北京航空航天大學
BEIHANG UNIVERSITY

Biogas Conversionh using Dielectric Barrier Discharge Non-thermal Plasma

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Outline

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

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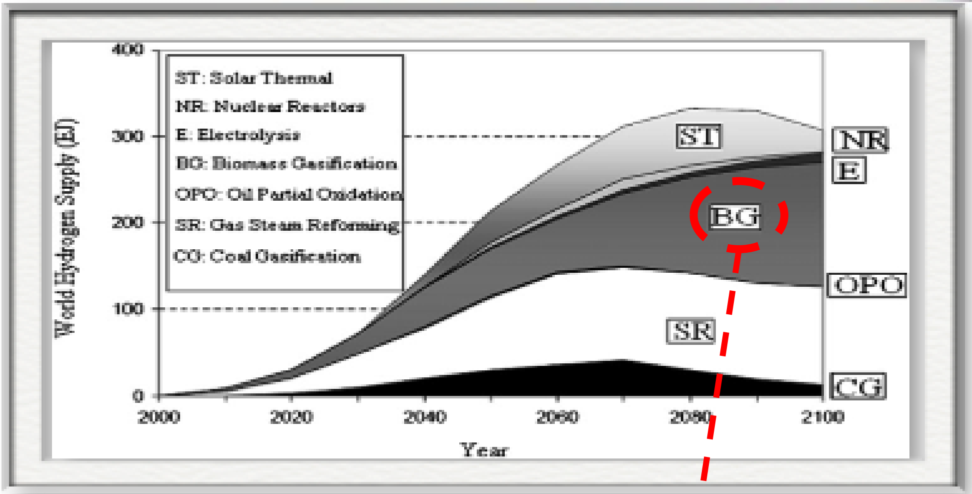
Energy status

Energy Crisis

- **Fossil energy: non-renewable energy**
- **Facing serious energy crisis**

(from World Energy Council, London, 2004)

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



BG: Biomass Gasification

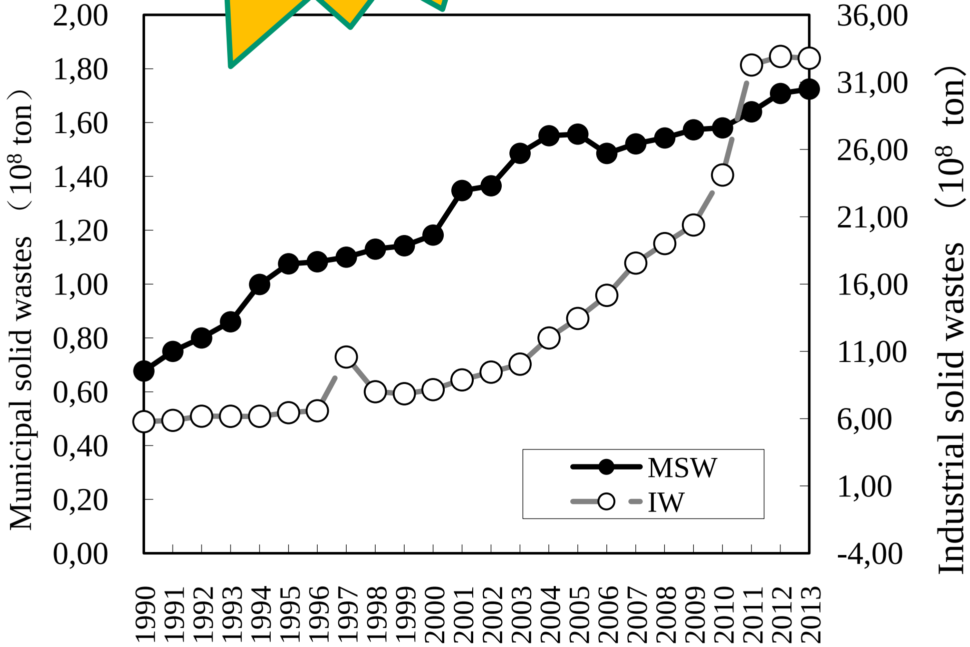
Source Change of Hydrogen in 21 Century

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

Biomass energy: renewable energy



Annual increment of MSW and IW in China

In 2013, the IW reached 3.3 billion tons in China.

Industrial biomass waste

- **xylogen**
- **cellulose**
- **hemicellulose**

Products of biomass pyrolysis

gas	**tar**	**char**

Reforming pyrolysis products by plasma

Gaseous products of biomass pyrolysis:

- H_2， CO， CH_4 and CO_2;
- Micromolecular hydrocarbon;
- Macromolecular hydrocarbon.

Reforming of pyrolysis gas

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

Reforming pyrolysis products by plasma?

