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Some temperature effects on stability and carbon formation in low temperature ac plasma conversion of methane

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Abstract

Methane conversion using a low temperature plasma generated by an ac corona discharge has recently been extensively studied. Different products can be produced: C_2, C_3, H_2, CO, CO_2 and coke. The understanding of the role of temperature has been limited. This paper discusses the use of an IR thermal imaging and measurement system to study the effects of temperature on the stability and carbon formation in low temperature ac plasma conversion of methane. Three types of coke are observed during the methane conversion process using plasma generated by an ac corona discharge under various conditions. The first type of coke is dark brown and powder coke. The second type of coke is dark greenish and forms a soft coating. The third type is coke filaments, which strongly affects the discharge stability by quickly connecting the two electrodes. In the partial oxidation or steam reforming of methane, the temperature is generally less than 300 °C under normal experimental conditions. Increasing the feed temperature in the steam reforming of methane increases the reactor temperature, causing the formation of coke filaments when the water concentration is not high enough. Therefore, feeding liquid water at room temperature into the reactor helps improve the stability.

Keywords: Plasma conversion; IR thermal imaging and measurement system; Plasma tubular reactor

1. Introduction

A substantial body of work by a number of investigators has shown that methane can be successfully converted to valuable products under a variety of conditions with relatively low power consumption [1–5]. A number of issues have arisen from these studies that impact the potential for development of a successful commercial process based on these phenomena. A key issue is understanding the role of temperature on the conversion and product distribution, including conditions that result in carbon formation [6]. One question is whether low temperature plasmas are really low in temperature, or rather the observed chemistry is the result of traditional high temperature gas phase radical reactions in small volumes, and therefore subject to the equilibrium constraints of a thermal system. The product distributions themselves can be inconclusive in some cases. Additionally, the range of conditions for which carbon formation occurs, and limits the stability and longevity of the plasma operation, has been found to be affected by temperature among other conditions. This paper examines the temperature distribution in the low temperature ac plasma conversion of methane under both steam reforming and partial oxidation conditions to assist in understanding the initiation of carbon formation. Under normal operation, coke formation is of course undesirable and conditions have been found where it can be minimized and non-coke carbon balances above 90% could be achieved in a number of cases.

2. Experimental

Fig. 1 shows a schematic of the ac plasma tubular reactor with a point to plate electrode configuration. The discharge occurred between two metal electrodes in a quartz or sapphire tube. In the temperature measurement experiments, the top electrode was a 3/16 in OD hollow tube made of stainless steel; and the bottom electrode was a circular stainless steel disk with 7 mm diameter and ~1.5 mm thick. There were four 1.5 mm i.d. holes on the disk to facilitate the flow of gas through the reactor. The sapphire tube's i.d. was 8 mm. The sapphire tube (ST) was used in the temperature measurement experiments because it was IR transparent. The gas

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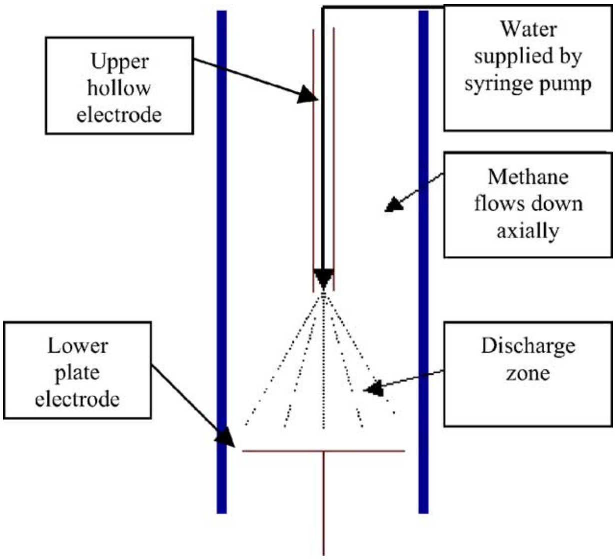

Fig. 1. The plasma reactor for methane steam reforming and partial oxidation.

gap between the two electrodes was always 10 mm. Fig. 2, produced from an Olympus model 740 digital camera using automatic settings, illustrates the geometry of the reactor and provides an orientation for the IR images, as shown in Fig. 3. The feed flowed axially downward inside the reactor. In the steam reforming of methane, liquid water at room temperature was pumped into the reactor via the top electrode by a Kid Scientific syringe pump model 100, where it then substantially vaporized. In the partial oxidation of methane, oxygen was mixed with methane before going into the reactor.

