Kinetic Modeling of Plasma Methane Conversion Using Gliding Arc

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Abstract: Plasma methane (CH\textsubscript{4}) conversion in gliding arc discharge was examined. The result data of experiments regarding the performance of gliding arc discharge were presented in this paper. A simulation which is consisted some chemical kinetic mechanisms has been provided to analyze and describe the plasma process. The effect of total gas flow rate and input frequency refers to power consumption have been studied to evaluate the performance of gliding arc plasma system and the reaction mechanism of decomposition. Experiment results indicated that the maximum conversion of CH\textsubscript{4} reached 50% at the total gas flow rate of 1 L/min. The plasma reaction was occurred at the atmospheric pressure and the main products were C (solid), hydrogen, and acetylene (C\textsubscript{2}H\textsubscript{2}). The plasma reaction of methane conversion was exothermic reaction which increased the product stream temperature around 30–50 °C.

Key words: plasma, gliding arc, methane conversion, reaction mechanism

1. Introduction

Conversion of methane into more valuable compounds, such as hydrogen, synthesis gas, acetylene, and other higher hydrocarbon or black carbon is still becoming a challenge [1]. Many studies have been done intensively for several decades especially for direct methane conversion. The major problem on this route came from the strong C—H bond of methane.

Many research groups used catalytic method to overcome this problem and reported some good results. But those were not free from any problems. Carbon solid deposition on catalyst surface that was produced by chemical reaction was reduced the catalyst performance and became the greatest barrier to transfer this technology from laboratory into industrial scale. The catalyst needed a specific temperature which was usually 100–200°C higher than room temperature to activate the catalytic site. It means heat supply was significantly required. Another reported problem was the small flow of injected raw gas.

Now days, more and more investigations have been deeply performed using non-conventional technology, like plasma technology. Plasmas, both thermal and non-thermal plasmas, have been extensively studied for methane conversion. Different kinds of plasmas and operation conditions produced different product distribution. This characteristic made it suitable for chemical synthesis selection. Methane utilization using glow discharge [2–4], dielectric barrier discharge (DBD) [5–11], Corona [3,12], spark [3], arc plasma-jet [13], RF plasma [14,15], thermal plasma [16,17] have been investigated. Another plasma variables effect on CH\textsubscript{4} plasma reaction such as plasma power generator [18,19], catalyst process-assisted [20,21], water vapor injection [22] were also experimentally investigated.

Cold plasmas such as corona, glow discharge, and DBD were very cheap and easy to handle. It becomes great possibility to be applied in industry. The main problem was the plasma density which is very low. It made rather difficult to achieve higher conversion at higher flow rate. However, hot plasmas which typically high temperature arc plasmas produced very
high density of plasma and capable to maintain high injection gas flow rate. But the instrument cost was very expensive and it spent higher power consumption.

To overcome those problems, plasma device which is located in transition region between glow and arc state was introduced. Gliding arc plasma at low current intensity, which is also called glowing arc, became a favor due to its characteristics under transition region, such as: higher electron density, higher flame overheating, and capable for high injection flow rate. Its applications have been increasing. Decomposition of $\text{H}_2\text{S}$ [23], $\text{N}_2\text{O}$ [24], $\text{CHCl}_3$ and $\text{CCl}_4$ [25,26], which were employing gliding arc as the destruction tool, have been investigated and studied. High percentage of destruction efficiency has been claimed using this method. Many papers were also discussing on the discharge behavior of gliding arc plasma. Theoretical and numerical study of gliding arc to describe it has been published with showing many mathematical equations [27–31].

In this study, the conversion of methane using gliding arc plasma was deeply studied. The experimental results were compared with the computational simulation ones in term of both kinetic reaction path way and thermodynamic calculation.

2. Experiment setup

The schematic diagram of experimental setup is shown in Figure 1. Details of each part of the system are described in the next section.

![Schematic diagram of experimental set up](image)

**2.1. Plasma reactor and applied power system**

The reactor was made from a quartz-glass tube of inner diameter 450 mm and total volume $5 \times 10^{-4}$ m$^3$. The upper part and bottom of the reactor supplied with a teflon seal comprised two electrodes made of stainless steel. The length of the electrodes was 150 mm. The separation of the electrodes in the narrowest section was only 1 mm. The gas mixture was introduced between the electrodes through a capillary of inner diameter 0.3 mm. A thermocouple, located 100 mm above the electrode, has been provided to measure the outlet gas temperature ($T_g$). A high frequency AC power supply (Auto electric, A1831) with a maximum voltage $10^3$ V and a maximum ampere $10^{-1}$ A was connected to the gliding arc electrode to generate plasma. The frequency could be adjusted from $1 \times 10^4$ to $2 \times 10^4$ Hz. Figure 2 shows typical waveforms of voltage and discharge current used in this experiment.

