CONTROL OF PRODUCT SELECTIVITY IN DIRECT METHANE CONVERSION BY ATMOSPHERIC PRESSURE NON-THERMAL PLASMA

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Abstract

Different types of non-thermal plasma, namely corona discharge, homogenous glow discharge and pseudo-glow discharge were studied in one reactor at atmospheric pressure and 1-2 kHz ac supply. The electrode configuration and input power controls the amplitude and duration of the discharge current pulses. The discharge conditions determined the product selectivity in direct methane conversion. The glow discharge produces acetylene, ethylene and ethane in approximately equal quantities, while the corona discharge is mainly selective to acetylene. In the pseudo-glow discharge the product distribution can be controlled by the power input.

1. Introduction

The direct conversion of methane into more valuable hydrocarbons has been studied intensively for more than 20 years. Thermal and catalytic methods however lead to low yields of the desired hydrocarbon products. A well-established process is the direct conversion of methane into acetylene in thermal arc plasma and this process has been developed and used for more than 40 years by Hüls. Non-thermal plasmas are currently being investigated as a promising alternative low temperature method to directly convert methane to higher hydrocarbons. Using microwave and RF plasmas at reduced pressure, a high selectivity towards acetylene were found. By combining the plasma with heterogeneous catalysts such as zeolites, it has been found that methane was converted mainly to acetylene over NaY zeolite in a dc corona discharge. A recent study has shown non-catalytic direct conversion of methane to acetylene by using dc pulse corona discharge at atmospheric pressure with a selectivity higher than 95%. It remains unclear if methane is converted to acetylene mainly through the discharge in a volume process or through a surface reaction on the catalysts inside the plasma.

In this paper we use an ac 1-2 kHz power supply and configure the electrodes in the reactor to realize different types of non-thermal plasma, corona discharge, homogenous glow discharge and pseudo-glow discharge at atmospheric pressure in order to study methane conversion and the product selectivity.

2. Experiment

a. Experimental Arrangement

A schematic diagram of the experiment is shown in Fig. 1. The experiment was carried out in a quartz glass tube with internal diameter 18 mm. Reactant gases controlled by mass flow...
controllers were fed at a constant flow rate. High voltage with a frequency between 1 and 2 kHz was applied to the electrodes. A digital oscilloscope recorded the voltages and current signals. The current was measured with a grounded resistor in series with the electrode. The power input to the discharge was calculated by:

\[ P_e = \frac{1}{T} \int_0^T V(t)I(t)dt, \]

where \( V(t) \) is the voltage drop across the electrodes, \( I(t) \) is the current through the plasma.

The feed gas and products from the reactor were analyzed on-line by GC-MS (HP G1800C GC). All the experiments were operated at atmospheric pressure. The concentrations of each species were calculated using calibrated gas mixtures as external standard, while the hydrogen concentration was estimated from the total gas balance (moles of \( \text{H}_2 \) formed = moles of total gas out - moles of \( \text{CH}_4 \) out and all \( \text{C}_x\text{H}_y \) products). The methane conversion \( C \), product selectivity \( S \), yield \( Y \) of \( \text{C}_2 \) hydrocarbons and hydrogen are defined as follows:

\[
\begin{align*}
C_{\text{H}_4} & = \frac{(\text{moles of } \text{CH}_4 \text{ consumed})}{(\text{moles of } \text{CH}_4 \text{ introduced})} \times 100\% \\
S_{\text{C}_2} & = \frac{(2 \times \text{moles of } \text{C}_2 \text{ product formed})}{(\text{moles of } \text{CH}_4 \text{ introduced})} \times 100\% \\
Y_{\text{C}_2} & = \frac{(2 \times \text{moles of } \text{C}_2 \text{ product formed})}{(\text{moles of } \text{CH}_4 \text{ introduced})} \times 100\% \\
S_{\text{H}_2} & = \frac{(0.5 \times \text{moles of } \text{H}_2 \text{ formed})}{(\text{moles of } \text{CH}_4 \text{ consumed})} \times 100\%
\end{align*}
\]

where \( \text{C}_2 \) represents \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \).

**b. Electrode Configurations and Electrical Characteristics**

The electrode configuration was varied in order to produce different kinds of non-thermal plasma and control the current pulse waveform. Fig. 2 shows the electrode configurations, and Fig. 3 shows the correspondant electrical characteristics of the plasma. Fig. 2a is the configuration used for the corona discharge (CD) and Fig. 3a shows a typical applied voltage and discharge current waveform. The discharge current is a short pulse with rise a time of less

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**Fig. 2** Two kinds of electrode configurations to produce: (a) corona discharge and (b) glow or pseudo-glow discharge at atmospheric pressure.
than 50 ns, reaching a maximum value of 100 A or more.