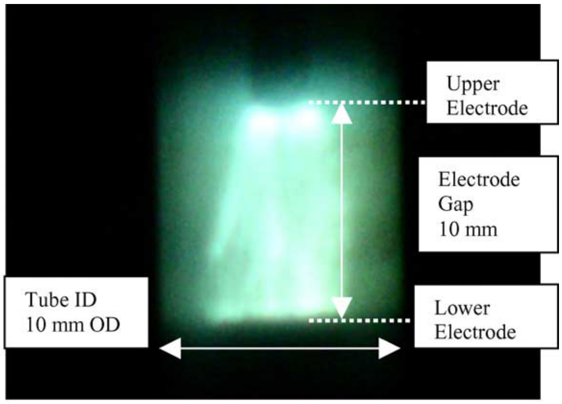

Fig. 2. Visible image of the ST reactor with discharge on.

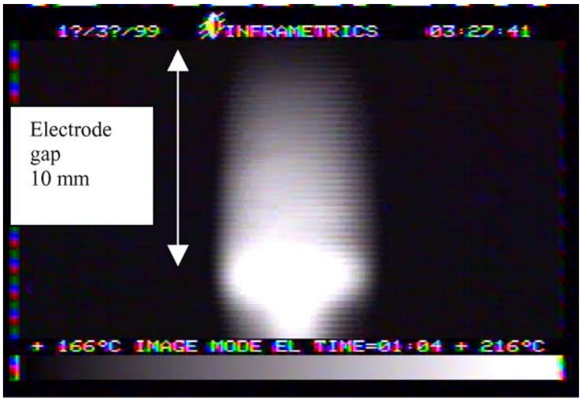

Fig. 3. IR image of the reactor with discharge on.

Details of the ac plasma experimental apparatus have been presented in detail elsewhere [4]. Feed gases were controlled by Porter mass flow rate controllers, model 201. The gases exiting the reactor flowed through two liquid traps in series using dry ice. The dry products then flowed either to a bubble meter for flow rate measurements or to a GC for composition analysis. A bubble meter and a stopwatch were used to measure the total feed flow rate and product flow rate. Either of the two similar online gas chromatographs (Carle Series 400 AGC, model 04157), each equipped with a thermal conductivity detector, an HTS system for hydrogen separation and analysis, and separation columns was used to analyze gas compositions from independent calibrations for each component. The liquid product, if present, was neither quantified nor analyzed in most experiments, but a few analyses of the liquid (water) showed the absence of organics under conditions used in this study. The methane conversion (%) was defined as $100 \times (\mathrm{CH}_{4\_\mathrm{in}} - \mathrm{CH}_{4\_\mathrm{out}})/(\mathrm{CH}_{4\_\mathrm{in}})$ and the oxygen conversion was calculated by the same method. Water conversion was actually based on an oxygen balance wherein oxygen not accounted for from the feed is assumed to be from converted water. With the feed water molar flow rate, water conversion may be calculated.

The discharge was generated by the ac power supplied by the power supply unit. The power supply unit consisted of an Elgar ac power supply model 251B, a Wavetek model 182A waveform generator, and a midpoint grounded Magnetec Jefferson high voltage transformer. Only a sinusoidal waveform was used. The frequency was set at 300 Hz. The consumed power on the low side of the transformer was measured with a Tektronics TDS 754 C oscilloscope equipped with an A622 current probe and a P6139A voltage probe, and therefore includes losses from the transformer, wiring and the reactor. Power was calculated as the product of the voltage and current waveform measurements.