**2.2. Input gas**

Methane with a purity of 99.97% was used as source of gas. Injection of methane gas was controlled by calibrated mass flow controllers: Tylan FC-280S, having real flowing capacity up to $3.34 \times 10^{-4}$ m$^3$/s and Bronkhorst Hi-Flow MFC, having real flowing up to $1.67 \times 10^{-5}$ m$^3$/s. Total gas flow rate was varied from 1 L/min ($=1.67 \times 10^{-5}$ m$^3$/s) to 3 L/min ($=5.0 \times 10^{-5}$ m$^3$/s). The mixture composition of the outlet reactor was analyzed before and after the plasma operation.
2.3. Measurement system

Two GCs have been used to analyze the quantitative amount of products. The content of hydrogen in the gas mixture after the reaction was measured by GC-TCD (YoungLin M600D, Column: SK Carbon). And for determination of hydrocarbons in the outlet gas mixture, a GC-FID (Hewlett Packard 5890, Column: Carbon Sieve 5A) was used. The flow of gas to the GC was measured first by bubble flow meter. Considering the expansion of gas, the end of main output line was connected to wet test meter (Ritter TG5) to measure the fluctuation of main flow after and before experiment running.

The evaluation of system performance, selectivity and conversion, were formulated as:

\[
\text{Selectivity for H}_2 = \frac{\text{moles of H}_2 \text{ produced}}{2 \times \text{moles of CH}_4 \text{ converted}} \times 100\% \quad (1)
\]

\[
\text{Selectivity for C}_x\text{H}_y = \frac{x \times \text{moles of C}_x\text{H}_y \text{ produced}}{\text{moles of CH}_4 \text{ converted}} \times 100\% \quad (2)
\]

\[
\text{Conversion of H}_2 = \frac{\text{moles of CH}_4 \text{ converted}}{\text{moles of initial CH}_4} \times 100\% \quad (3)
\]

The waveform of voltage and current were captured by oscilloscope (Agilent 54641A) with a high voltage probe (Tektronix 6015A) and current monitor (Pearson 4997). The amount of supplied power was calculated by following equation:

\[
W = \int (V(t) \times I(t))dt \times \text{frequency} \quad (4)
\]

3. Simulation Model

To explain the reaction pathway, a model simulation based on chemical kinetic reaction has been performed. The gas-phase reaction mechanism consists of the 28 reactions listed in Table 1. These 28 reactions were obtained and chosen by summarizing the literatures [32–34]. The model was assumed to be at constant pressure and the order of the reaction was one. Rate constants were formulated in a modified Arrhenius form,

\[
k_i = A_i T_i^{n_i} \exp(-E_i/RT_i) \quad (5)
\]

The model was deeply concerning on the visible products in the output stream. Experimentally hydrogen and acetylene selectivity were compared with simulation results because these gases were existed mostly in the product stream.

To satisfy the process analysis, calculation of heat balance of the system was done. Energy that has been produced by plasma reaction and supplied by power supply has changed the heat balance of the system. Produced heat by reaction was possible to be calculated based on heat of formation of the compounds. However, the supplied energy from power supply.
Table 1. Chemical kinetic reaction for conversion of methane

