Review

CH$_4$–CO$_2$ reforming by plasma – challenges and opportunities

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ABSTRACT

CH$_4$–CO$_2$ reforming is of rapid growing interest for reasons of the continuous decrease of petroleum resources and the emphasis on the environmental situation for greenhouse gas mitigation. Plasma technology is considered to be one of potential ways for CH$_4$–CO$_2$ reforming. This paper presents an overview of CH$_4$–CO$_2$ reforming by cold plasmas and thermal plasma. The evaluations for their performances and the key factors in different plasmas are given. In particular, the attention is focused on how to achieve higher conversions at high feed-gas flow rate, so as to lessen the energy consumption in the process by plasma to meet the requirements of industrial application. To obtain the aim, three key factors, electron density, plasma temperature and reactor configuration related to the process are emphasized. Considering the current status of CH$_4$–CO$_2$ reforming by plasma, there is an opportunity to improve the energy conversion efficiency and the treatment capacity of the process by optimizing both plasma form and reactor design in future work.

Contents

1. Introduction

Synthesis gas (or "syngas"), a mixture of carbon monoxide and hydrogen, is an important intermediate for various synthesizing chemicals and environmentally clean fuels, such as ammonia, methanol (MeOH), acetic acid, methyl formate, dimethyl ether (DME), synthetic gasoline, and diesel [1]. Generally, it is required for various H$_2$/CO ratios of syngas to synthesize different products. For example, H$_2$/CO ratio of 2/1 is needed to synthesize methanol, and 1/1 to synthesize acetic acid or methyl formate.

Synthesis gas can be produced from coal, petroleum coke, natural gas, biomass and even from organic wastes. Though

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significant quantities of synthesis gas are being made from coal [2], nature gas is the largest source of synthesis gas at present and its use for this purpose is growing because of its lowest cost routes and environment-friendship [3].

There are several technologies available for synthesis gas production depending on natural gas, such as steam reforming of CH_4, partial oxidation of CH_4, CO_2 reforming of CH_4 and a combination of them, which result in different H_2/CO ratio. The traditional and potential industrial process for synthesis gas production has been steam reforming of methane (1), which is so called wet reforming and makes syngas with H_2/CO of about 3 or higher. Steam reforming of methane is suitable for synthesizing ammonia, but results in redundant hydrogen for methanol synthesis and many other synthesis processes. Meanwhile, it needs at least 1 mol methane to form 1 mol CO in this reforming reaction.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = 206 kJ/mol \quad (1)$$
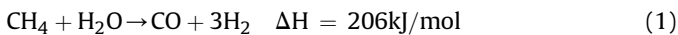
Since the continuous decrease of petroleum resources and the emphasis on the environmental situation, as well as the chemical energy transmission [4–6], much of the forward-looking consideration of synthesis gas production has been focused on CH_4–CO_2 reforming (also called dry reforming) during the past decade.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H = 247 kJ/mol \quad (2)$$
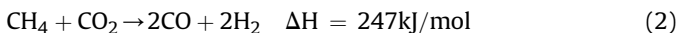
CH_4–CO_2 reforming becomes more attractive because it not only lessens methane consumption but also makes use of carbon dioxide. Stoichiometrically, reaction (2) shows that it could save half of the methane required to obtain the same amount of CO compared with steam reforming and partial oxidation, since CO_2 is also a carbon source in the reforming process. Though CH_4–CO_2 reforming results in H_2/CO ratio equaling 1/1, the H_2/CO ratio can be relatively easily controlled by adjusting the CH_4/CO_2 ratio in the feed. Therefore, the synthesis gas from CH_4–CO_2 reforming can not only be used in synthesis of acetic acid or methyl formate, but also meet H_2/CO ratio required by various products process when combining with steam reforming of CH_4 process. Besides, CH_4–CO_2 reforming is more befitting for high CO_2-containing natural gases, biogases and coal bed methane [7,8].

However, CH_4–CO_2 reforming reaction is a highly endothermic reaction; it usually needs special methods to achieve a considerable reaction rate to meet industrial requirements. Catalytic and plasma technology are considered to be potential. Nevertheless, these techniques have not been practically commercialized so far.