The temperatures inside the reactor were analyzed using an IR thermal imaging and measurement system model 600 made by Inframetrics Inc. with a temperature range of 0–1000 °C. The IR was calibrated by adjusting its emissivity until the recorded temperature equaled the known temperature of the electrode (260 °C) that was placed inside the sapphire tube and heated only by an external heater.

3. Coke and coke formation conditions

There were at least three types of coke formed during the methane conversion process using the plasma generated by this ac discharge, depending on the feed conditions. Different frequencies than used here changed the range of conditions under which coke was found to form. One type of coke was dark brown and powder coke, similar to the type of coke produced from acetylene decomposition. Generally, this type of coke did not cause any serious problem with the discharge stability. However, if a thick layer of this coke was formed on the electrode surfaces, the methane conversion decreased. The discharge then concentrated on one point over the electrode surface. Eventually, a coke filament grew from that point. Under high water or oxygen mole fraction feed conditions (≥67 mol% water or 33 mol% O_2), conditions that usually resulted in a low acetylene selectivity and a high carbon monoxide selectivity, this type of coke was generally not seen. In the partial oxidation of methane, under experimental conditions where the temperature inside the reactor was high, a large amount of this type of carbon was also observed below the bottom electrode.

The second type of "coke" was dark greenish and formed a soft coating on the reactor wall that is easily removed. This type of coke was usually seen when the water mole fraction in the feed was less than 50%, which usually resulted in a high acetylene selectivity. Even though it did not directly disrupt the discharge, once the film was thick enough, it provided an alternate conductive path for electricity from the top electrode to the bottom electrode. The power consumption would increase and the methane conversion would then decrease. Eventually, the discharge went from the top electrode to the reactor wall where the coke film was. In the steam reforming of methane, this change is usually irreversible. However, in the partial oxidation of methane, it can be reversible because the decrease in the feed conversions allows more oxygen to oxidize the coke layer resulting in long-term stability (several hours).

The third type of coke was a coke filament that was visually observed to grow from one or both electrodes toward the other electrode. The filaments caused discharge instability in both the steam reforming and partial oxidation of methane. It was formed when the discharge did not move over the electrode surface but concentrated on a spot, as seen in Fig. 4. The discharge looked like an arc connecting the two electrodes. A coke filament started to form at the point where the discharge originated. The concentration of heat over a small point on an electrode caused the average temperature at that spot to rise to above 300 °C. The temperature increase could cause methane to decompose to carbon, which quickly nucleates and grows to form coke filaments. Once the carbon filament started to grow, the methane conversion decreased, and eventually reached zero, when the filament connected the two electrodes.

4. Temperature measurements in the steam reforming of methane

The temperatures of the top and bottom electrodes and the bulk gas between them in the steam reforming of methane were measured using the IR camera. The feed consisted of 25 sccm of methane and 50 sccm of water. Unless otherwise specified, water was pumped directly into the reactor via the top electrode, similar to all of the steam reforming experiments presented in this paper. The input power was 16 W at 85 V low side voltage and was 17 W at 100 V low side voltage.