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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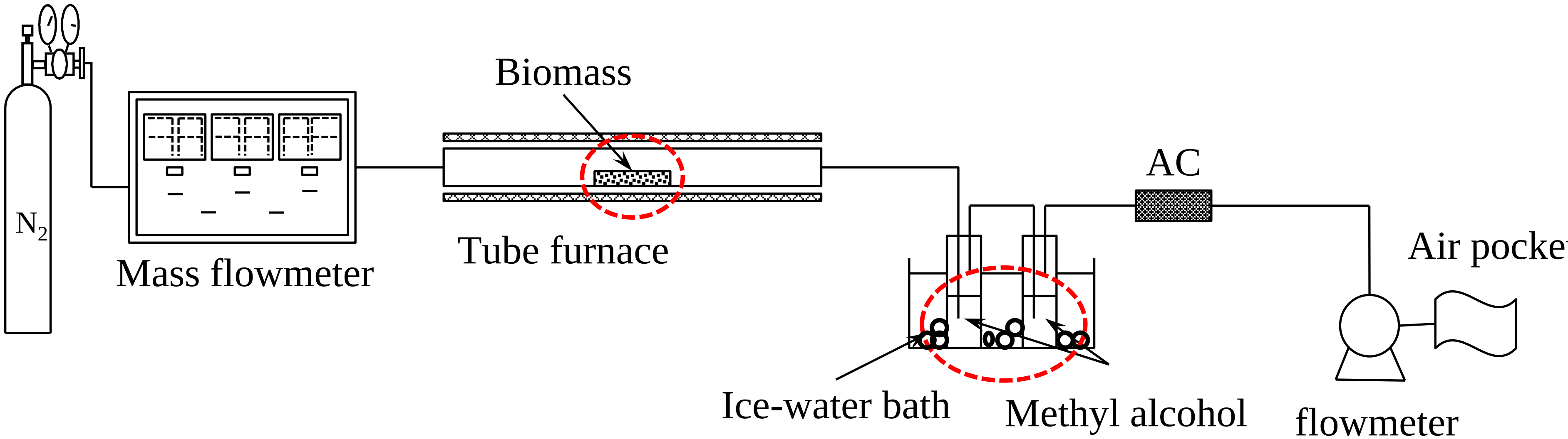
Pyrolysis process of biomass wastes