Catalytic CH_4–CO_2 reforming was investigated as early as 1888 [9] and was thoroughly explored by Fischer and Tropsch in 1928 [10]. A. T. Ashcroft et al. [11] and M. C. J. Bradford et al. [9] emphasized its environmental significance. In catalytic reaction process, the mixture of CH_4–CO_2 is fed into a tubiform fixed-bed reactor filled with catalysts, and the thermal energy required for the reaction is supplied by combustion of natural gas outside the reactor. Though the reactor for CH_4–CO_2 reforming can be used with reference to that of steam reforming of CH_4, the greatest barrier to transfer catalytic CH_4–CO_2 reforming process from laboratory to the industrial scale is carbon deposition on catalyst surface which leads to the deactivation of the catalysts [12–14].
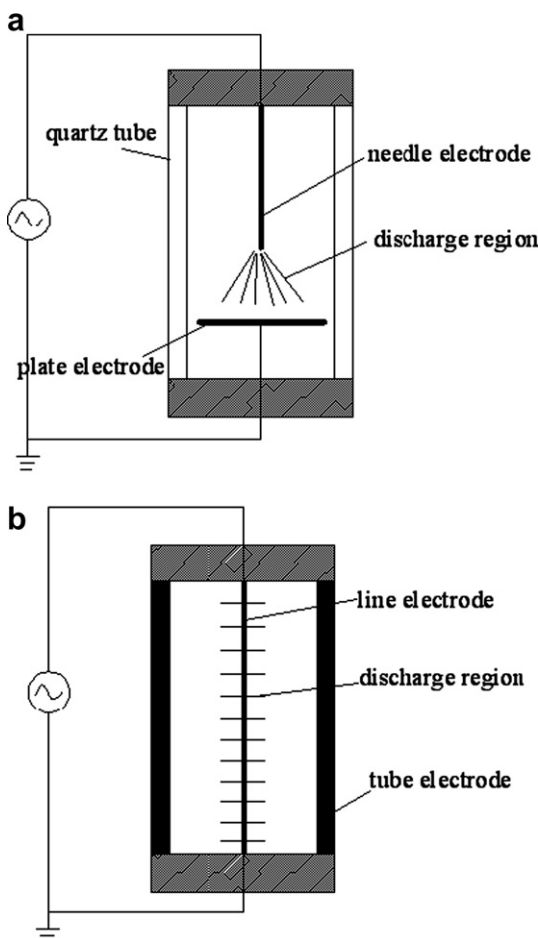

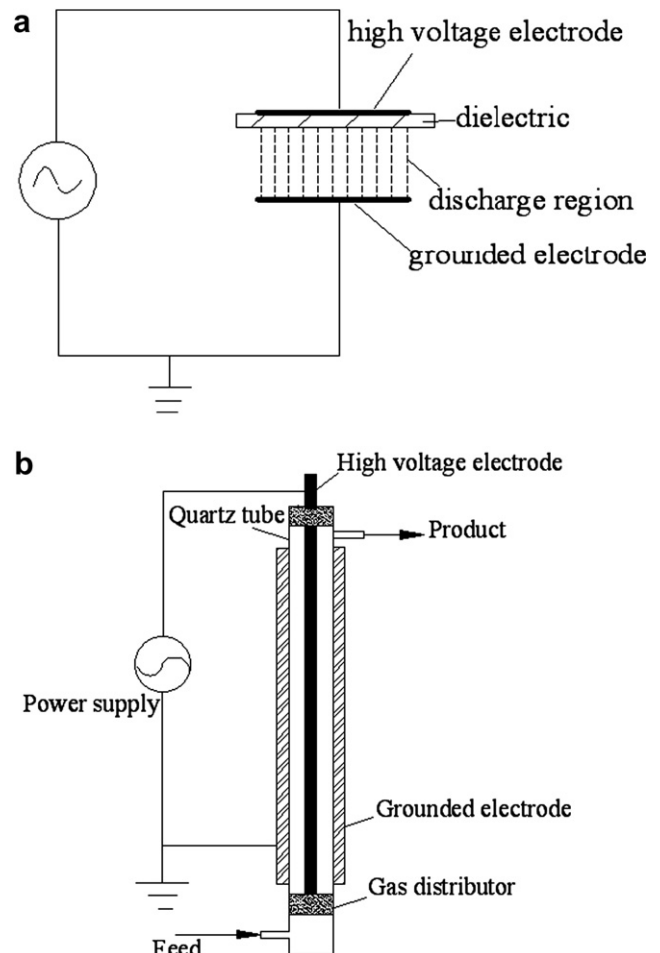**Fig. 1.** Schematic diagram of the corona discharge reactor.

Fig. 2. Schematic diagram of the DBD reactor.

CH_4–CO_2 reforming by plasma was demonstrated first in a controlled-arc in 1986 [15,16]. Compared with the catalytic reaction, CH_4–CO_2 reforming by plasma with its electron-induced chemistry and thermo-chemical reactions can obtain high conversions and selectivity without catalyst, and without concern about carbon deposition. Therefore, it has drawn increasing attentions in the past ten years though the energy use now is still a problem.

Based on our knowledge of CH_4–CO_2 reforming to synthesis gas by plasma, this paper summarizes the development in this field. The aim is to find a way to resolve the key problems, which are how to achieve high conversions at higher feed-gas flow rate, and obtain high energy efficiency in the process, so as to meet the requirement of industrial application.

2. Evaluation of plasma technologies for CH_4–CO_2 reforming

There has been much enthusiasm for CH_4–CO_2 reforming in terms of global CO_2 emission restriction. However, the reforming process demands on energy. In plasma process, the energy is provided by electricity, and production of electricity will release CO_2. In response to plasma technologies for CH_4–CO_2 reforming, one of the most important things is to estimate the amount of CO_2 released in the whole process, and compare it with conventional steam reforming of CH_4.

