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**Plasma Assisted Reforming of Methane:
Two Stage Perfectly Stirred Reactor
(PSR) Simulation**

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Abstract

Plasmatron fuel converters have been investigated for the conversion of a wide range of fuels. This paper is one of a series describing an experimental and computational study of plasmatron methane reformers. A simple model using a two step process has been proposed for investigating homogeneous reformation of methane using partial oxidation reactions. In the first step, a fraction of the fuel is combusted, while during the second the rest of the fuel is reformed. The purpose of the simple model is to provide limited understanding of uncatalyzed methane reformation using plasma fuel reformers. The implications of kinetic rates, as well as mixing rates, are explored. This paper describes model and results of simple two step process, used to provide guidance to experiments as well as more sophisticated calculations in an accompanying papers. Comparison with experimental results with a plasmatron methane reformer are also presented.

1. Introduction

Hydrogen generation from natural gas has been performed using mainly steam reforming. Although steam reforming has substantial advantages from a system point of view, partial oxidation can have advantages in certain circumstances, particularly where pure hydrogen is not required, and where the hydrogen rich gas will not be compressed downstream from the reformer. [see, for example, 1-8]

In the fuel reformation of natural gas the use of catalysts is widespread. The catalyst reduces the required temperatures, increases conversion and maximizes the hydrogen yield. However, the catalyst is expensive and needs to be regularly exchanged, at substantial cost. It has been estimated that the capital cost of the catalytic reformer is on the order of 1/3-1/2 of the cost of the plant.

The conversion of natural gas without the use of a catalyst is attractive. Plasma-driven catalysts have been explored for the conversion of methane and other fuels. Our group at the Plasma Science and Fusion Center at MIT has been investigating the conversion of a wide range of fuel into hydrogen rich gas.

This paper is one of a series of papers to investigate the performance of plasmatron methane converters. The accompanying papers describe the experimental performance of the device, both at steady state conditions [9] and during start-up [10], as well as papers describing the fluid dynamics of the device [11] and a modeling paper describing the results from a Partially Stirred Reactor model [12]. An additional paper describes the results from steady state and transient reforming of propane [13]. The purpose of this paper is to develop a simple chemical model of the process with methane, based upon a two stage, Perfectly Stirred Reactor.

Section 2 describes the chemical model. Section 3 applies the model to our configuration. Section 4 looks at the effect of reactor size and varying residence time. Discussions and comparison with the experimental results are presented in Section 5. Finally Section 6 provides the conclusions.

2. Chemical model

Chemkin 4.0 [14] was used to simulate a fuel converter based on a plasmatron. The plasmatron fuel converter and experimental results have been described in accompanying papers, for steady state [9] and start-up [10] conditions.

The simple model described in this paper assumes that a fraction of the fuel is consumed in stoichiometric combustion and these combustion products mix perfectly with the rest of the room temperature air/fuel mixture. The model is consistent with observations in the plasmatron fuel converter [9, 10], in which if the methane and the air are premixed, there is no conversion, and the conversion is a strong function of the methane/air stratification in the plasma region.

The process, as presently understood, is thus a two step process, with pure combustion in the first step which releases enough heat to drive the partial oxidation reactions in the second step.

The simple model uses an equilibrium reactor to combust the stoichiometric methane/air mixture. This mixture is then fed to a perfectly stirred reactor (PSR) that has a secondary input consisting in additional fuel and air (with $O/C = 1$) at room temperature. The overall O/C ratio is then substantially higher than for stoichiometric partial oxidation (since the first stage has substantially higher O/C).

The fuel is methane. The GRI 3.0 mechanism was used in the calculations [15]. 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 stage is about 2200 K. At this temperature, substantial levels of NO and nitrogen-carbon compounds are made. Nitrogen chemistry is followed.