Pyrolysis setup of Biomass wastes

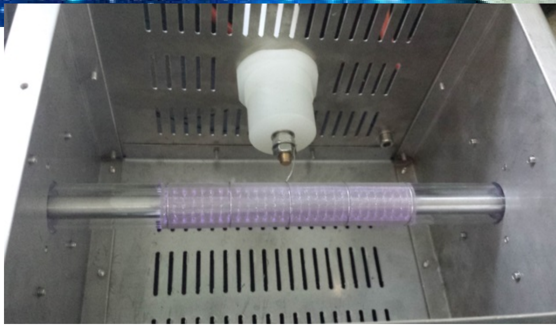


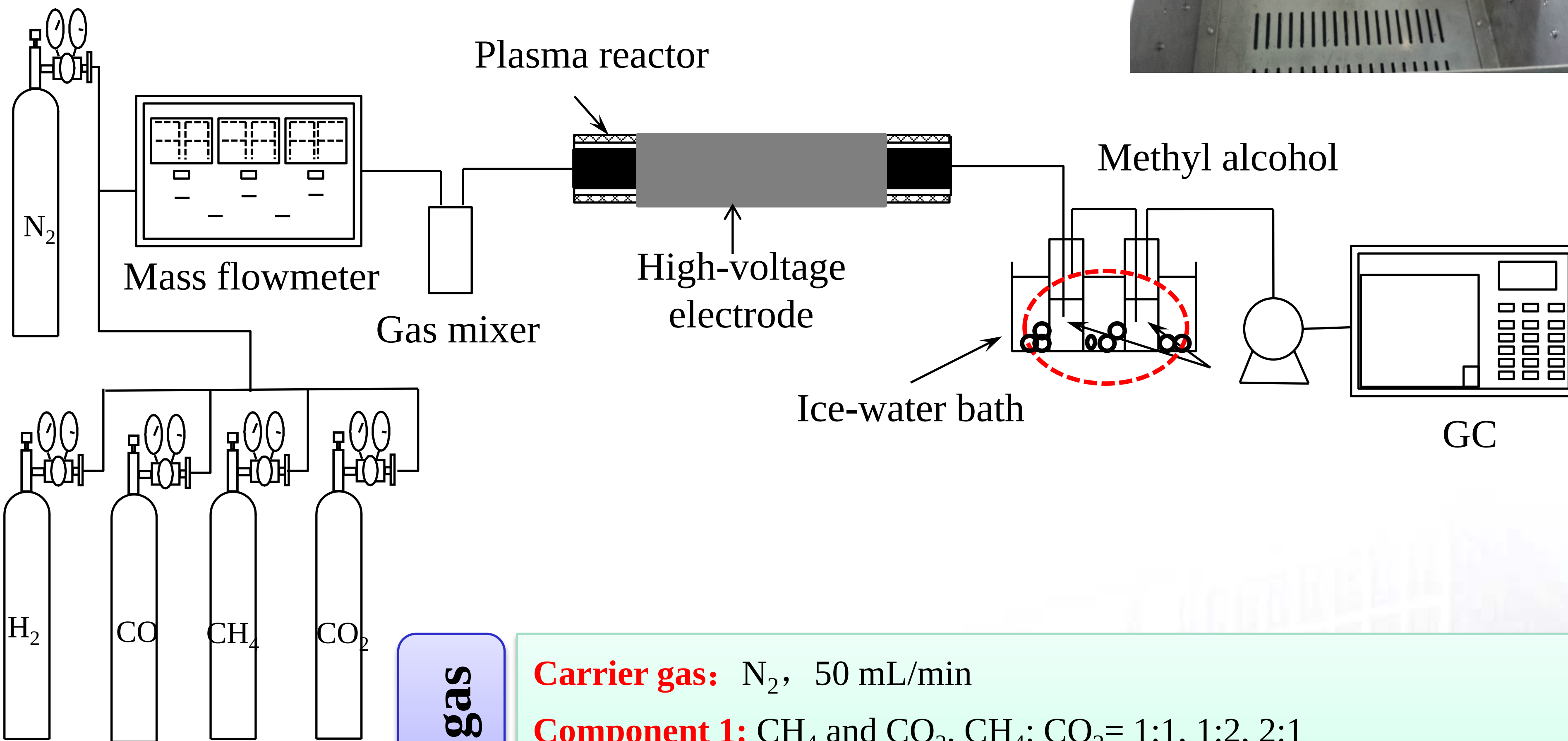
Experimental conditions

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

Pyrolysis process of biomass wastes

Reforming setup by plasma





Feed gas

Carrier gas: N_2, 50 mL/min

Component 1: CH_4 and CO_2, CH_4: CO_2= 1:1, 1:2, 2:1

Component 2: CH_4, CO_2 and CO, CH_4: CO_2: CO= 1:1:3, 1:2:2, 2:1:2

Component 3: CH_4, CO_2 and H_2, CH_4: CO_2: H_2= 1:1:1, 1:2:1, 2:2:1

Analytical methods

experimental material

pine sawdust

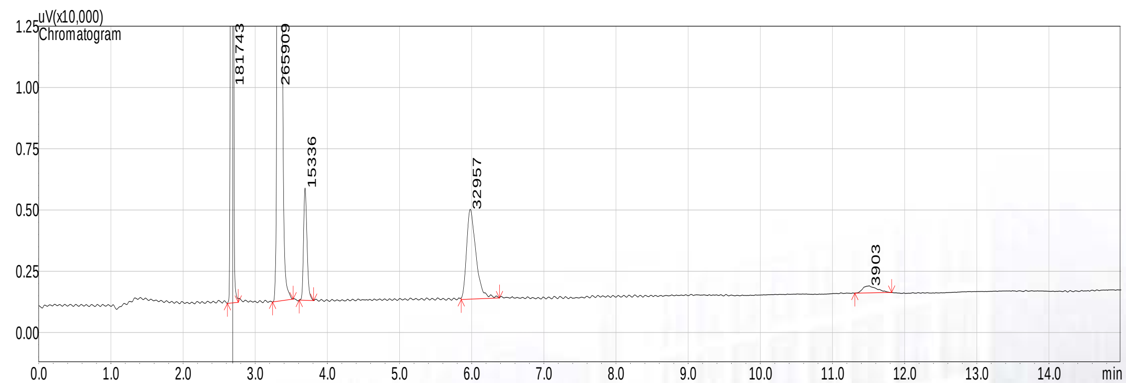
Grinding and selecting the pine sawdust with appropriate particle size，

Drying at 105 ºC for 24h before use,

4g for each experiment dosage.

Analysis and test

Test targets	test methods
Total amounts of gas products	gas flowmeter
CO_2, CH_4, CO, H_2	GC-TCD (Carboxen-1010 PLOT)



Target gas	H_2	N_2	CO	CH_4	CO_2
retention time /min	2.7	3.3	3.7	6.0	11.5

Evaluation index of plasma reforming

The calculation methods of conversion of CO_2 and CH_4 (*X*), selectivity of H_2 and CO (*S*) and carbon balance (*B*) is as follows:

$$X(CO_2)(\%) = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100\%$$

$$X(CH_4)(\%) = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100\%$$

$$S(CO)(\%) = \frac{[CO]_{out}}{[CH_4]_{in} + [CO_2]_{in} - [CH_4]_{out} - [CO_2]_{out}} \times 100\%$$

$$S(H_2)(\%) = \frac{0.5 \times [H_2]_{out}}{[CH_4]_{in} - [CH_4]_{out}} \times 100\%$$

$$B(C) = \left(1 - \frac{[CO]_{out} + [CH_4]_{out} + [CO_2]_{out}}{[CH_4]_{in} + [CO_2]_{in}}\right)$$