As shown in Eq. (2), it requires at least 123.5 kJ energy and 0.5 mol methane to remove 0.5 mol CO_2 to get 1 mol CO. In plasma reforming process, considering electricity is from combustion of methane (combustion value of 890 kJ/mol), 42% of combustion energy converts to electricity, 67% of electric energy is utilized by the reforming reaction, to get 1 mol CO, it would burnt 0.5 mol of methane and 0.5 mol CO_2 released at power plant. However, these CO_2 would be balanced by that removed during the reforming process. The similar discussion is for steam reforming of CH_4 in Eq. (1), where it requires at least 206 kJ energy and 1 mol methane to obtain 1 mol CO. If 70% of caloric from burning of natural gas outside the tubular reactor is utilized by the reforming reaction, it would burn 0.33 mol of methane and 0.33 mol CO_2 released. In one word, to obtain 1 mol CO in CH_4–CO_2 reforming by plasma process, it expends 1 mol of methane without CO_2 released; in steam reforming of CH_4, it expends 1.33 mol of methane and 0.33 mol of CO_2 released.

Reforming reaction (2) is not only a process of substance conversion, but a process of energy conversion, it is important that the novel technology for CH_4–CO_2 reforming should be with high conversions, large treatment capacity and easy to enlarge. In order to discuss in convenience, specific energy (3) and energy conversion efficiency (4) are defined as below.

Specific energy (SE)

$$SE = \frac{P}{[CO + H_2]_{produced}} \qquad (3)$$

where, P refers to the input power of plasma in kW; $[CO + H_2]_{produced}$ refers to moles of ($CO + H_2$) produced per second (mol/s). SE expresses the energy consumption for producing 1 mol of ($CO + H_2$). The larger SE is, the higher energy consumption of the reforming process is. The standard enthalpy change of CH_4–CO_2 reforming reaction is 247 kJ/mol, which means that the minimum specific energy to produce 1 mol ($CO + H_2$) is equal to 61.75 kJ/mol.

Energy conversion efficiency (ECE)

$$ECE = \frac{n_{H_2} \times LHV_{H_2} + n_{CO} \times LHV_{CO}}{P + n'_{CH_4} \times LHV_{CH_4}} \qquad (4)$$

Where, n_i refers to the moles of the product i (mol); n'_{CH_4} the moles of methane converted (mol); P the input power of plasma in kW; LHV [17] the lower heating value of substance in kJ/mol. ECE expresses the lower heating value (LHV) of synthesis gas produced in the reforming process divided by the input energy, which is the summation of the input power of plasma and the LHV of methane converted. According the definition of (4), the ECE in the reforming process is less than 1, the larger ECE is, the lower energy consumption of the reforming process is, and the desirable value is equal to 1.

SE and ECE appear to be good indicators for describing reforming process. These two parameters can be calculated with conversion and selectivity of the different plasma reforming processes in order to compare their different performances.

$$SE = \frac{P}{(n_{CH_4} \times x_{CH_4} + n_{CO_2} \times x_{CO_2}) \times S_{CO} + n_{CH_4} \times x_{CH_4} \times 2 \times S_{H_2}} \qquad (5)$$

$$ECE = \frac{n_{CH_4} \times x_{CH_4} \times 2 \times S_{H_2} \times LHV_{H_2} + (n_{CH_4} \times x_{CH_4} + n_{CO_2} \times x_{CO_2}) \times S_{CO} \times LHV_{CO}}{P + n_{CH_4} \times x_{CH_4} \times LHV_{CH_4}} \qquad (6)$$

where, n_i refers to the moles of i component (mol); x_i and S_i are conversion and selectivity of i component, respectively.

3. Plasma technologies for CH_4–CO_2 reforming

3.1. Plasma

Plasma is a more or less ionized gas produced mainly by electric field, which consists of a mixture of electrons, ions, neutral particles, and so on. The term of plasma was first introduced by Irving Langmuir in 1928 [18,19]. Since the mass of ions and neutral particles are much larger than that of electrons in plasma, electrons are called light particles, while ions and neutral particles are called heavy particles.
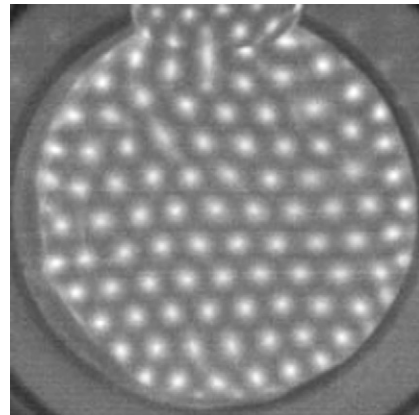

