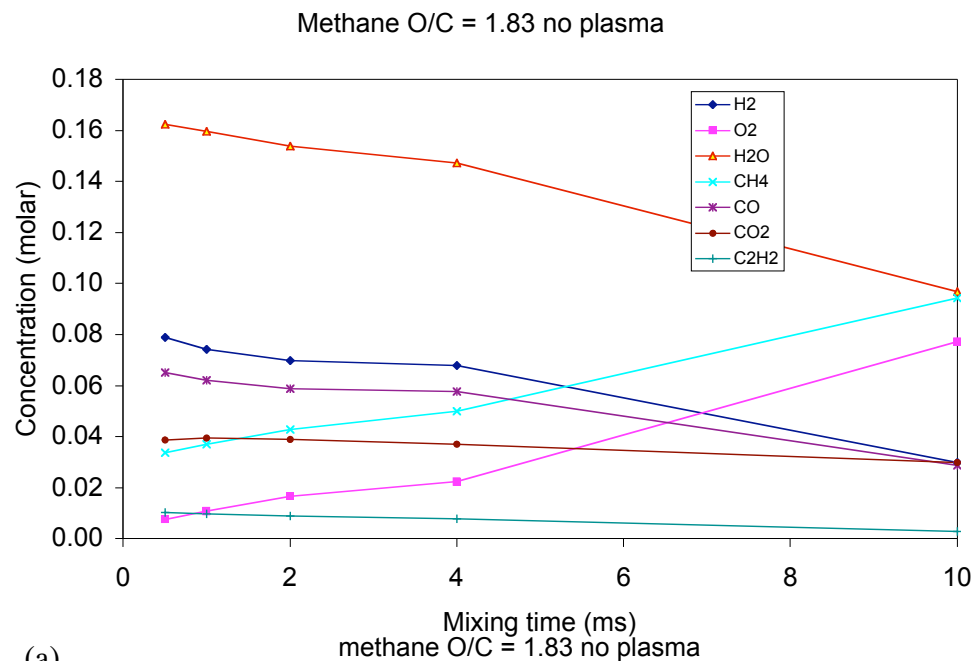
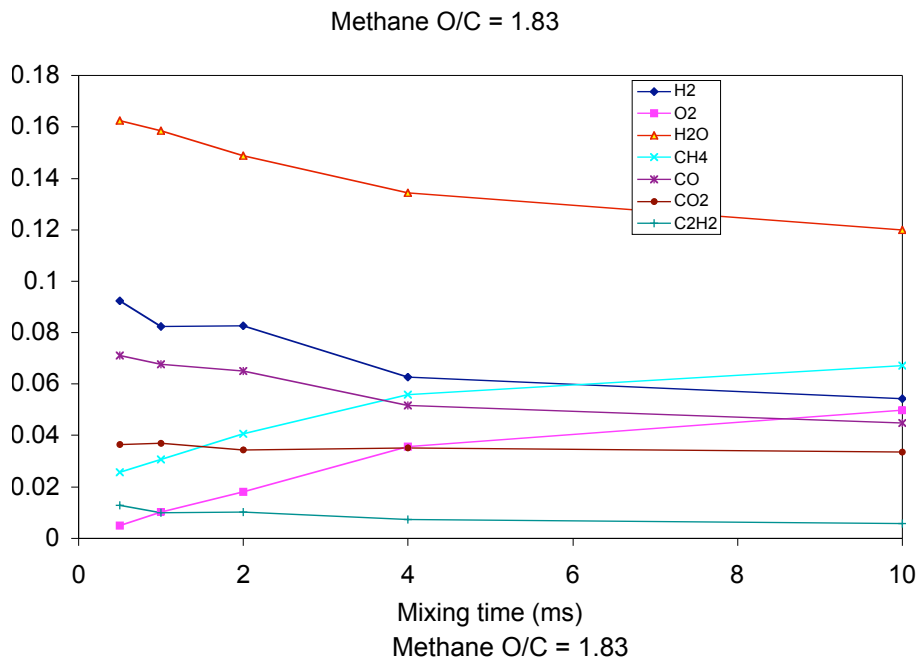