It is assumed that the reactor is adiabatic and has a volume of 1000 cm^3 . Although the volume of the reactor is easy to establish, the region with good mixing is not, and we have performed calculations for various reactor sizes. The residence time varies depending on the temperature of the gases as well as the mass flow rate. It has been assumed that the mass flow in the PSR is $\sim 5 \text{ g/s}$ (corresponding to a few hundred l/min).

The stoichiometric flow rate to the equilibrium reactor is varied in order to investigate the effect of additional enthalpy. The secondary flow (with $O/C = 1$) is held constant. In the experiments, the methane flow rate was constant [9,10].

The reactor network used in the simulation is schematically shown in Figure 1. There is no preheating of any of the reagents. The object of the plasma is to ignite the stoichiometric methane/air fuel mixture, but in terms of energy balance it provides only a small fraction of the exothermic energy of the partial oxidation reaction and is actually not included in the model.

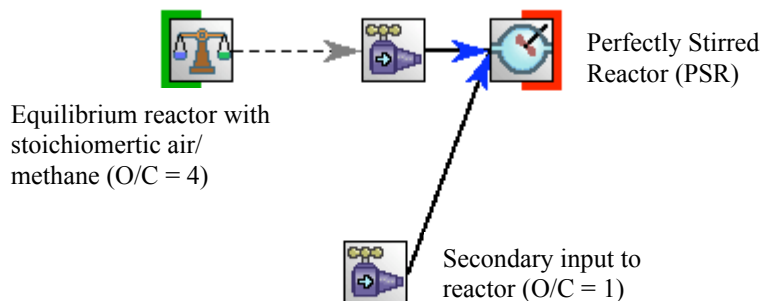


Figure 1. Schematic diagram of the process

3 Two Stage PSR results

The composition of the output from the PSR is shown in Figure 2 for the case of a reactor with 1000 cm^3 . The secondary input flow rate (with $O/C = 1$) was 3 g/s , and the stoichiometric flow rate was varied to vary the overall O/C . It is clear that the hydrogen production and methane conversion processes experience a discontinuous jump around an $O/C \sim 1.4$ (corresponding to 1.5 g/s of stoichiometric air/methane mixture). There is very little hydrogen in the output for $O/C < 1.4$, and relatively constant after the transition. The amount of hydrogen produced in this homogeneous system is about 7-8%, relatively independent on the overall O/C ratio. It should be noted that with increased stoichiometric mass flow rate (more combustion), the residence time decreases, both because of the increased mass flow rate as well as increased temperature.

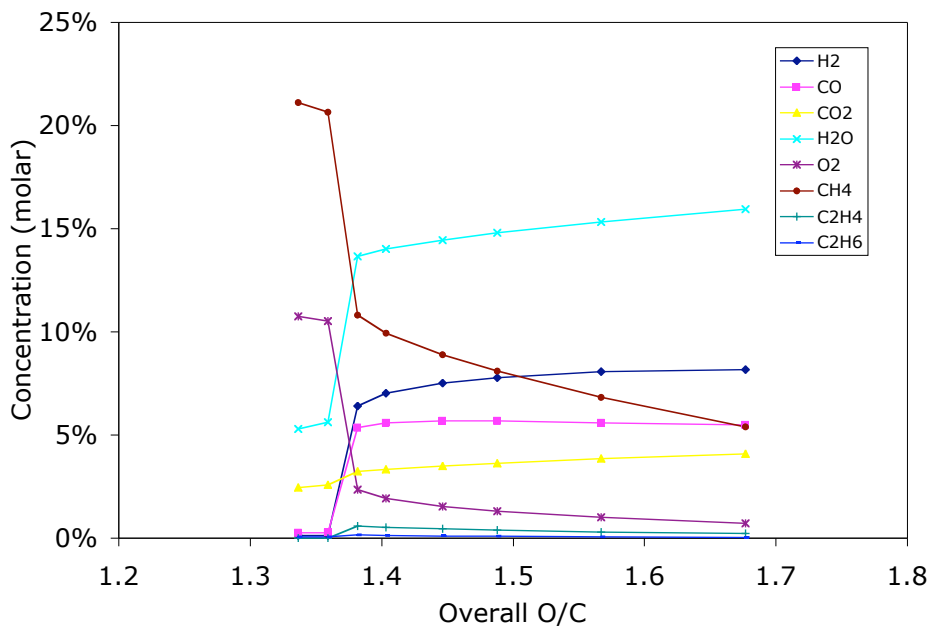


Figure 2. Composition of the exhaust as a function of the overall O/C ratio.