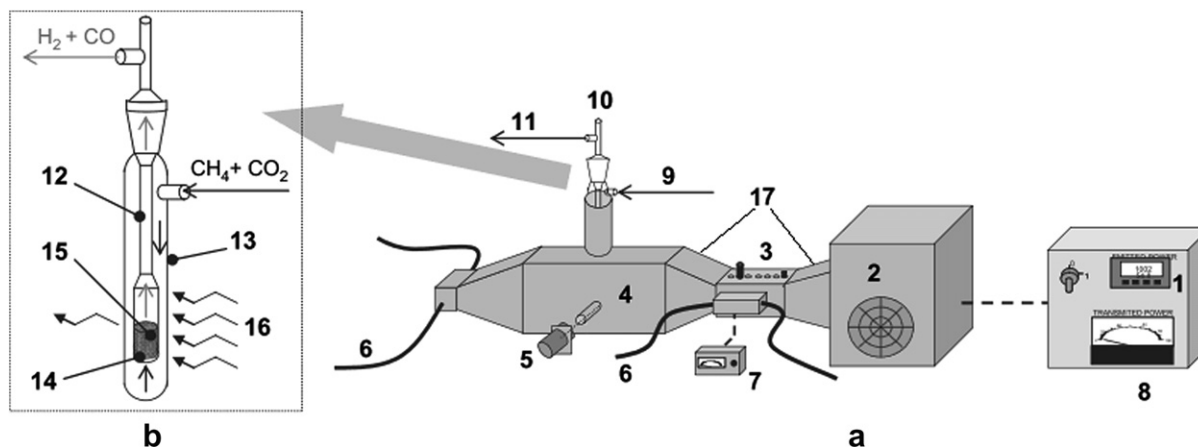**Fig. 3.** The pattern of discharge imprint on dielectric surface [31].

Fig. 4. (a) Schematic diagram of microwave discharge setup. (b) Close-up view of the set quartz reactor-jacket [49]. 1. Input power control; 2. Microwave generator or magnetron; 3. Manual 2-stub unit; 4. resonance cavity; 5. Optical pyrometer; 6. Water sink; 7. Reflected power control; 8. Transmitted power control; 9. Inflow gas line; 10. Set quartz reactor-jacket and catalyst/microwave receptor; 11. Outflow gas line; 12. Quartz reactor; 13. Quartz jacket; 14. Porous plate; 15. Catalyst and microwave receptor bed; 16. Microwave radiation; 17. Waveguide.

Depending on the energy density level, temperature and electron density, plasma applied for CH_4–CO_2 reforming is classified as thermodynamic non-equilibrium plasma and thermodynamic equilibrium plasma. The thermodynamic non-equilibrium plasma is also called cold plasma, in which the thermal kinetic energy of electrons is much larger than that of heavy particles; the weighted-average temperature of plasma is near room temperature [20]. The chemical reaction in cold plasma is mainly induced by energetic electrons. Due to action of electric field, electrons are accelerated and energized. Through electron-impact dissociation, excitation and ionization of gas molecules, the energetic electrons transfer their energy to the gas molecules upon inelastic collision, and excited species, free radicals, ions, as well as additional electrons are produced [14], then the desired plasma chemical reactions take place. The thermodynamic equilibrium plasma is simply called thermal plasma, in which the temperature of heavy particle is close to that of electrons at the range of thousands K. Because the electron density in thermal plasma is higher than that in cold plasma, by large amount of impact between electrons and heavy particles, the electron energy from electric field goes into heating heavy particles to achieve the thermodynamic equilibrium in electrons and heavy particles. The chemical reactions in thermal plasma are both electron-induced reactions and thermo-chemical reactions.

3.2. CH_4–CO_2 reforming by cold plasma

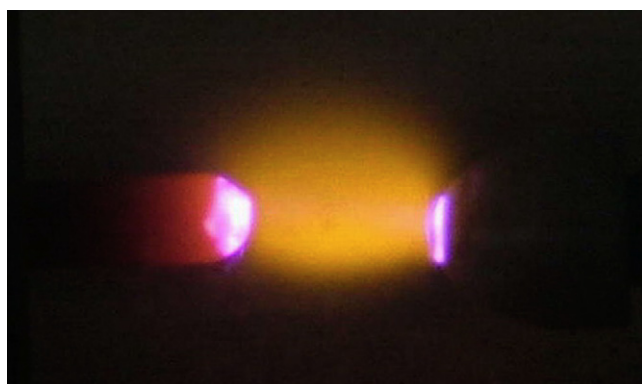Several kinds of cold plasmas have been tested in CH_4–CO_2 reforming, such as corona discharge, dielectric barrier discharge (DBD), microwave discharge, atmospheric pressure glow discharge (APGD) and gliding arc discharge. Due to different discharge modes, the electron temperature of cold plasmas can vary from 1 to 10 eV while the temperature of heavy particles is in the range of hundreds K; the local electron density is in the range of 10^{15}–10^{20} m^{-3}.