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

B(C) represents the ratio of conversion of CH_4 and CO_2 in the air inflow to non-CO carbon (containing tar, char, and et.al)

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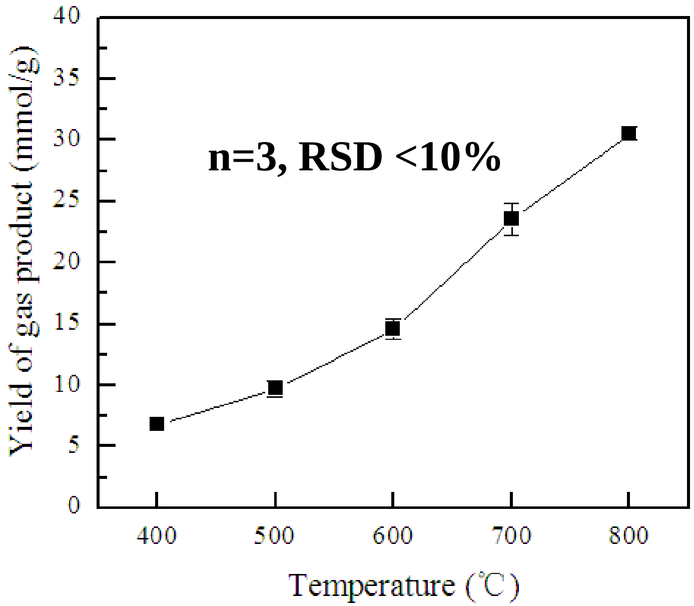
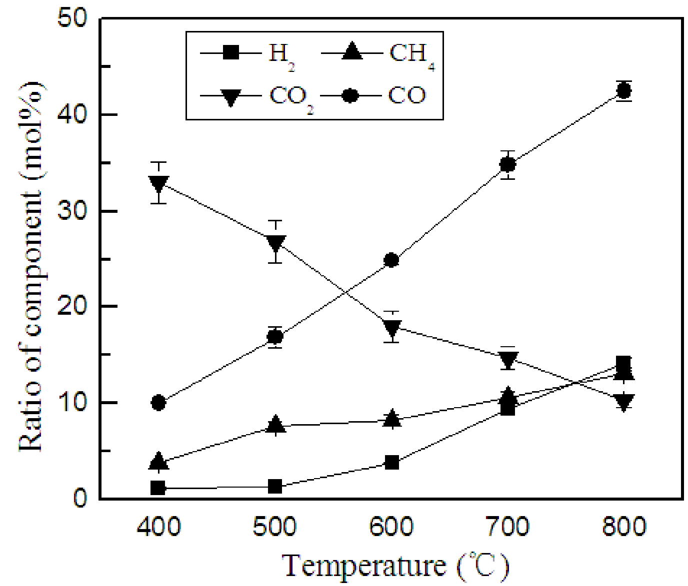
Pyrolysis of biomass wastes