The PSR temperature and residence time are shown in Figure 3. The temperature increases with increasing stoichiometric flow rate. The temperature of the PSR reaches values where substantial reactions can take place, at which point the fuel rich mixture in the PSR ignites. The steady state temperatures of the PSR are on the order of $1400\text{-}1500 \text{ K}$. The residence time varied from about 80 ms at the conditions of the lowest O/C values considered, to about 30 ms to the highest flow rates.

The corresponding stoichiometric flow rate is plotted in Figure 4 as a function of the calculated O/C ratio. Substantial precombustion of the methane is required in order to drive the reforming reaction. A stoichiometric flow rate of 1.5 g/s is required for a secondary flow rate of 3 g/s , corresponding to an overall O/C of about 1.4 . These conditions result in large enough temperatures to maintain the reaction.

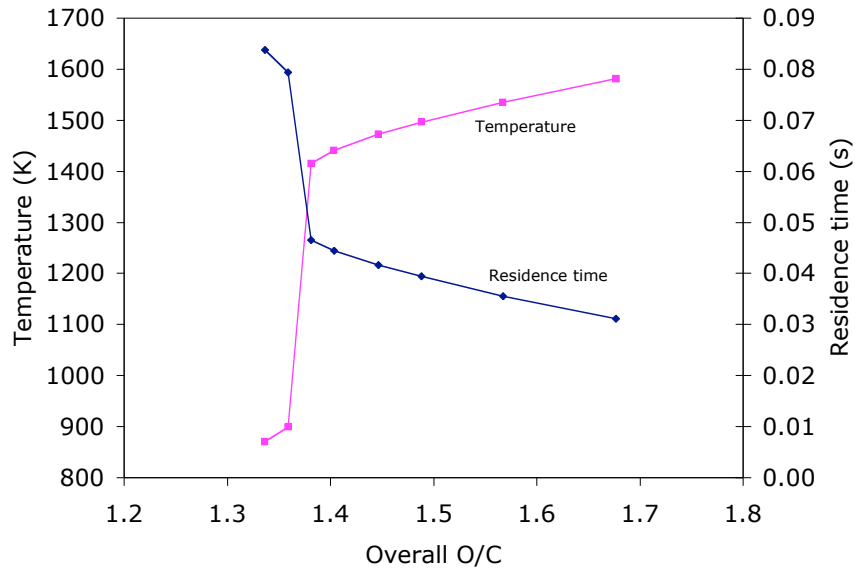


Figure 3. Reactor temperature and residence time as a function of the O/C ratio)

It should be noted that once the PSR is ignited, the concentrations are relatively insensitive to further increases in the overall O/C. (see figure 2). In addition, it is not expected that the size of the reactor, nor the flow (which affect the residence time), will have a large impact. This will be discussed later in section 4.