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Forward rate coefficient(^1)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(CH_4 = CH_3 + H)</td>
<td>1.31E+34</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>(CH_4 + H = CH_3 + H_2)</td>
<td>2.2E+4</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>(CH_3 + H = CH_2 + H_2)</td>
<td>1.8E+12</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>(CH_2 + H = CH_2 + H)</td>
<td>3.00E+13</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>(CH_2 + H_2 = CH_3 + H)</td>
<td>7.23E+13</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>(CH_3 + CH_2 = C_2 H_4 + H)</td>
<td>5.00E+13</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>(CH_3 + CH_3 = CH_4 + CH_2)</td>
<td>1.70E+09</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>(CH_3 + CH_3 = C_2 H_5 + H)</td>
<td>5.00E+12</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>(H + H_2 = H_2 + H)</td>
<td>9.70E+16</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>(CH_3 + H_2 = CH_4 + H)</td>
<td>4.13E+04</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>(CH_3 + CH_3 = C_2 H_5 + H)</td>
<td>5.62E+00</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>(C_2 H_5 + H = C_2 H_4 + H_2)</td>
<td>1.30E+37</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>(C_2 H_5 = C_2 H_4 + H)</td>
<td>1.25E+38</td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>(C_2 H_4 + H = C_2 H_3 + H_2)</td>
<td>3.16E+11</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>(C_2 H_4 + CH_3 = C_2 H_5 + CH_4)</td>
<td>4.20E+11</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>(C_2 H_4 + H + C_2 H_5 + H_2)</td>
<td>7.54E+17</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>(C_2 H_4 + H_2 = C_2 H_4 + H + H_2)</td>
<td>7.54E+17</td>
<td></td>
</tr>
<tr>
<td>18.</td>
<td>(C_2 H_4 + H_2 = C_2 H_5 + H_2)</td>
<td>3.00E+13</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>(C_2 H_4 = C_2 H_3)</td>
<td>1.13E+36</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>(CH_2 + C_2 H_4 = C_2 H_6)</td>
<td>1.80E+13</td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td>(CH + H = C + H_2)</td>
<td>1.50E+14</td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>(C + CH_3 = C_2 H_2 + H)</td>
<td>5.00E+13</td>
<td></td>
</tr>
<tr>
<td>23.</td>
<td>(CH + C_2 H_2 = C_2 H_3 + H)</td>
<td>1.1E+13</td>
<td></td>
</tr>
<tr>
<td>24.</td>
<td>(C_2 H_2 + H = C_2 H_3)</td>
<td>6E+12</td>
<td></td>
</tr>
<tr>
<td>25.</td>
<td>(C_2 H + H_2 = C_2 H_4)</td>
<td>8E+12</td>
<td></td>
</tr>
<tr>
<td>26.</td>
<td>(CH_3 + H_2 = CH_4 + H)</td>
<td>4.13E+2</td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>(C_2 H_4 + C_2 H_3 = C_4 H_6 + H)</td>
<td>6.21E+11</td>
<td></td>
</tr>
<tr>
<td>28.</td>
<td>(CH_3 + CH_3 = C_2 H_5 + H_2)</td>
<td>2.9E+5</td>
<td></td>
</tr>
</tbody>
</table>

Note: \(^1\) \(k = AT^n \exp(-E/RT)\)

could be known from oscilloscope measurement,

\[
\dot{Q} = (\Delta H_{f,reactant} - \Delta H_{f,product}) + W
\]

(6)

In this experiment, reactant compound was (reacted) methane and the products were higher hydrocarbon (acetylene) and hydrogen. The heat of formation is calculated equal to the sum of the bond energies in the molecules, \(\sum E(b)\),

\[
\Delta H_f = \sum E(b)
\]

(7)

Bond energy data of compounds could be found in Table 2. Moreover, increment of gas temperature due to energy changes could be calculated as,

\[
\dot{Q} = \sum \left[ (m \cdot C_p)_{un-reacted \ species} + \sum (m \cdot C_p)_{products} \right] (T_g,t - T_g,0)
\]

(8)

Table 2. Compounds parameters

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>Chem. Struct.</th>
<th>(\sum E(b)_{T=298K}/(J/mol))</th>
<th>(C_{P,T=333K}/(J/(mol \cdot T)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Methane</td>
<td>CH\textsubscript{4}</td>
<td>1.66 \times 10^6 [35]</td>
<td>37.6</td>
</tr>
<tr>
<td>2.</td>
<td>Acetylene</td>
<td>C\textsubscript{2}H\textsubscript{2}</td>
<td>1.64 \times 10^6 [36]</td>
<td>46.3</td>
</tr>
<tr>
<td>3.</td>
<td>Hydrogen</td>
<td>H\textsubscript{2}</td>
<td>4.22 \times 10^5 [35]</td>
<td>29.0</td>
</tr>
</tbody>
</table>
Heat balance could be checked by comparing temperature of outlet gas \( T_g \) between experimental and theoretical calculation. The model was assumed free from environmental disturbance (closed system).

The simulation model was coded and numerically solved using MATLAB® program. MATLAB® modules (ode23s and fmins) were utilized to solve the coupled differential equations and minimize the absolute error [38].