Pyrolytic characteristics of biomass wastes at different temperatures



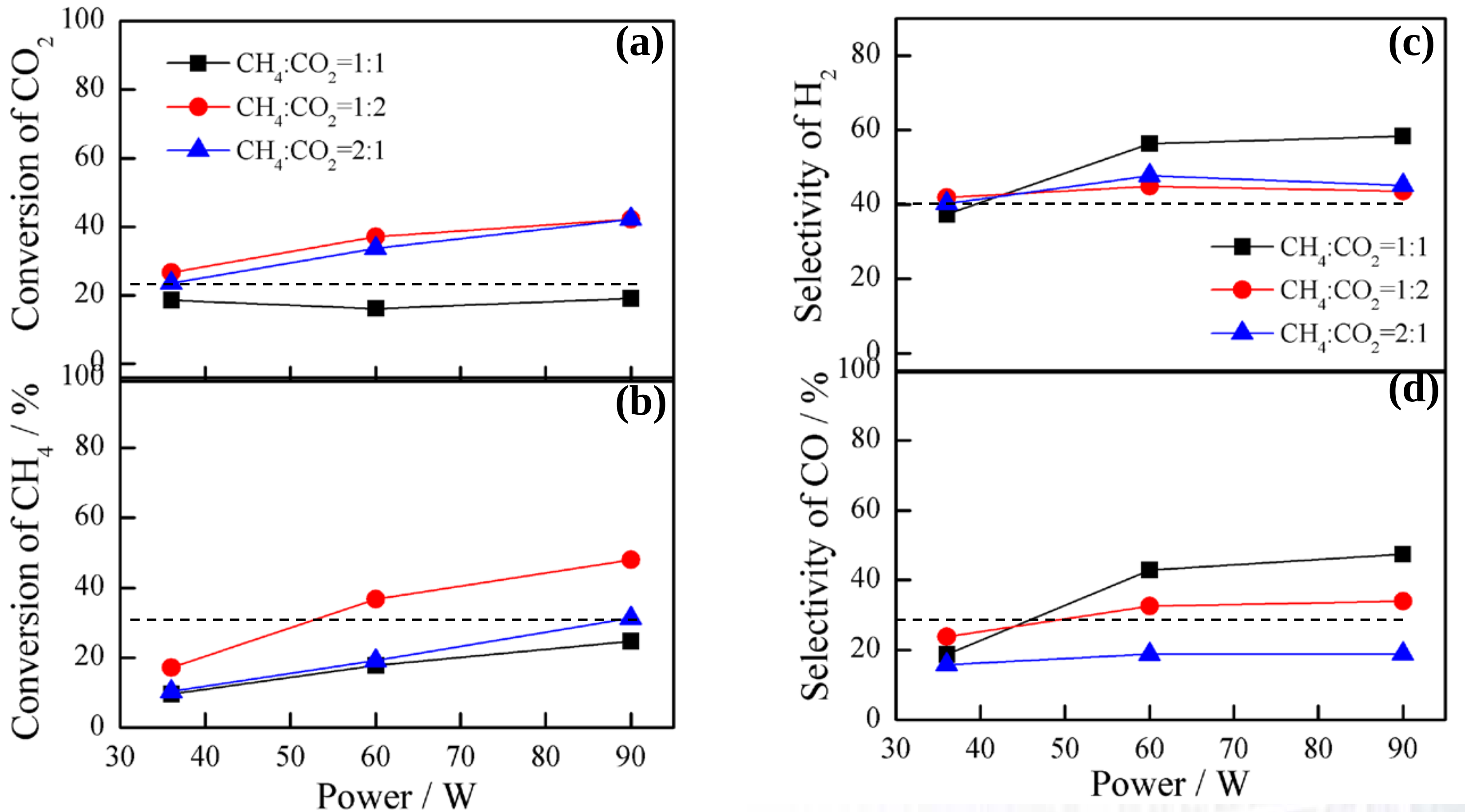


Temperature (°C)	400	500	600	700	800
H_2+CO (mol%)	11.24	16.35	29.63	44.99	56.71
H_2/CO (mol/mol)	0.12	0.08	0.16	0.27	0.34

With temperature increasing to 800 ºC, 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