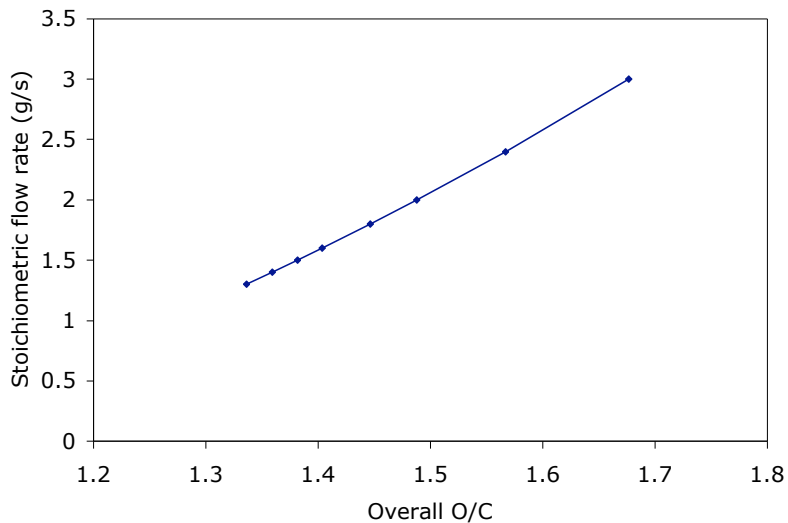


Figure 4. Stoichiometric flow rate as a function of overall O/C ratio (overall) (secondary flow rate to the PSR is 3 g/s)

In Figure 5, the concentration of fixated nitrogen compounds are shown as a function of the overall O/C ratio. NO (generated in the stoichiometric combustion process) shows a large discontinuity at the point where the PSR ignites, and there is a simultaneous increase of HCN and NH₃, as would be expected from a system with a reducing environment.

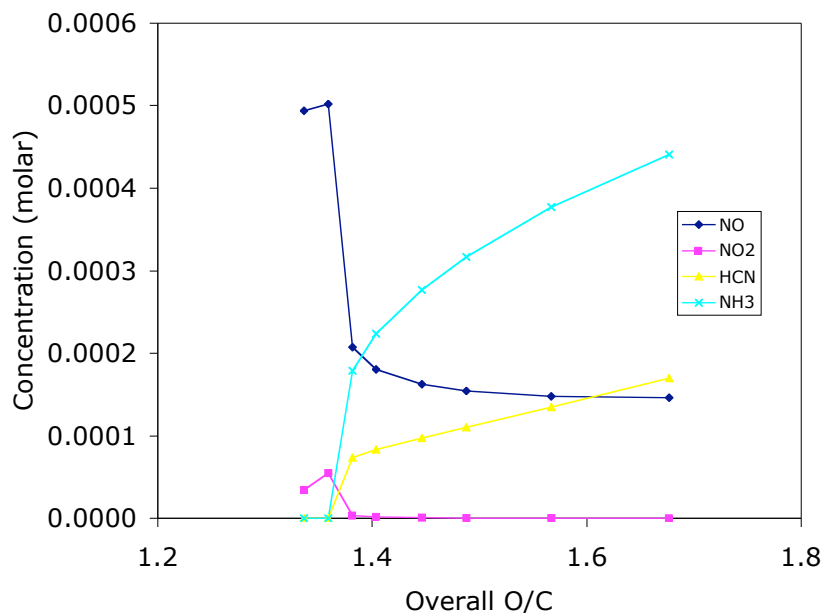


Figure 5. Fixated nitrogen as a function overall O/C (secondary flow rate is 3 g/s)

It would be useful to determine whether the fixated is generated in the equilibrium reactor or in the PSR. The equilibrium reactor generates, at a flow rate of 1.5 g/s, an NO flow rate of 10^{-4} moles/s. The output from the PSR has about $0.9 \cdot 10^{-4}$ moles/s. Thus, most of the NO from the equilibrium reactor flows to the output of the PSR when there is little reforming in the PSR. Nor surprisingly, as it is in the equilibrium reactor where the nitrogen is fixated.

4 Effect of residence time in the conversion

In order to determine the effect of residence time, the flow rates were scaled down, with fixed reactor volume. These flow rates do correspond to more realistic flow rates in the experiment.

The total gas flow rate was varied from 2.5 g/s total to 20 g/s. The results are shown in Figure 6. Increasing the residence time only slightly increases the hydrogen yield and the methane conversion. The model suggests fast initial chemistry, followed by slow chemistry.