Generally, cold plasmas are inhomogeneous in discharge space which results in limited reaction region. So the conversions and the treatment capacity are restricted. For increasing reaction conversion rate, catalytic process may be introduced in CH_4–CO_2 reforming by cold plasma. There are two ways to introduce catalysts in cold plasma; one is to place catalysts in the discharge space, and the other after the discharge space.

3.2.1. Corona discharge

Corona discharge (Fig. 1) is an inhomogeneous discharge with low current density [21]. It could be generated at atmospheric pressure and has high electric field intensity for ionizing or decomposing feed-gas particles. Corona discharge usually involves two asymmetric electrodes; one high curvature, such as a small diameter wire or even a sharp tip, and the other low curvature, such as a plate or a cylinder. When a voltage applied exceeds a certain value, the electric breakdown is caused near the high curvature electrode locally, and the corona discharge is brought on. The electron temperature of corona plasma is in the range of 3.5–5 eV while the gas temperature is less than 400 K and the electron density is about 10^{15}–10^{19} m^{-3} [22]. However, high electron density mainly occupies the region around the high curvature electrode.

CH_4–CO_2 reforming was carried out by corona discharge [23–25]. When the discharge power was 46.3 W, flow rate of feed gases was 43 mL/min and the mole ratio of CH_4/CO_2 was 1:1, the conversions of CH_4 and CO_2 were 62.4% and 47.8%, and the
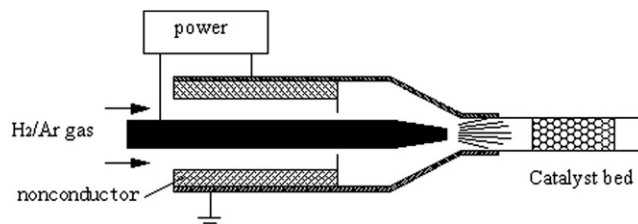

Fig. 5. Atmospheric pressure glow discharge phenomena [52].

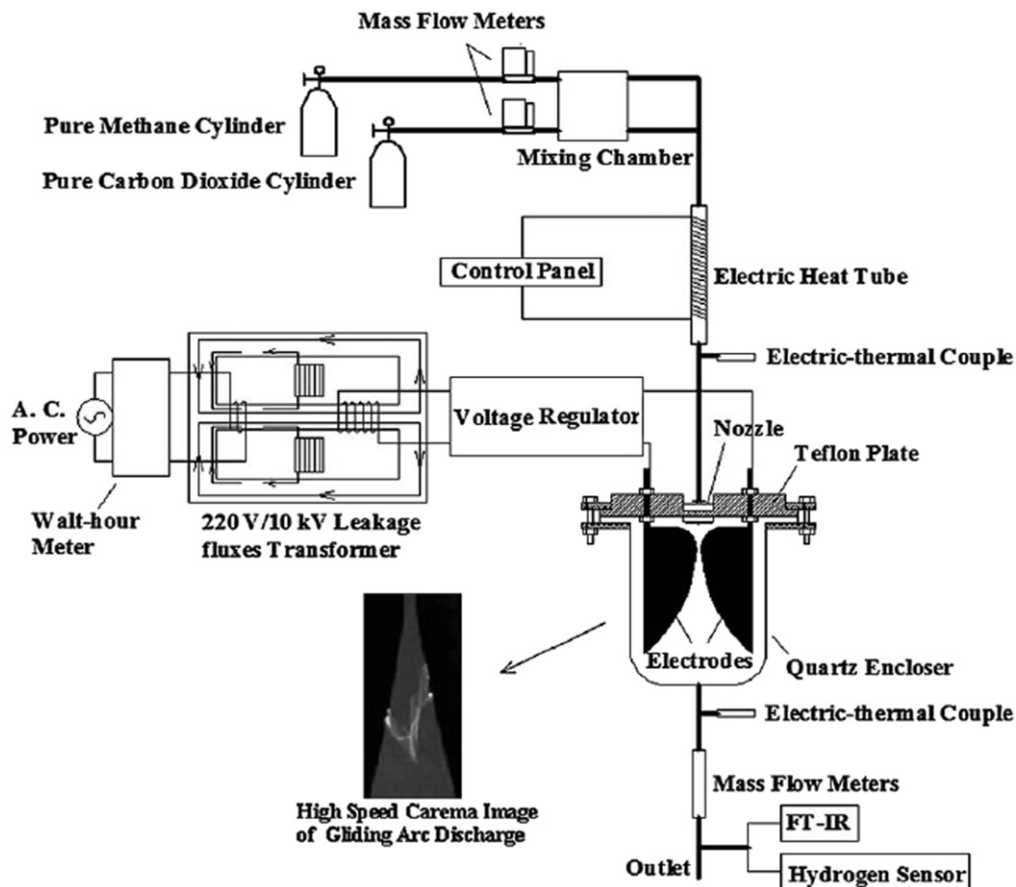**Fig. 6.** Schematic diagram of APGD plasma jet [59].