The electrode configuration shown in Fig. 2b can produce glow or pseudo-glow discharges. These discharges are stabilized by inserting a resistance of ~100 kΩ into one of the electrodes. Fig. 3b shows the voltage and current wave forms of the homogenous or true glow discharge. It is of a pulse-less nature and extends over a whole ac cycle, visually appearing as a diffuse glow over the entire inter-electrode space. Although it is shown here in methane, it can also be realized in air. Increasing the input voltage will usually change it to pseudo-glow discharges. The typical applied voltage and discharge current are shown in Fig. 3c, having features common to both corona and glow discharges. The current pulses are longer (~40 μs) compared to the corona discharge and also a continuous component of the current is observed, in the example of Fig. 3c during the negative half wave. In one half cycle one pulse or at high power input several pulses were observed, the pulse current ranging between 40 and 200 mA.

3. Results and Discussion

The results of methane conversion are plotted against the input energy per methane molecule in Fig. 4. In the experiments shown, the gas flow rate was 30 sccm. The real glow discharge (GD) may only be operated at low energy input below 6 eV/molecule, upon increasing power, in most cases the discharge switches to a pseudo-glow discharge (PD). The methane conversion increases with the energy input. Comparing PD, GD and CD at about 5 eV/molecule, PD and GD have almost the same methane conversion for similar energy.
input, but CD gives a higher conversion, this means that the spark is more efficient in converting methane even at lower average power input. At about 19 eV/molecule energy input the methane conversion can reach up to 60% in a CD and even up to 70% in a PD.

Fig. 5 shows the $C_2$ yields and Table 1 lists the selectivities. The types of discharges investigated have their own product selectivities and yields. In a glow discharge (e.g. GD, PD) the selectivity to $C_2H_2$, $C_2H_4$ and $C_2H_6$ are almost the same. The behavior of the pseudo-glow discharge (PD) changes with the energy input, at power a similar product selectivity as in a GD is found, but with higher $C_2H_6$ yields. Long time (~40 µs) low current pulses (~40 mA) with an energy per pulse of about 1.1 mJ as in PD are produce preferentially all $C_2$ products. Upon further increasing the power or energy input, the reaction becomes mainly selective towards acetylene with small amount of $C_2H_4$, $C_2H_6$ and other hydrocarbons like $C_4H_2$ and $C_4H_6$. Long time (~40 µs) current pulse larger than ~80 mA with energy per pulse ~3.2 mJ as in PD or short time (~50 ns) and higher current pulse (~80 A) with energy per pulse ~3.3 mJ as in CD produce preferentially $C_2H_2$. The selectivity to acetylene was significant, for example in CD or PD with an energy input of about 19 eV/molecule, 60 or 73% methane was converted, yielding 31 or 43% acetylene and 8 or 11% other hydrocarbons, as well as 22 or 17% soot or carbon deposition in the reactor. The PD is even more efficient than a CD in methane conversion at about 19 eV/molecule energy input.

![Graph](image1.png)

Fig. 4: Methane conversion against the input energy density in different kinds of non-thermal plasma at atmospheric pressure.

![Graph](image2.png)

Fig. 5: $C_2$ hydrocarbon yield against the input energy in different kinds of non-thermal plasma at atmospheric pressure.

In our earlier experiments, the dielectric barrier discharge (DBD) was mainly selective to $C_2H_2$ and $C_1H_4$ with small amount of $C_2H_4$, $C_2H_6$ and other hydrocarbons like n-C$_4$H$_{10}$. The short time (~100 ns) and low current pulses (~200 mA) with energy per pulse ~0.1 mJ as in a DBD produce preferentially saturated hydrocarbons. Fig. 6 illustrates schematically the results of selectivity vs. pulse energy.
Table 1: Products selectivity in different kinds of non-thermal plasma at atmospheric pressure and ambient room temperature, pure methane gas flow rate: 30 sccm. GD—glow discharge, PD—pseudo-glow discharge, CD—corona discharge.