4. Results and discussion

4.1. Products and product stability

In order to determine the products and product stability, 1.5 L/min of methane was injected to the reactor and frequency was kept constant at 20 kHz. Product samples were taken in different sampling time. To ensure the reproducibility of the products, every point of sample has been done by two times experiment. Figure 3(a) shows that the conversion of methane reached 45%–50%. The products mainly consisted of hydrogen, around 40% of selectivity, and acetylene, 20% of selectivity (Figure 3(b)). Other higher hydrocarbon products, such as propylene (C\(_3\)H\(_6\)) and propane (C\(_3\)H\(_8\)), were also detected but the concentration was quite low (less than 1% of total gas product stream). Instead of gaseous products, carbon (C) was numerously produced as the solid product. Based on this experimental result, it could be suggested that the plasma chemical reaction of methane conversion in gliding arc could be:

\[
\text{CH}_4 = \text{C} + 2\text{H}_2 \quad (9)
\]

\[
2\text{CH}_4 = \text{C}_2\text{H}_2 + 3\text{H}_2 \quad (10)
\]

In terms of stability of the conversion and product distribution, Figure 3 shows the plasma reaction has given stable result. The results were almost independent from reaction time or sampling time.

4.2. Effect of total gas flow rate

The effect of total gas flow rate, which was related to the residence time of methane and passed through between the electrodes, was investigated. Experiments were performed by varying the total gas flow rate from 1 to 3 L/min with interval 0.5 L/min. In this experiment, the total consumed power could not be adjusted manually. The power was a function of breakdown voltage and changed into stable-equilibrium state automatically. The number of consumed power was captured by oscilloscope as function of voltage and current and changed into power by applying formula 4.

![Figure 3. Stability performance of (a) methane conversion and (b) product distribution on reaction time](image)

(1) Hydrogen, (2) Acetylene

![Figure 4. Effect of total gas flow rate on (a) methane conversion and (b) products yield](image)

(1) Hydrogen, (2) Acetylene
Figure 4 shows that the conversion of methane was decreased when the total gas flow rate increased. The conversion was decreased from 50% at total gas flow rate 1 L/min to 38% at 3 L/min. The increment of total gas flow rate reduced the residence time of CH\textsubscript{4} to collide with electrons and other energetic species. However, increasing of total gas flow rate was also decreased the production ratio (yield) of hydrogen and acetylene.

4.3. Effect of frequency

The power supply frequency is related to the supplying total power of AC power supply to the plasma system. Generally, higher frequency produces higher total power because of increasing number of pulse per cycle of voltage and current waveform. In this study, frequency was varied from 15 to 20 kHz.

As shown in Figure 5, the conversion of methane tent to be increased with increasing of frequency, from 41% at 15 kHz to 48% at 20 kHz. Reducing supplied power to the plasma system, as told before, has become the main reason of this phenomena. Increasing value of conversion was effecting on production yield of hydrogen and acetylene, the amount of which was slightly getting to increase with increasing value of frequency.

4.4. Reaction mechanism

The main gaseous products of methane conversion using gliding arc plasma were hydrogen and acetylene. To investigate the methane reaction mechanism, 28 reactions were used to approach the amount of the final products. The model simulations, as told above, consisted of two parts: kinetic reaction and heat balance model. This model results were compared to the experimental results which were produced by varying total gas flow rate and applied frequency.

Figure 6 shows the comparison of simulation and experimental result where the total gas flow rate was adjusted as the variable. Figure 6(a) shows the selectivity for hydrogen and acetylene as a function of total gas flow rate at frequency of 20 kHz. The selectivity for hydrogen and acetylene were slightly decreased around 3%–5% with the increasing of total gas flow rate from 1 L/min to 3 L/min. However, kinetic simulation showed electron collision has an important role on the conversion of methane and initiate plasma reaction rather than other radical or energetic species.

Initiated with methane and electron reaction, the concentration of CH\textsubscript{3} radical (CH\textsubscript{3}·) was increased sharply at the beginning (Figure 6(b)) although in the next step, it would be consumed and reacted to form higher mass molecules or smaller ones. At the same time, the production of hydrogen radical (H·) was also increased but not as much as CH\textsubscript{3}·. It was because H· has high possibility to react simultaneously with methane after it was produced. When the concentration of CH\textsubscript{3}· getting high, reaction of CH\textsubscript{3}·+H· became favor to produce other radical species, such as CH\textsubscript{2}· and H\textsubscript{2}. It made the concentration of CH\textsubscript{3}· dropped quickly. In case of H·, although it was consumed and reacted with other radical species, many other radical reactions produced H· as the intermediate species. That was the reason that made the concentration of H· was not drop sharply. Instead of these two radical species, other species were not so significant amount and effect to the reaction pathway.