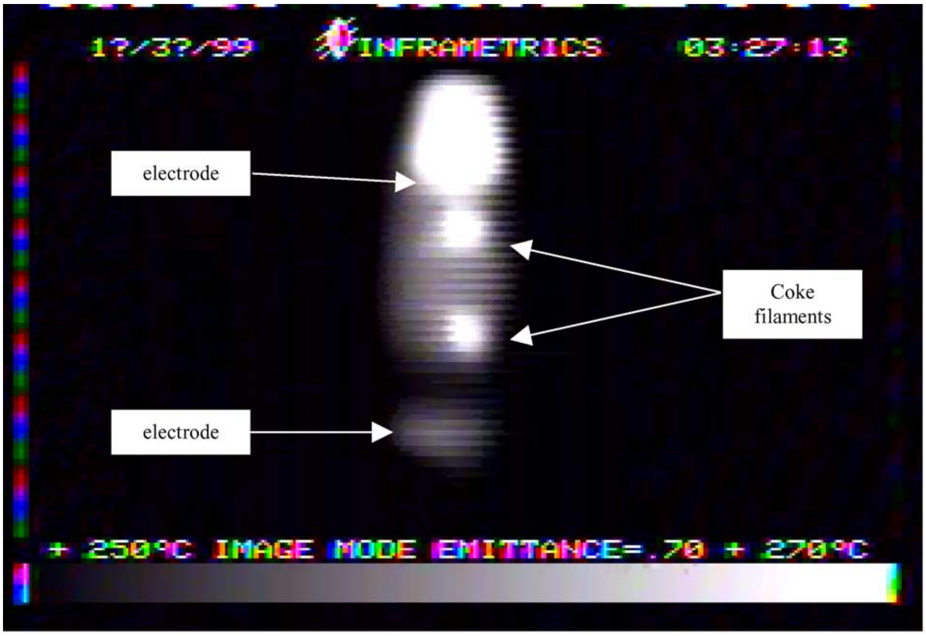

Fig. 4. IR image of the ST reactor with discharge on, coke filament being formed.

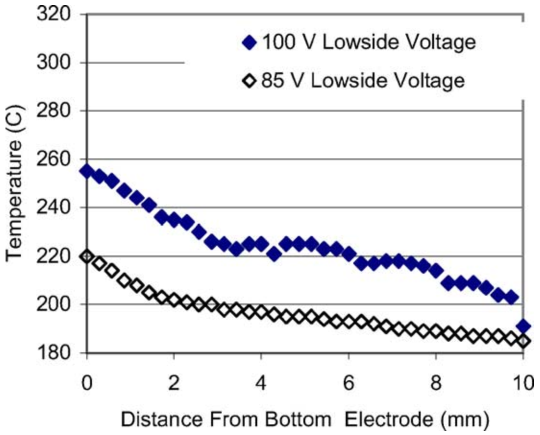

Fig. 5. Axial temperature profile of the reactor at tube center liquid water fed in via the top electrode.

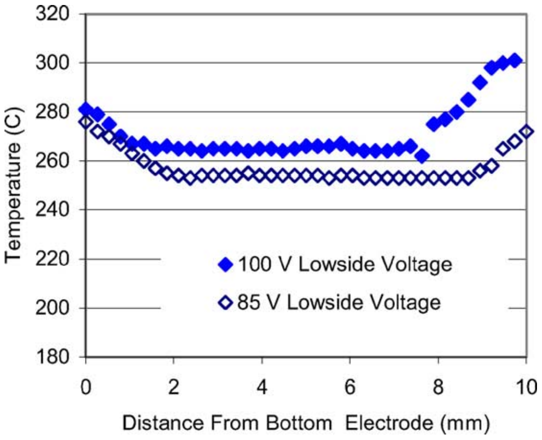

Fig. 6. Axial temperature profile of the reactor at tube center vapor water mixed with methane before reaching reactor.

In the steam reforming of methane using the non-equilibrium plasma using the ac discharge, when water was pumped into the reactor via the top electrode, the bottom electrode temperature was always the highest temperature inside the reactor. It looked the brightest on the IR image. It should be noted that on the visible image (Fig. 2), the bottom electrode was not emitting any visible light. In other words, the bottom electrode was not glowing. The temperatures at the center of the tube were always higher than the temperatures at other positions closer to the wall, confirming the visual observation that in methane steam reforming the visible discharge moved well over the electrode surfaces. The space that the visible discharge covered was the whole volume between the two electrodes. However, when the applied voltage was increased, or the input power was increased, the visible discharge coverage was observed to decrease. This decrease in the discharge coverage could be seen in Fig. 5: the recorded temperatures at 100 V low side voltage fluctuated a little more than the recorded temperatures at 85 V low side voltage. It should be noted that as the bulk gas temperature and electrodes temperatures increased, the visible discharge coverage decreased.