Fig. 7. Schematic diagram of gliding arc discharge setup [61].

selectivity of CO and H_2 was 66.8% and 70% [23], while the ECE was 13% and SE was 1798 kJ/mol, respectively.

Corona discharge has been tested with combination of catalysts for CH_4–CO_2 reforming by Chang-jun Liu et al. [26,27]. Under the conditions of corona discharge power 8.4 W, zeolites catalyst of 0.1 g held on the lower plate electrode, total flow rate of 25 mL/min and CH_4/CO_2 of 1/1 [26], the conversions of CH_4 and CO_2 were 56.3% and 22.8%, respectively; the selectivity of CO, C_2H_2, C_2H_4 and C_2H_6 was 9.1%, 15.0%, 1.9% and 1.8%, respectively. Since the products were complex, it was difficult to estimate the ECE and SE by Eq. (5) and (6).

Since corona discharge is characterized of localized breakdown which restricts the available reaction volume, it is difficult to achieve a large treatment capacity in CH_4–CO_2 reforming by corona discharge.

3.2.2. Dielectric barrier discharge (DBD)

DBD (Fig. 2), also called silent discharge, was first reported by Siemens in 1857 [28,29]. Its main application is production of ozone. DBD typically involves two planar electrodes. The two electrodes are placed parallelly with a gap of several millimeters, and at least one electrode is covered by dielectric with a thickness of one or 2 mm. The dielectric can be made from glass, quartz, ceramics, polymers or other materials of low dielectric loss and high breakdown strength [22]. It is the use of dielectric in the discharge gap that restricts electric currents and prevents the formation of spark and arc [30]. DBD is also an inhomogeneous discharge at atmospheric pressure and requires alternating voltages for its operation. The discharge is characterized by many micro-discharge filar channels of 0.1–0.2 mm in diameter (Fig. 3 [31]). The number of micro-discharge channels is proportional to the voltage applied on the electrodes, and the distance among filar channels is about several millimeters. The activation of reactant is mainly induced in the micro-discharge channels, in which the electron temperature is in the range of 1–10 eV [32,33] while the gas temperature in the gap is only hundreds K. Though the electron density in the micro-discharge channels is about 10^{18}–10^{21} m^{-3}
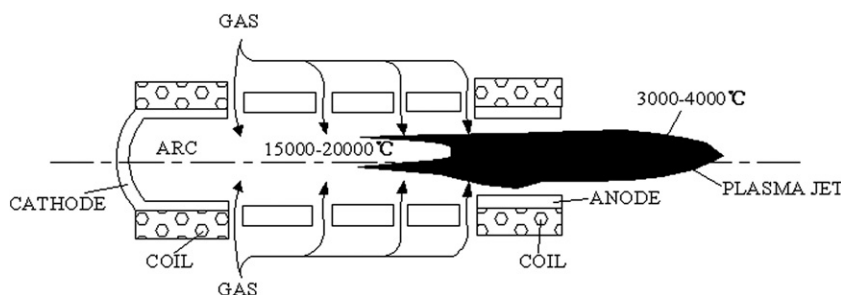

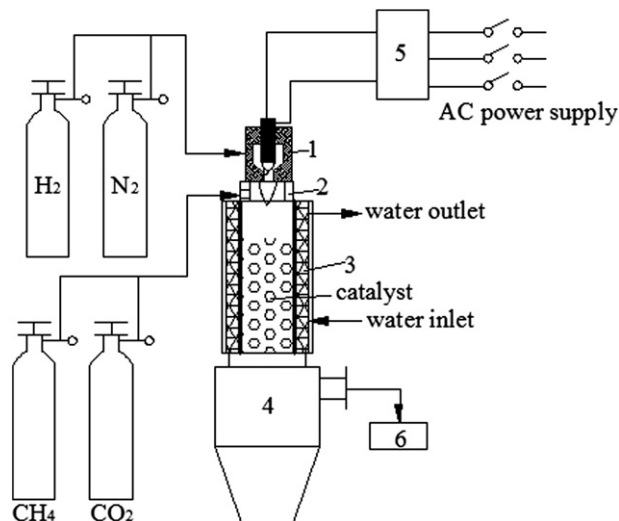**Fig. 8.** Schematic diagram of DC thermal plasma torch [63].

Fig. 9. Schematic diagram of experimental setup with single-anode thermal plasma [66]. 1. plasma generator; 2. feed inlet ring; 3. adiabatic fixed-bed reactor; 4. cooling system; 5. DC power supply; 6. gas chromatograph.

[34,35], the average electron density in the gap volume is still much lower.