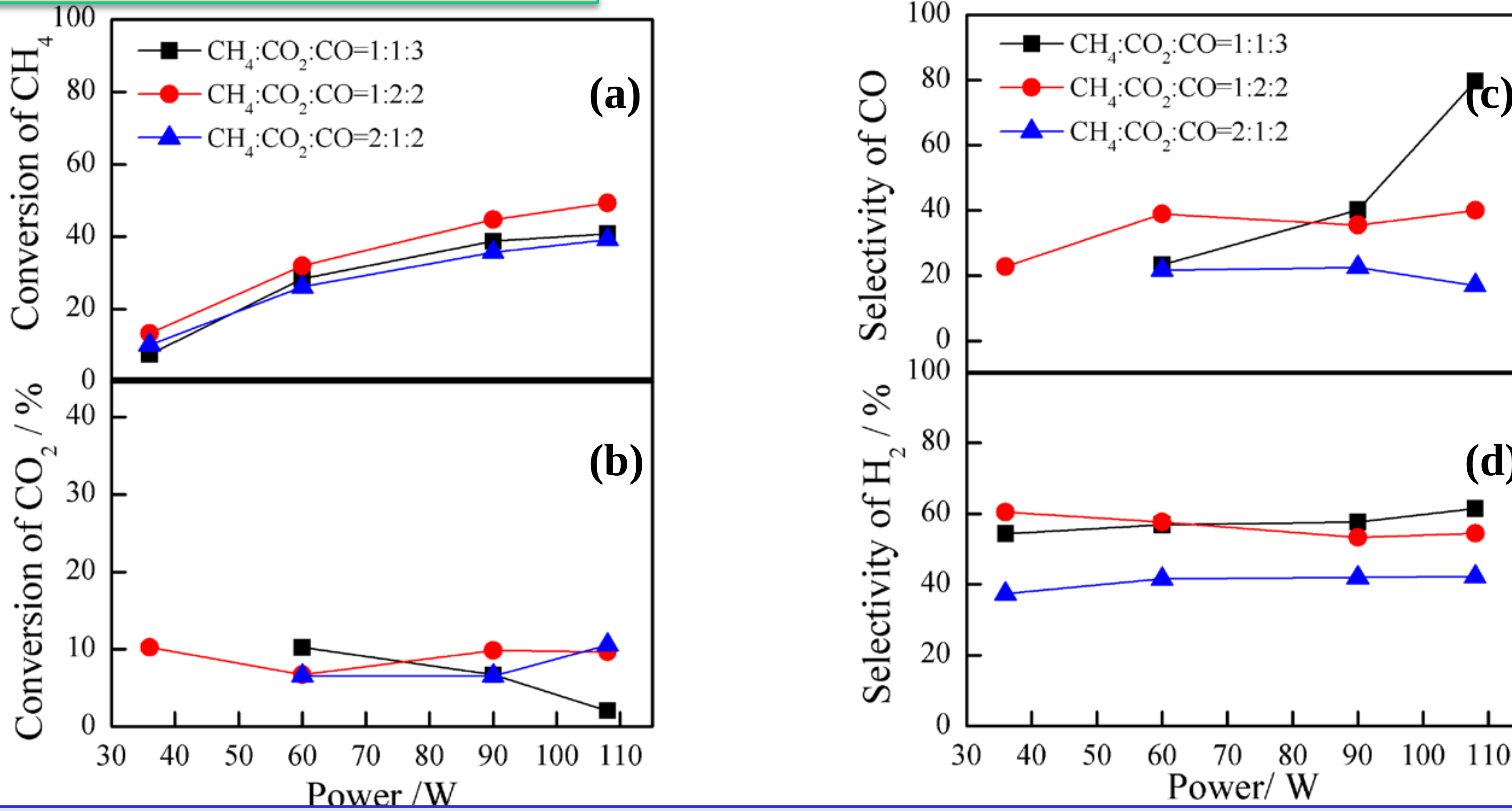
Reforming CH_4 and CO_2



Conversion of CH_4 and CO_2 and selectivity of CO and H_2 both increased with the addition of discharge powers.

Influence of discharge powers

Reforming CH_4, CO_2 and CO



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.

Influence of discharge powers

Reforming CH_4, CO_2 and CO

The total reforming reaction is as follows:

$$CH_4 + CO_2 \rightarrow CO + H_2$$

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.

$$CO_2 + e \rightarrow CO + O\cdot + e$$

$$CH_4 + e \rightarrow CH_3\cdot + H\cdot + e$$

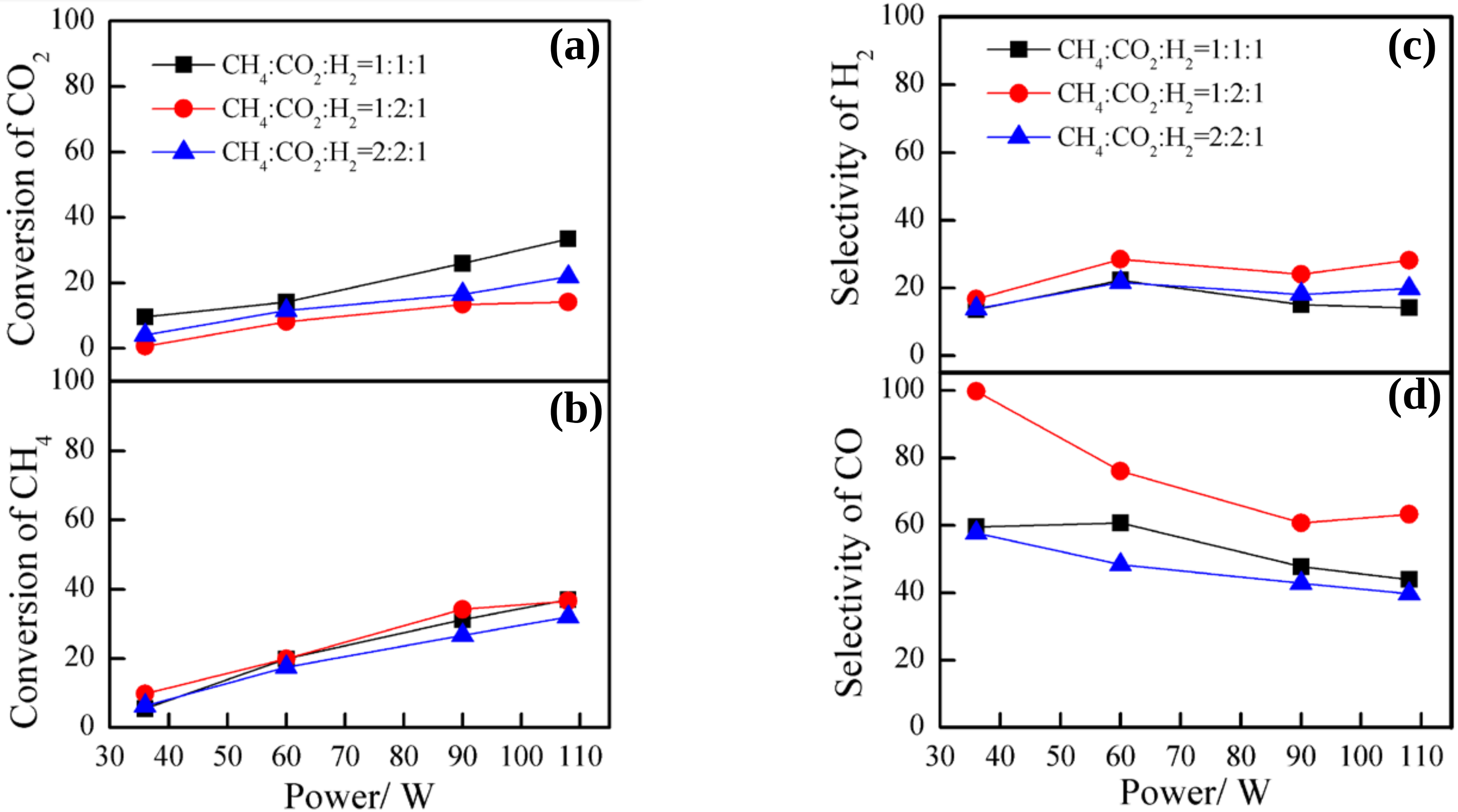
$$CH_4 + e \rightarrow CH_2\cdot + H_2 + e$$