The reason water was introduced into the reactor in the liquid form was that coke filaments formed if water was vaporized and mixed with methane before reaching the reactor and the water mole fraction was below 50%. If water was fed in the liquid form, the discharge stability could still be maintained even at water mole fractions less than 25%. An experiment in which the feed consisted of 25 sccm of methane, and 50 sccm of water (vaporized and mixed with methane) was conducted. The discharge was monitored by the IR camera to understand the cause of carbon formation when water was fed into the reactor this way. At this feed condition, there was no problem with carbon formation. The reactor wall was clean and almost free of coke. The axial temperature profile is shown in Fig. 6. The temperature profile when water was fed in the vapor form is different from the temperature profile when water was fed in the liquid form. In the former case, the temperatures of both the top and bottom electrodes were both the highest inside the reactor. In the later case, only the temperature of the bottom electrode was the highest. Theoretically, the feed temperature when water was fed in the liquid form should be at least 75 °C less than the feed temperature when water was fed in the vapor form. It is consistent with the experimental results that the temperature of the top electrode, when water was fed in liquid form, was about 100 °C lower than the temperature of the top electrode when water was fed in vapor form. Furthermore, if a coke filament were to be formed when water was fed in the liquid form, it would grow from the bottom electrode, whose temperature was the highest inside the reactor. If a coke filament were to be formed when water was fed in the vapor form, there would be two filaments forming on each electrode and growing toward one another. As a result, it could be concluded that because feeding liquid water into the reactor kept the reactor temperatures lower, it helped distribute the discharge over the electrode surfaces. Because the discharge was well distributed, and the temperature was lower, there was no hot spot for a coke filament to form. Therefore, the discharge stability could be achieved when water was fed in the liquid form at substantially lower water fractions.

In summary, the temperatures inside the plasma reactor were generally less than 300 °C under stable steam reforming conditions. When water was fed in the liquid form, it helped decrease the reactor and electrode temperatures; therefore, coke filament formation did not occur to disrupt the discharge stability.

5. Temperature measurements in the partial oxidation of methane

The temperatures inside the reactor for conditions of the partial oxidation of methane were also measured using the IR camera. The feed consisted of 266 sccm of methane and 134 sccm of oxygen (2/1 ratio). The input power was 12 W

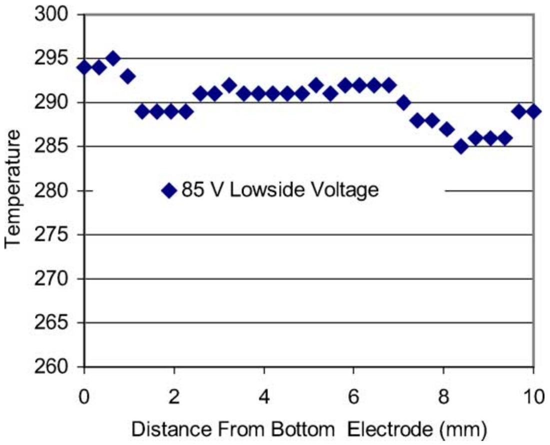

Fig. 7. Axial temperature profile at reactor center.

at 85 V low side voltage. The temperatures on various positions inside the reactor were measured. The axial temperature profile at the reactor center is presented in Fig. 7.

It is seen that under the described experimental conditions, the temperature inside the plasma reactor generated by ac discharge was less than 300 °C. It was also found that if the reactor was cooled by a water jacket at 10 °C, the discharge was not affected. These results confirm that the plasma generated by the ac discharge is a low temperature, non-equilibrium, plasma even under conditions of exothermic reactions.

The axial temperature profile at the reactor center (Fig. 7) and the IR image (Fig. 8) show that the temperature differences between the top and bottom electrodes were small. The partial oxidation reactions producing CO, CO_2, and H_2O are exothermic. On the other hand, the coupling reactions producing C_2 hydrocarbons and the steam reforming reactions are endothermic. As a result, the bulk gas temperature is increased by the heat released from the exothermic reactions and decreased by the endothermic reactions. The decrease in the axial temperature profile at the reactor center near the bottom electrode suggests that either more endothermic reactions or less exothermic reactions occurred in this region. From the GC results, that show that the oxygen conversion was above 90%, it can be inferred that oxygen became limited before the gases reached the bottom electrode. If the methane conversion was not high, a large fraction of hydrogen produced could be oxidized further to water, which is undesirable, in the early reactor stage.