The composition of the fixated nitrogen compounds for different residence times is shown in Figure 7. There are changes in the composition of the fixated nitrogen, with NO decreasing and NH₃ increasing. As with the composition of the major components, slow

chemistry follows relatively fast chemistry. For residence times larger than about 20 ms, the rates of conversion are very slow and the concentration rate of change is slow. It is interesting that the total fixated nitrogen does not change much over the range of residence times.

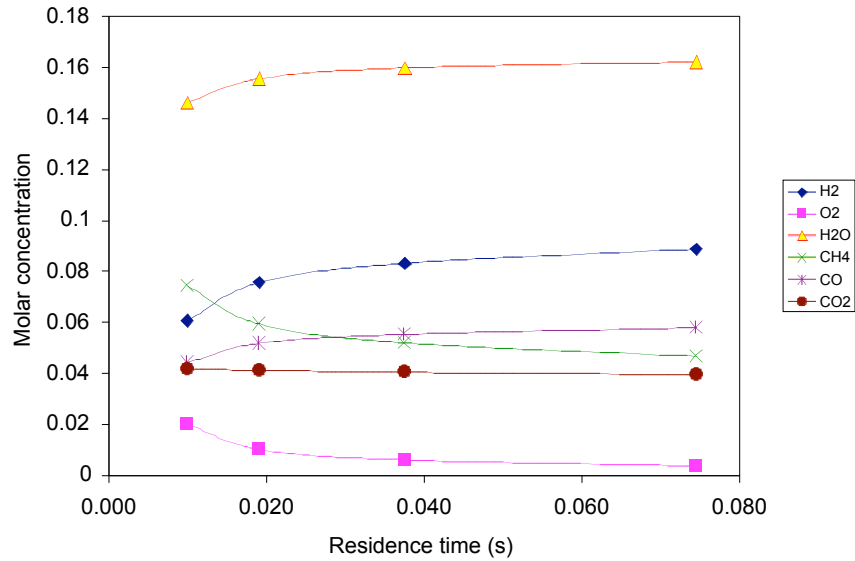


Figure 6. Molar concentration of major components as a function of the residence time.

The concentration of fixated nitrogen compounds is about 1400 ppm. The fixated nitrogen was not measured experimentally. However, measurements by Khadya [16] and Stevens [17] are in agreement with these measurements.

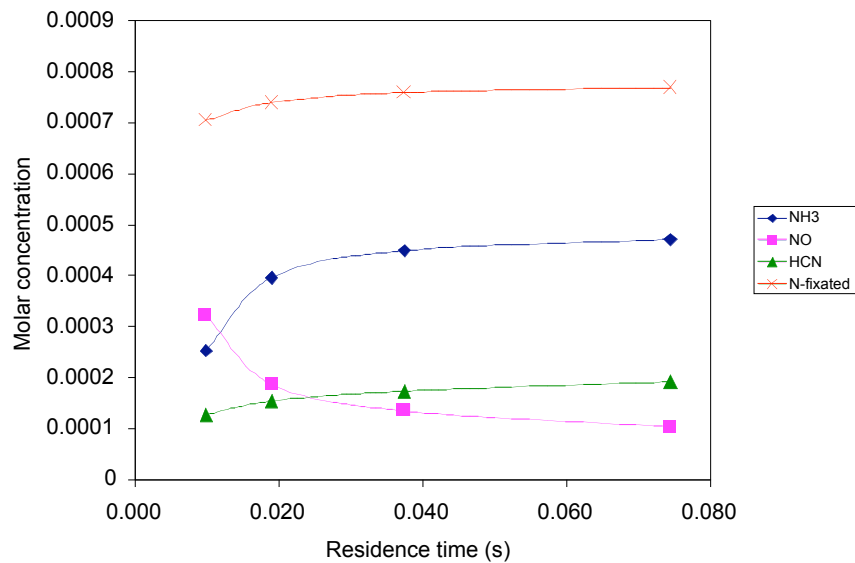


Figure 7. Molar concentration of fixated nitrogen.

It is likely that these compounds, when the reformat is used in a combustion process, will turn to nitrogen oxides.