DBD was employed to CH_4–CO_2 reforming by several researchers [36–43]. However, the selectivity of syngas is reported low and products are usually complex, moreover the conversion of reactants is low in most cases. Q. Wang et al. [43] investigated conversion of CH_4 and CO_2 in a coaxial DBD reactor. The main products were syngas, but C_2H_6 and trace amount of other hydrocarbons were also formed. The conversion of CH_4 and CO_2 and also the selectivity of CO and H_2 increased with the increasing input power, while the selectivity of C_2H_6 decreased sharply. When the input power was 107.4 W, discharge gap of 1.95 mm, electrode length of 20 cm, total feed flux of 20 mL/min and CH_4/CO_2 of 1/1, the conversions of CH_4 and CO_2 were 72.8% and 44.4%, the selectivity of CO, H_2 and C_2H_6 was about 82%, 70% and 8.8%, respectively, while the corresponding ECE and SE were 4% and 7289 kJ/mol, respectively.

DBD was also investigated with combination of various catalysts for CH_4–CO_2 reforming due to its high electron density in the micro-discharge channels. Hyung Keun Song et al. [44] reported CH_4–CO_2 reforming by DBD over Ni/γ-Al_2O_3 catalyst. Catalysts were packed in the bottom of plasma region. The main products were CO, H_2, C_2H_6, C_3H_8 and C_4H_{10}. Compared with reactions without catalysts, CH_4 conversion decreased from 57.63% to 55.71%,

and CO_2 conversion increased from 30.95% to 33.48% at the discharge power of 130 W, total flow rate of 30 mL/min and the CH_4/CO_2 ratio of 1.

There may be two reasons why the reaction performances weren't changed significantly by the combination of plasma and catalysts in DBD. When catalysts are put in the discharge zone, the electron density in discharge space would decrease with the charged particles recombination on catalysts according to the theory of plasma sheath, a uniform filar discharge is difficult to achieve. What is more, DBD without assisted heat can not provide enough gas temperature for catalytic activity [45–48].

The reasons why hydrocarbons occur in DBD process may be due to the intrinsic characteristics of DBD. The molecules of CH_4 are easily cracked into CH_x radicals in the filar channel with high electron energy and electron density. These radicals diffuse rapidly out of the channel into free-discharge region. This process seems a quench. In free-discharge region, the radicals couple to form hydrocarbons.

3.2.3. Microwave discharge

Microwave discharge plasma can be operated at a frequency range of GHz and a wide pressure range. The microwave plasma reactor involves a microwave generator, waveguides, a resonance cavity inserted a quartz tube where the reactants are led into and the plasma is generated as shown in Fig. 4. At atmospheric pressure, microwave discharge has larger discharge space and better discharge uniformity than that of corona discharge and DBD; the electron temperature is approximately 0.4–0.6 eV while the heavy particle temperature is around 2000 K [13].

Atmospheric pressure microwave discharge (Fig. 4) is also considered for CH_4–CO_2 reforming [49–51]. The products by pulsed microwave plasma [50] included synthesis gas, C_2H_2 and C_2H_4. Under the conditions of flow rate of 200 mL/min (CH_4/$CO_2 = 1.5$:1), peak microwave power of 120 W and pulsed duty factor of 100/100 ms, conversions of CH_4 and CO_2 were 70.8% and 68.8%, and the selectivity of CO, C_2H_2, C_2H_4 was 75%, 17.8% and 4.1%, respectively, free of carbon deposition, and the ECE and SE were 47% and 307 kJ/mol, respectively. Here, the appearance of hydrocarbons was due to the excessive CH_4 in feed.

CH_4–CO_2 reforming by microwave discharge shows higher conversions and selectivity, larger treatment capacity, as well as higher energy efficiency, which benefit from its larger discharge space and better discharge uniformity. The chemical reaction in microwave plasma is induced by energetic electrons and high gas temperature. However, the equipment of microwave discharge is more complicated and bulky, it is difficult to obtain large equipment suited for industrial requirements.
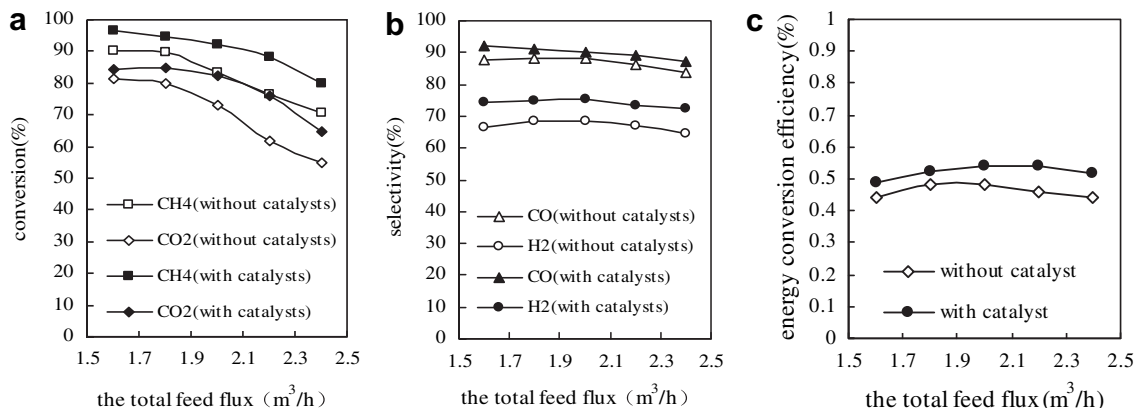