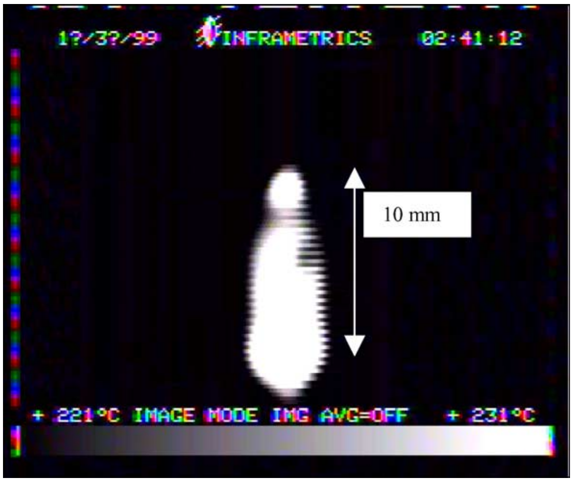

Fig. 8. IR image of the reactor with discharge on.

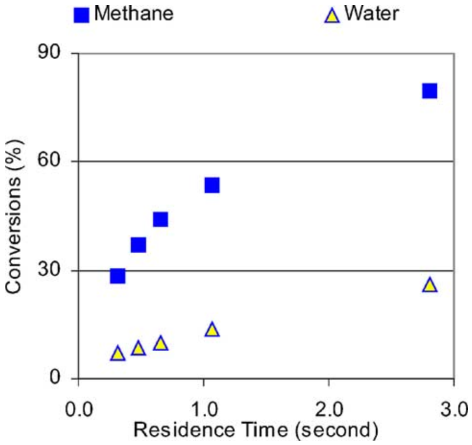

Fig. 9. Conversion vs. residence time in steam reforming 10 mm i.d., 67% H_2O, 33% CH_4, ∼15 W.

6. Summary and conclusions

Under these low temperature and atmospheric pressure conditions, thermodynamics do not predict high methane conversion, whether it is steam reforming or partial oxidation of methane. However, the highest methane conversion experimentally obtained at quite short residence times so far is 80% in the steam reforming of methane and 68% in the partial oxidation of methane using the non-equilibrium plasma generated by the ac discharge. In both cases, the methane conversion depends strongly on the residence time (Figs. 9 and 10).

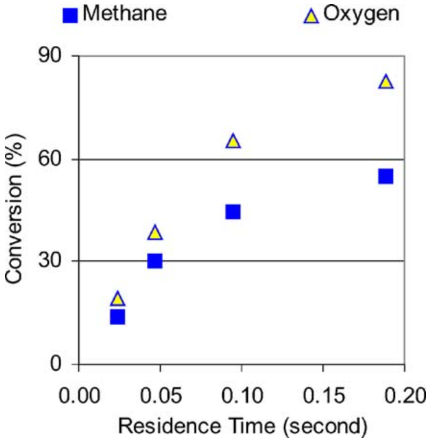

Fig. 10. Conversion vs. residence time in partial oxidation 4.5 mm i.d., 67% CH_4, 33% O_2, ∼10 W.

C_2 hydrocarbons are not the products thermodynamically favored from steam reforming or partial oxidation of methane. However, the C_2 selectivity could be very high over a wide range of methane conversions when methane is converted using the non-equilibrium plasma generated by the ac discharge. The C_2 selectivity was 30–40%, in the partial oxidation of methane. In the steam reforming of methane, at 67% water mole fraction, the selectivity toward C_2 hydrocarbons could be as high as 45%. Furthermore, at 50% water mole fraction, this C_2 selectivity could be as high as 60%. This study shows confirming evidence for non-equilibrium behavior in the conversion of methane by plasma activation at low temperatures.

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