The effect of changing the residence time has little effect upon the conversion, as shown in Figure 6. However, it has a substantial effect on the critical flow required for igniting the PSR. Figure 8 shows the overall O/C required for ignition corresponding to reactor sizes varying from 150 to 1000 cm³, for a total mass flow rate of 4.5 g/s. As the reactor size decreases, the required temperature for ignition increases to compensate for the decreased residence time, increasing the required stoichiometric flow rate and thus the overall O/C.

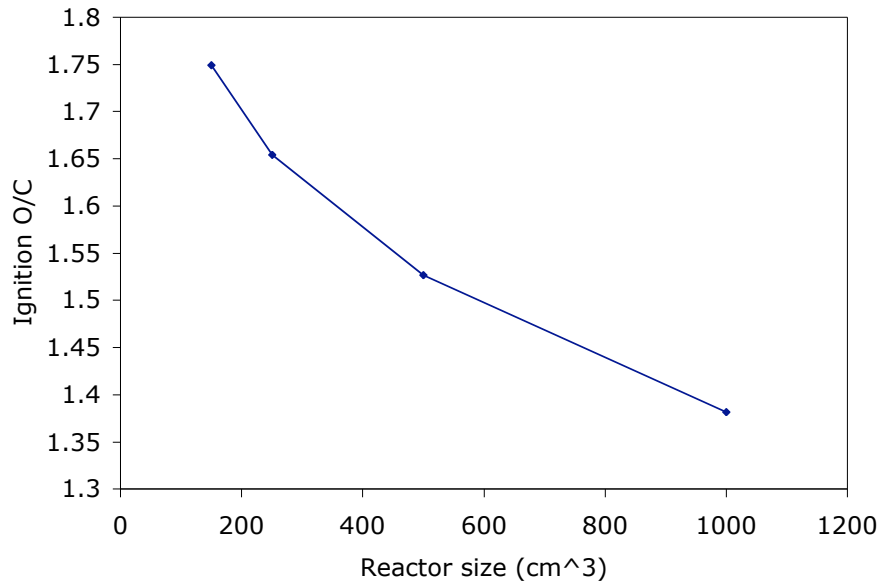


Figure 8. Required overall O/C for ignition of a PSR of various sizes, for a constant mass flow rate of 4.5 g/s

5 Discussion

In this section a comparison between the model and the experimental results is presented.

Results that illustrate the ignition-like behavior of the plasmatron methane reformer are reproduced in Figure 9 (from reference [9]). As explained in reference [9], there is a problem determining the O/C ratio, which has a ~10% spread. The results in Figure 9 show a required overall O/C of about 1.6 for ignition. Section 4 found that the overall O/C for ignition was closer to 1.4 for a reactor size of 1000 cm³, but as discussed above, the physical reactor size may be substantially larger than the PSR, as the downstream sections of the actual reactor may be closer to plug-flow, rather than perfectly-stirred. Using results from Figure 8, a reactor needs to be about 250 cm³ in order to match the experimentally obtained O/C ~ 1.6. It is not unlikely that the actual size of the PSR be this size, as recirculating flow (that generated the idea of the PSR model instead of Plug-Flow model), occur over substantially smaller sections of the actual reactor, as shown in

the paper on fluid simulation [11]. Although those simulations [11] did not include chemistry, the existence and size of the recirculation zone was suggested.

The model has been successful in predicting the experimental result that at relatively high values of O/C (> 1.6) there is a sudden increase the methane conversion. The experimental program was designed to test this hypothesis.