The main reactions that responsible to the hydrogen production were,
\begin{equation}
CH\textsubscript{3}·+H· = CH\textsubscript{2} + H\textsubscript{2} \quad (11)
\end{equation}
\begin{equation}
H·+H·+H\textsubscript{2} = H\textsubscript{2}+H\textsubscript{2} \quad (12)
\end{equation}

and for acetylene was,
\begin{equation}
C·+CH\textsubscript{3}· = C\textsubscript{2}H\textsubscript{2}+H· \quad (14)
\end{equation}
In order to satisfy and check the model, total C and H atom balance were also calculated. Calculation was done by totaling the number of C and H atom from products and compared to the total of input C and H atom. Figure 6(c) shows the model result was quite good because the ratio of C and H atom before and after reaction was closed to 1 (equilibrium).

Another way to analyze the phenomena of plasma reaction was using heat balance calculation. The calculation was done by totaling the incoming input power to the system and produced heat caused by reaction. These energies could change the temperature of the system higher than before reaction. The experiment result shows the temperature of outlet gas stream has increased around 30–50 °C. Calculation of methane reaction (bond energy method) stated that the plasma reaction was an exothermic reaction.

Figure 6(d) shows the comparison of outlet gas temperature ($T_g$) before and after reaction. By increasing the total gas flow rate, the gas temperature was decreased. Higher flow rate means increasing volume of gases that could accept or transfer the heat to raise the temperature in specific time dimension. Higher volume of gas heat acceptor made the increment of $T_g$ becoming lower and lower. However, the heat that produced from plasma reaction was the main reason of the increment of the temperature rather than supplied energy from AC power supply. By comparing the total produced energy, energy from AC power supply just contributed 20%–30% to the increment of gas temperature. The importance of external energy was used to initiate the breakdown of methane gas to initiate the plasma reaction.

In case of frequency as the adjusted variable, the overall phenomena was not significantly different. Figure 7 shows the simulation results compared to the experimental ones as a function of total gas flow rate 1.5 L/min. As shown in Figure 7(a), the selectivity for hydrogen and acetylene were relatively stable with increasing frequency. It means, although the energy that supplied to the plasma system was difference, the reaction pathway was almost similar where the electron collision was still the main
factor on initiating the reaction. Reducing energy could cause the decrease in methane conversion (Figure 5(b)). In case of intermediate radical species concentration, the main reaction was mainly done by CH\textsubscript{3} and H. Those radical species has important role on the reaction direction (Figure 7(b)). Similar with the previous result, this model also gave a satisfactory result on the calculation of total C and H balance (Figure 7(c)).

Figure 7. Simulation and experimental result of methane plasma reaction as a function of frequency at total gas flow rate 1.5 L/min
(a) Gaseous product selectivity, (b) Simulation of radical species concentration as a function of reaction time, (c) Simulation C and H atom balance, (d) Gas temperature ($T_g$) profile

Figure 7(d) shows the comparison of gas temperature between model calculation and experimental result. Increasing frequency refers that the increasing input power would increase the temperature of outlet gas after plasma reaction. This could be explained by two factors. First, increasing input power could produce more conversion of methane and produce more energy from plasma reaction. Second one was due to higher input power itself. Some portions of input power energy contribute to the increasing temperature although this contribution was not so high.

5. Conclusions

The performance of methane conversion in gliding arc plasma at atmospheric pressure was studied both experimentally and theoretically. The effect of total gas flow rate and input power frequency were experimentally investigated. The maximum conversion of methane was 50% for total methane flow rate 1 L/min. Hydrogen and acetylene were the major product of plasma reaction. The selectivity for hydrogen could reach max 40% and acetylene reach max 18%.

Energetic electron has an important role to initiate the plasma reaction. However, CH\textsubscript{3} and H were the radical species that lead the direction of the reaction and product distribution. Hydrogen was produced via CH\textsubscript{3}, CH\textsubscript{4}, H while acetylene existed by reaction between C and CH\textsubscript{3}. In term of temperature analysis, the experiment shows that the temperature of product stream has increased 30–50°C. Exothermic plasma reaction contributed 70%–80% of increment of product gas temperature while the rest was caused by input power.
Nomenclature

\( A \) frequency factor of modified Arrhenius (cm\(^3\)/(mol·s))

\( C_p \) specific heats at constant pressure (J/(mol·K))

\( I \) current (A)

\( k \) rate constant (s\(^{-1}\))

\( \dot{n} \) flow of compounds (mol/s)

\( n \) order of temperature to rate constant

\( \dot{Q} \) total input energy (J/s)

\( t \) time (s)

\( T \) temperature (K)

\( V \) voltage (V)

\( W \) supplied power by power supply (W)

\( \Delta \dot{H} \) enthalpy of compound (J/s)

Suffixes

\( \text{r} \) reaction

\( \text{g} \) gas

\( \text{i} \) species

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