<table>
<thead>
<tr>
<th></th>
<th>C₂H₂ (%)</th>
<th>C₂H₄ (%)</th>
<th>C₂H₆ (%)</th>
<th>C₃H₂ (%)</th>
<th>C₆H₆ (%)</th>
<th>H₂ (%)</th>
<th>eV/mol.</th>
<th>Energy per pulse (mJ)</th>
<th>Energy per cycle (mJ)</th>
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<tr>
<td>GD 0</td>
<td>14.0</td>
<td>15.9</td>
<td>24.3</td>
<td>-</td>
<td>-</td>
<td>44.1</td>
<td>2.06</td>
<td>-</td>
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<td>17.0</td>
<td>18.2</td>
<td>28.4</td>
<td>-</td>
<td>-</td>
<td>38.8</td>
<td>3.62</td>
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<tr>
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<td>20.0</td>
<td>25.9</td>
<td>28.1</td>
<td>-</td>
<td>-</td>
<td>47.6</td>
<td>5.71</td>
<td>-</td>
<td>11.1</td>
</tr>
<tr>
<td>PD 0</td>
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<td>15.9</td>
<td>29.8</td>
<td>-</td>
<td>-</td>
<td>47.5</td>
<td>1.99</td>
<td>~0.07</td>
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<tr>
<td>PD 1</td>
<td>16.3</td>
<td>17.3</td>
<td>33.9</td>
<td>-</td>
<td>-</td>
<td>40.5</td>
<td>3.34</td>
<td>~0.09</td>
<td>7.2</td>
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<tr>
<td>PD 2</td>
<td>15.4</td>
<td>16.7</td>
<td>33.6</td>
<td>-</td>
<td>-</td>
<td>42.5</td>
<td>4.34</td>
<td>~1.1</td>
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<td>33.4</td>
<td>12.1</td>
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<td>4.2</td>
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<td>70.9</td>
<td>7.40</td>
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<td>PD 4</td>
<td>45.8</td>
<td>4.7</td>
<td>1.9</td>
<td>3.4</td>
<td>2.9</td>
<td>84.3</td>
<td>9.24</td>
<td>~3.2</td>
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</tr>
<tr>
<td>PD 5</td>
<td>60.3</td>
<td>6.3</td>
<td>2.0</td>
<td>5.0</td>
<td>2.6</td>
<td>84.4</td>
<td>19.32</td>
<td>~4.1</td>
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<tr>
<td>CD 1</td>
<td>34.0</td>
<td>3.5</td>
<td>1.9</td>
<td>9.4</td>
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<td>79.0</td>
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<tr>
<td>CD 2</td>
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<td>7.3</td>
<td>1.5</td>
<td>77.7</td>
<td>18.80</td>
<td>~5.8</td>
<td>40.6</td>
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</table>

Fig. 6: Summary of the relationship between energy per pulse and product selectivity.

Different products and selectivities reflect that each kind of discharge has its own plasma chemistry. In our study we have shown that the main product in a DBD is C₂H₆, followed by higher aliphatic hydrocarbons. The product distribution and computer simulations indicate that the main radical formed by electron impact dissociation of methane is CH₃. Its main reaction is the recombination and hydrocarbon chain growth. With increasing pulse energy in the discharge, de-hydrogenation becomes a more important reaction path. A possible reason could be that the distribution of primary radicals is shifted from mainly CH₃ to CH₂ and CH under these conditions.

Table 1 also lists the hydrogen selectivities. It amounts to about 50% where hydrogen-rich products are predominantly formed and up to approx. 80% in a CD or PD. There hydrogen is a byproduct from acetylene formation and methane decomposition to solid carbon (CH₄→C(s)+2H₂). The de-hydrogenation of methane in this non-thermal plasma could also have a potential application for hydrogen production.
Fig. 7 shows the energy required per CH₄ molecule converted against the input energy in the non-thermal plasmas investigated. At about 5 eV/molecule energy input, the CD is the most effective discharge for methane dissociation. The DBD investigated in our earlier study requires 90–130 eV/molec. The energy required PD and GD are similar and lie between the CD and the DBD. It is expected that large-area PD or GD with multiple electrodes will have latent potentials in practical use similar to the DBD.

4. Conclusions

In non-thermal ac plasmas the duration and amplitude of the current pulses have been controlled, giving a transition between glow, pseudo-glow and corona discharge. Each type of plasma has its own plasma chemistry and product selectivity. A homogeneous glow discharge and a pseudo-glow discharge at low energy input produces almost the same amount of ethane, ethylene and acetylene; while high methane conversions were found in corona and pseudo-glow discharges at > 8 eV/molec. energy input. In the latter case the main product was acetylene and hydrogen. Non-thermal plasma methods could possibly open new ways of acetylene synthesis and hydrogen fuel production by direct methane conversion at low temperature. Glow and pseudo-glow discharges are more efficient than the dielectric barrier discharge concerning energy costs and have latent potential in practical use.

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