$$CH_4 + e \rightarrow CH\cdot + H\cdot + H_2 + e$$

$$CH_4 + e \rightarrow C + 2H_2 + e$$

Influence of discharge powers

Reforming CH_4, CO_2 and H_2

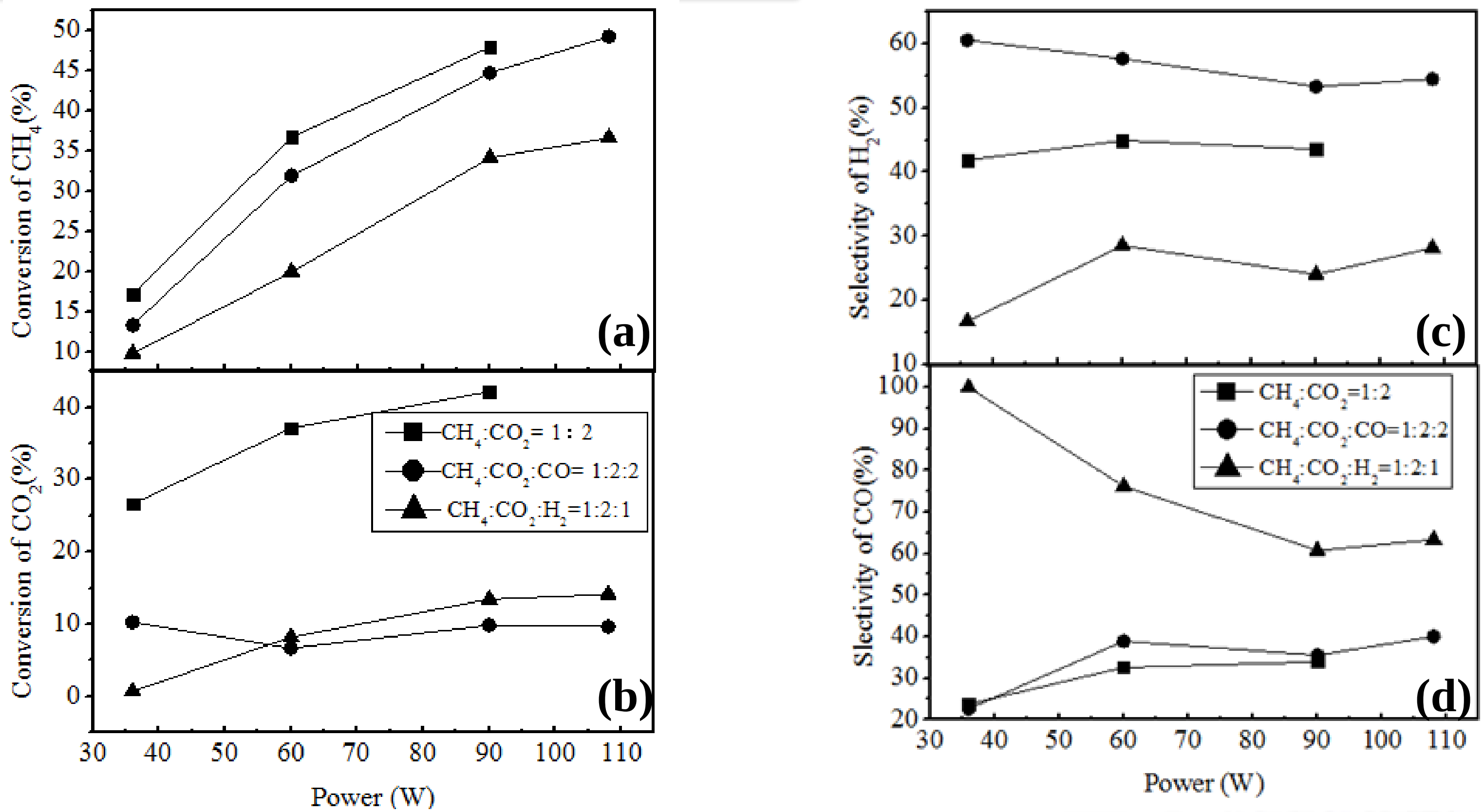


The selectivity of CO decreased with the increase of discharge powers (d). It indicates that CO may react to form other products at higher powers.

confirms the consumption of non-unique transformation paths of CH_4.

