Biogas Conversion using Dielectric Barrier Discharge
Non-thermal Plasma

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1. Background
2. Materials and Methods
   - Pyrolysis process of biomass wastes
   - Reforming of biogas using dielectric barrier discharge non-thermal plasma
   - Analytical methods
3. Results and Discussion
   - Pyrolytic characteristics of biomass wastes at different temperatures
   - Influence of discharge powers on the reforming products
   - Influence of gas components on the reforming products
4. Conclusion
Outline

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Energy status

1. Background

Fossil energy: non-renewable energy
Facing serious energy crisis

- oil 40 years
- gas 60 years
- coal 200 years

→ BG: Biomass Gasification

Source Change of Hydrogen in 21 Century

Gasification technology would be the primary pattern of biomass energy conversion. Moreover, hydrogen production by gasification would be the main pathway to obtain renewable energy.

Industrial civilization relying on fossil energy is just a scene of the history of human civilization. The time of renewable energy is a kind of historical regression and necessity.
Industrial wastes of China

1. Background

Industrial biomass waste
- cellulose
- xylogen
- hemicellulose

Products of biomass pyrolysis
- gas
- tar
- char

Annual increment of MSW and IW in China

In 2013, the IW reached 3.3 billion tons in China.
Reforming pyrolysis products by plasma

1. Background

Gaseous products of biomass pyrolysis:
- $\text{H}_2$, CO, CH$_4$ and CO$_2$;
- Micromolecular hydrocarbon;
- Macromolecular hydrocarbon.

Reforming of pyrolysis gas

- Catalytic reforming
- Steam reforming
- Partial oxidation
- Plasma reforming

- Plasma reforming
  - Free radical and ionic reaction
  - Higher conversion of CH$_4$

- Progress of modern reactor design
  - Lower energy consumption of non-thermal plasma
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Pyrolysis process of biomass wastes

2. Materials and Methods

Pyrolysis setup of Biomass wastes

Pyrolysis temperatures: 400, 500, 600, 700, 800 ºC

Experimental conditions
2. Materials and Methods

**Pyrolysis process of biomass wastes**

**Reforming setup by plasma**

- **Carrier gas:** N₂, 50 mL/min
- **Component 1:** CH₄ and CO₂, CH₄: CO₂ = 1:1, 1:2, 2:1
- **Component 2:** CH₄, CO₂ and CO, CH₄: CO₂: CO = 1:1:3, 1:2:2, 2:1:2
- **Component 3:** CH₄, CO₂ and H₂, CH₄: CO₂: H₂ = 1:1:1, 1:2:1, 2:2:1
2. Materials and Methods

Analytical methods

<table>
<thead>
<tr>
<th>Test targets</th>
<th>test methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total amounts of gas</td>
<td>gas flowmeter</td>
</tr>
<tr>
<td>products</td>
<td></td>
</tr>
<tr>
<td>CO₂, CH₄, CO, H₂</td>
<td>GC-TCD (Carboxen-1010 PLOT)</td>
</tr>
</tbody>
</table>

Analysis and test

Grinding and selecting the pine sawdust with appropriate particle size,
Drying at 105 °C for 24h before use,
4g for each experiment dosage.

Target gas

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>N₂</th>
<th>CO</th>
<th>CH₄</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>retention time /min</td>
<td>2.7</td>
<td>3.3</td>
<td>3.7</td>
<td>6.0</td>
<td>11.5</td>
</tr>
</tbody>
</table>
The calculation methods of conversion of $\text{CO}_2$ and $\text{CH}_4$ ($X$), selectivity of $\text{H}_2$ and $\text{CO}$ ($S$) and carbon balance ($B$) is as follows:

$$X(\text{CO}_2)(\%) = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100\%$$

$$X(\text{CH}_4)(\%) = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100\%$$

$$S(\text{CO})(\%) = \frac{[\text{CO}]_{\text{out}}}{[\text{CH}_4]_{\text{in}} + [\text{CO}_2]_{\text{in}} - [\text{CH}_4]_{\text{out}} - [\text{CO}_2]_{\text{out}}} \times 100\%$$

$$S(\text{H}_2)(\%) = \frac{0.5 \times [\text{H}_2]_{\text{out}}}{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}} \times 100\%$$

$$B(C) = \left(1 - \frac{[\text{CO}]_{\text{out}} + [\text{CH}_4]_{\text{out}} + [\text{CO}_2]_{\text{out}}}{[\text{CH}_4]_{\text{in}} + [\text{CO}_2]_{\text{in}}} \right)$$

Where $[X]_{\text{in}}$ represents the flow of target gas in the air inflow, whereas, $[X]_{\text{out}}$ represents the flow of target gas in the air out.