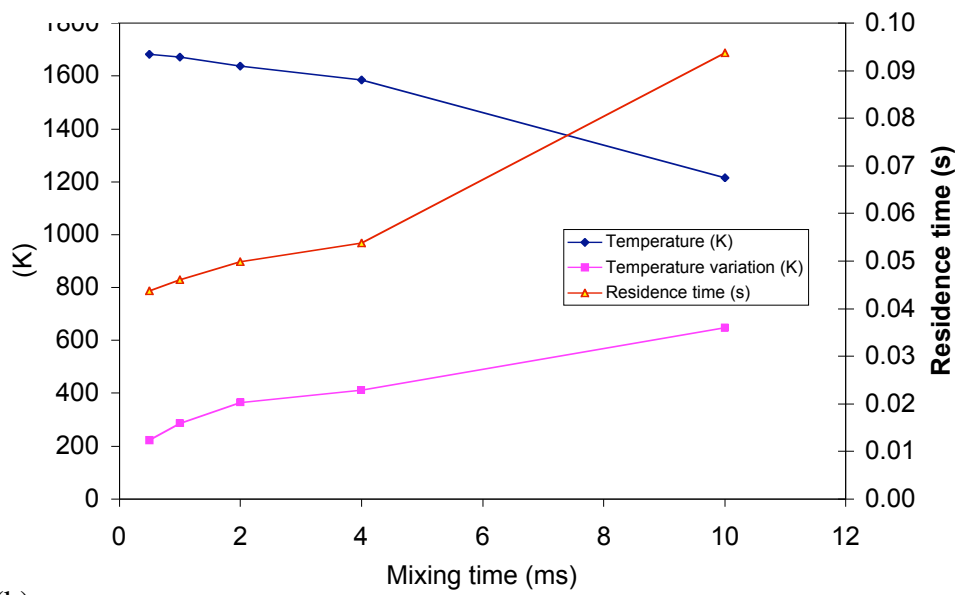
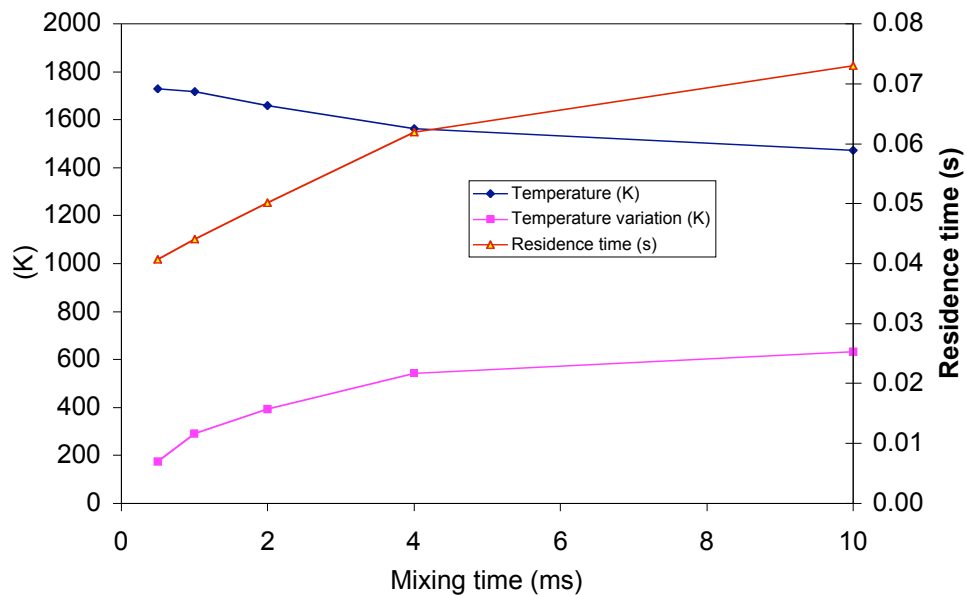