Influence of gas components

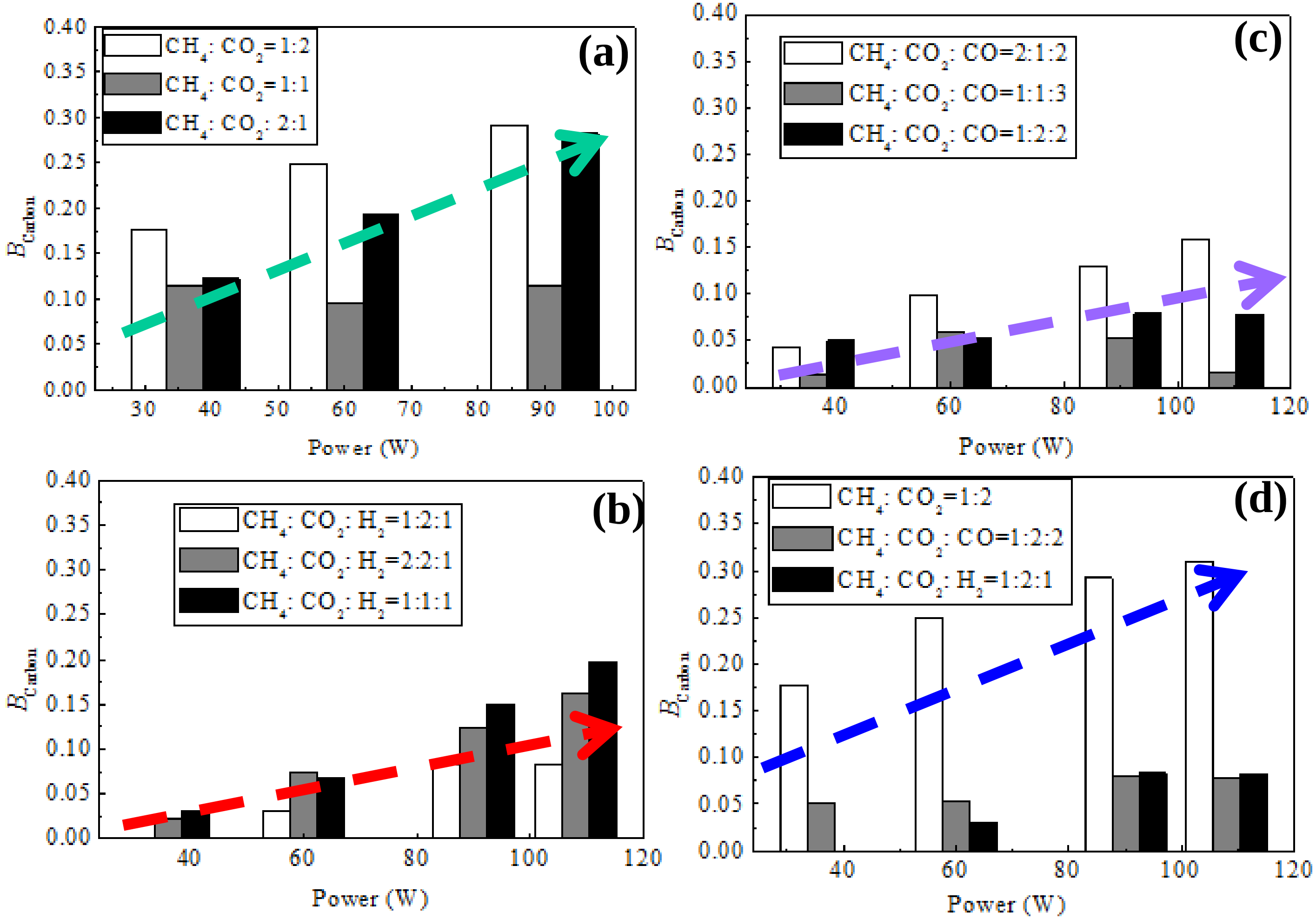
Reforming gas of different components



The conversion of CH_4 increased with the discharge power increasing, whereas the addition of CO and H_2 had tiny influence on the conversion of CH_4 (a).

The conversion of CO_2 decreased through adding both CO and H_2 in the reaction gas (b).

Carbon balance



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.

Acknowledgement

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Group Students


Thank you