$B(C)$ represents the ratio of conversion of $\text{CH}_4$ and $\text{CO}_2$ in the air inflow to non-CO carbon (containing tar, char, and et.al)
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Pyrolytic characteristics of biomass wastes at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$+CO (mol%)</td>
<td>11.24</td>
<td>16.35</td>
<td>29.63</td>
<td>44.99</td>
<td>56.71</td>
</tr>
<tr>
<td>H$_2$/CO (mol/mol)</td>
<td>0.12</td>
<td>0.08</td>
<td>0.16</td>
<td>0.27</td>
<td>0.34</td>
</tr>
</tbody>
</table>

With temperature increasing to 800 °C, the ratio of H$_2$+CO and CH$_4$ among total gas products increased to 56.71 mol% and 13.10 mol%, respectively. Moreover, the ratio of H$_2$/CO increased to 0.34.
Influence of discharge powers

Reforming CH$_4$ and CO$_2$

Conversion of CH$_4$ and CO$_2$ and selectivity of CO and H$_2$ both increased with the addition of discharge powers.
The addition of CO into CH$_4$ and CO$_2$ in the plasma reforming process would inhibit the conversion of CO$_2$ (b), however, it had tiny influence on the conversion of CH$_4$ (a). It can be concluded that CO$_2$ might have the unique transformation paths, however, CH$_4$ might have non-unique transformation paths.
Reforming CH$_4$, CO$_2$ and CO

The total reforming reaction is as follows:

$$\text{CH}_4 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2$$

It can be concluded from the results that CO$_2$ might have the unique transformation paths, however, CH$_4$ might have non-unique transformation paths.

$$\text{CO}_2 + e \rightarrow \text{CO} + \text{O} \cdot + e$$
$$\text{CH}_4 + e \rightarrow \text{CH}_3 \cdot + \text{H} \cdot + e$$
$$\text{CH}_4 + e \rightarrow \text{CH}_2 \cdot + \text{H}_2 + e$$
$$\text{CH}_4 + e \rightarrow \text{CH} \cdot + \text{H} \cdot + \text{H}_2 + e$$
$$\text{CH}_4 + e \rightarrow \text{C} + 2\text{H}_2 + e$$
Influence of discharge powers

3. Results and discussion

Reforming CH\(_4\), CO\(_2\) and H\(_2\)

The addition of H\(_2\) into CH\(_4\) and CO\(_2\) would inhibit the selectivity of H\(_2\) (c) and improve the selectivity of CO (d). However, it still had tiny influence on the conversion of CH\(_4\) (b). This result confirms the consumption of non-unique transformation paths of CH\(_4\).

The selectivity of CO decreased with the increase of discharge powers (d). It indicates that CO may react to form other products at higher powers.

Additionally, CO may react to form other products at higher powers.
Influence of gas components

3. Results and discussion

Adding CO in the reaction gas, the selectivity of H₂ increases (c), and the selectivity of CO shows little change (d); Adding H₂ in the reaction gas, the selectivity of H₂ decreases (c), and the selectivity of CO increases (d).

Reforming gas of different components

The conversion of CH₄ increased with the discharge power increasing, whereas the addition of CO and H₂ had tiny influence on the conversion of CH₄ (a).

The conversion of CO₂ decreased through adding both CO and H₂ in the reaction gas (b).
3. Results and discussion

$B(c)$ increased with the increase of discharge power. It means that it will produce more non-CO products at higher discharge power.
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- The increase of pyrolysis temperature of biomass contributes to the formation of syngas ($H_2+CO$);

- The conversion of $CH_4$ is mainly influenced by the discharge power, whereas, the addition of CO and $H_2$ will reduce the conversion of $CO_2$;

- Adding CO in the reaction gas, the selectivity of $H_2$ increases, and the selectivity of CO shows little change; Adding $H_2$ in the reaction gas, the selectivity of $H_2$ decreases, and the selectivity of CO increases.

- The decomposition of $CO_2$ has the only path; however, the decomposition of $CH_4$ might have multiple paths. Free radical reaction is the main reaction mechanism. With the discharge power increasing, it will produce $H_2O$, carbon deposition and even some organic liquids.
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Group Students