Figure 4. Same as Figure 4 but for O/C = 1.63.



(a)



(b)

Figure 5. Same as Figure 4 but for O/C = 1.83.

Again, for increased O/C, the hydrogen concentration decreases, while the methane conversion increases. In the case of O/C ~ 1.83, the conversion increases by about 40% from than of O/C ~ 1.63. However, some of the conversion is to water, and the result of this increased combustion is increased temperature.

5 Discussion

The comparison between the experimental results and the modeling results are shown in Table 2. Because the experimental results do not measure water content, the results are shown for dry gas composition.

Table 2
Comparison of experiments and modeling results ($\tau_{\text{mix}} = 0.5$ ms)
Experiments with plasma on

		5/2/2005-1	PaSR	5/2/2005-2	PaSR	5/2/2005-3	PaSR
Power in	W	375	375	375	375	375	375
Axial air	g/s	2.16	2.16	2.59	2.59	3.02	3.02
Swirl air	g/s	0.86	0.86	0.86	0.86	0.86	0.86
Swirl methane	g/s	0.45	0.45	0.45	0.45	0.45	0.45
O/C ratio		1.43	1.43	1.63	1.63	1.83	1.83
Composition							
H2	vol.%	12.1	12.7	13.5	11.5	13.9	11.1
O2	vol.%	0.7	0.8	0.5	0.8	0.5	0.6
N2	vol.%	68.9	66.5	69.8	69.2	71.4	70.9
CH4	vol.%	4.2	5.8	1.9	4.3	1.7	3.1
CO	vol.%	9.1	9.1	9.6	8.4	10	8.5
CO2	vol.%	3.8	3.3	4	4.0	4.1	4.4
C2H4	vol.%	0.9	0.0	0.8	0.0	0.7	0.0
C2H2	vol.%	0.2	1.8	0	1.7	0	1.5
Σ C in	mole/min	1.69	1.69	1.69	1.69	1.69	1.69
Σ C out	mole/min	1.44	1.70	1.42	1.64	1.57	1.75
Δ C/C		0.15	-0.01	0.16	0.03	0.07	-0.04

The modeling results agree quantitatively with the experimental ones. One point of small disagreement is in the hydrogen concentration and the methane conversion, which are slightly underestimated in the modeling results for higher O/C ratios. The trend of the calculations also indicates that the hydrogen concentration peaks at low O/C ratios, while the experiments indicate that they peak at the higher O/C ratios, but the peaks, in any case, are rather broad.

It should be noted that the experimental results shown in Table 2 correspond to a series of experiments from [2] where there was good reforming at O/C ~ 1.43. Additional experiments in [2] show that there is a cliff in the methane conversion at O/C ~ 1.63, and poor conversion at O/C ~ 1.43. As described in the paper, the issue has to do with reproducibility of the measurement of the O/C ratio, which could be off by as much as 25%.

The code does not reproduce the experimental results with the C₂ compounds. The modeling indicates that the highest conversion is to acetylene, with small yields of C₂H₄ and C₂H₆ (about 0.1% molar each). The experimental results indicate the opposite, with substantial concentration of C₂H₄ and/or C₂H₆ (C₂H₄ and C₂H₆ are not separated by our chromatographic column) and very small concentration of C₂H₂. The impact on the methane conversion and hydrogen yields are, however, small.

Also shown in the table are the carbon balance, for both the modeling and the experiments. The last three rows of Table 2 show the sum of the carbon in the input (i.e., the methane), and the carbon sum of the output, and their relative differences. The carbon balance in the experiments are about 10-15%, while in the computation the carbon balance is within 1-4% (due to statistics).

It should be noted that in order for the chemistry to take place, mixing has to be at the molecular level. The effects of turbulence on mixing at this level are still not understood. However, it seems that high Reynolds numbers, higher than laminar-to-turbulent transition, are required ($Re > 10,000$) to achieve mixing at the molecular level [Dimotakis]. For reference, the Reynolds number in the plasmatron head region of the device is $Re \sim 6000$ (prior to chemistry).

The cases analyzed in Figure 3-5 without plasma show different quantitative results than the experiments. Good performance is only obtained in the experiments by operating at higher values of O/C than the numerical results. It is not clear why this is the case.

Two possible alternative explanations have been conceived to explain the difference observed between the experimental and numerical calculations without the plasma and at low O/C. The first one is that there are power losses not accounted by the code. The code models an adiabatic reactor. At conditions of lower O/C the exothermicity of the reaction is decreased, and reforming would be more sensitive to losses. The absence of the losses would thus explain both the good numerical reforming without the plasma as well as at the lower O/C ratio

The second possible explanation is the implication of the PaSR code itself. The code allows for a single mixing time. There is substantial recirculation in the reactor, but it is not as assumed in the code. When the exothermicity is high, decreased mixing may not affect as much the results. This behavior is shown in Figures 3-5. On those cases in the presence of the plasma (on the left of the figures), as mixing time increases, reforming degrades but asymptotes to good reforming (that is, the rate of change decreases with increasing mixing time). This is changing for the conditions without the plasma, where as the mixing time increases there no asymptote but instead the rate of change increases. Thus the reforming without the plasma is more sensitive to poor mixing than the case with plasma.

6.0 Conclusions

A model of a plasmatron methane reformer where limited mixing is included has produced quantitative agreement with experimental results. The process uses only gas phase chemistry, without the use of a catalyst. The model reproduces the hydrogen and other main components of the reformat, as well as the methane conversion.

The model also has been used to determine the effect of the plasma at steady state conditions. It has been shown that the plasma increases the hydrogen concentration by about 20%, but the reaction continues at lower temperatures even in the absence of the plasma. As the cold reagents are introduced into the hot reactor gas, they are heated and release sufficient energy to maintain the reaction, although at decreased temperature.

The composition of the reformat is accurately described by the model. However, there are regimes (low O/C, absence of plasma) where there is only qualitative agreement with the observations. Additional modeling is needed that includes losses or improved description of the fluid dynamics, mainly for the case without plasma.

Acknowledgements

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