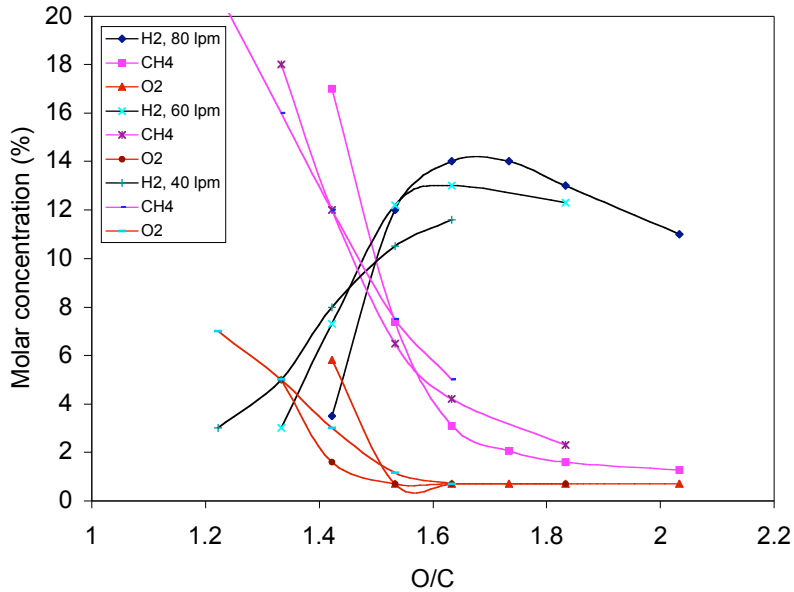


Figure 9. Experimental results (from reference [9]),

Table 1. Comparison between experimental and model results

Power in	W	5/2/2005-2	PaSR	PSR	
Axial air	g/s	375	375		
Swirl air	g/s	2.59	2.59		
Swirl methane	g/s	0.86	0.86		
O/C ratio		0.45	0.45		
		1.63	1.63		
Composition		Experiment		Composition	Dry gas composition
H2	vol.%	13.5	11.5	8.2	9.6
O2	vol.%	0.5	0.8	0.7	0.8
N2	vol.%	69.8	69.2	58	67.8
CH4	vol.%	1.9	4.3	5.4	6.3
CO	vol.%	9.6	8.4	5.5	6.4
CO2	vol.%	4	4.0	4.1	4.8
C2H4	vol.%	0.8	0.0	0.2	0.2
C2H2	vol.%	0	1.7	1.5	1.8

Table 1 shows typical results from the experiment, and compares with the results obtained in this paper. The experimentally obtained dry gas composition of the reformate is under the column labeled 5/2/2005-2. The PSR results have been those calculated of the O/C ~ 1.65 from Section 3. Two columns are indicated, the first one for the actual composition, and the second one for dry gas composition (to compare with the experiments). Also shown are the modeling results from the PsAR calculation [12].

The models underestimate the concentration of hydrogen (the PSR by about 40%, while the PaSR by about 20%). The assumption in this paper of very fast combustion in the first stage, followed by very fast mixing in the second stage, are crude approximation for the system. The PaSR model, which includes finite rate mixing, does a better job. A full fledged model using CFD and chemistry is outside the scope of the work.

It is not clear how large is the well mixed reactor, as there are regions in the downstream section of the physical reactor that resemble more a plug flow reactor than a well mixed reactor.

6 Conclusions and Summary

A 2-stage model has been developed for the homogeneous reforming of methane. The model was investigated using a simple Perfectly Stirred Reactor (PSR) with multiple inputs. It was determined that the reforming process ignited the overall O/C ratio is between 1.4 and 1.6. About 10-15% of the methane needs to be stoichiometrically combusted.

The actual composition of the reformate in the calculations underestimate the hydrogen concentration and the methane conversion. The PaSR model does better in predicting the composition of the reformate.

The results show a lack of sensitivity of the conversion to residence time. Increased conversion is difficult through the use of larger reactors. Instead, increased temperature is a more effective way to achieving high conversion of methane. The same results are obtained by increasing the reactor size by a factor of 8 or increasing the O/C ratio from 1.6 to 2. However, there is a minimum PSR size (defined as the section of the actual reactor with good mixing) for good reforming, and increased O/C ratio is needed to compensate for smaller well-mixed reactors.

Acknowledgement

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