Fig. 10. Effect of total flux on performance of single-anode thermal plasma with or without catalysts.
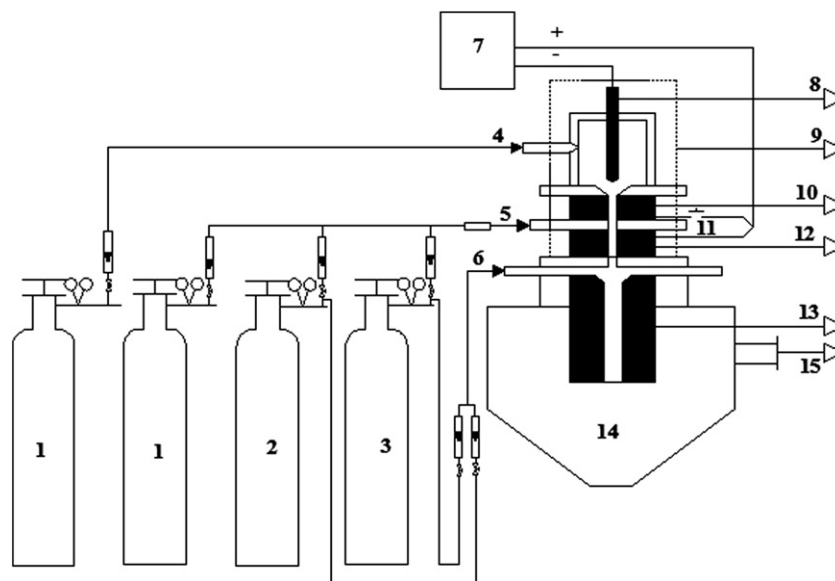
Fig. 11. Schematic diagram of experimental setup with binode thermal plasma [67]. 1. Ar; 2. CH_4; 3. CO_2; 4. gas inlet I; 5. gas inlet II; 6. gas inlet III; 7. DC power supply; 8. cathode; 9. plasma generator; 10. the first anode; 11. contactor; 12. the second anode; 13. graphite tube reactor; 14. collector; 15. gas outlet (Mode I is to introduce the feed gas, mixture of CH_4/CO_2, only into the gas inlet II; Mode II is to keep the same state, and introduce another part of feed gases into the plasma jet from the exit of plasma generator (gas inlet III)).

3.2.4. Atmospheric pressure glow discharge (APGD)

The term "glow" indicates that the plasma of the discharge is luminous in contrast to the relatively low-power dark discharge [18]. Glow discharge can operate over a wide pressure range. Atmospheric pressure glow discharge (APGD) is an arc-like discharge as shown in Fig. 5 [52], obtained by applying a few hundred volts to a few kilovolts between the two electrodes [53] with a ballast circuit to avoid the transition of glow to arc. The electron temperature of APGD is in the range of 1–2 eV while the gas temperature and the electron density are about 2000 K and $10^{18}-10^{19}$ m^{-3} [54,55], respectively.

APGD has been applied to CH_4-CO_2 reforming [12,55–59]. A. M. Ghorbanzadeh et al. [57] reported CH_4-CO_2 reforming by pulsed plasma. The products mainly consisted of syngas and C_2 hydrocarbons. At discharge power of 23 W, frequency of 4 kHz, feed-gas flow rate of 120 mL/min and CH_4/CO_2 of 1:1, the conversions of CH_4 and CO_2 were 61% and 50%, and the selectivity of H_2, CO, C_2H_2 and C_2H_4 was about 77.5%, 63%, 15% and 9%, respectively, while the ECE and SE were 44% and 313 kJ/mol, respectively. This process is more advantageous in energy conversion efficiency which benefits from higher electron density.

Cold plasma jet is one kind of APGD developed by H. Koinuma et al. [60]. Long Huali [59] presented CH_4-CO_2 reforming by AC cold plasma jet of 20 kHz (Fig. 6). The 12% $Ni/\gamma-Al_2O_3$ was put after the plasma discharge zone. At the total flow rate of 1.67×10^4 mL/min (1.0 m^3/h) ($CH_4 = 0.2$ m^3/h, $CO_2 = 0.3$ m^3/h, $N_2 = 0.5$ m^3/h) and the input power of 770 W, the conversions of CH_4 and CO_2 were 60.06% and 40.35%, and the selectivity of CO and H_2 was 96.79% and 96.87%, respectively. Compared with that without catalysts, the conversions were increased by 14.38% and 6.32%, and the selectivity was increased by 11.38% and 18.76%, respectively. The ECE increased from 63% to 80% while the SE decreased from 202 kJ/mol to 134 kJ/mol.

Obviously, the energy conversion efficiency in the investigation by cold plasma jet is raised significantly compared to that of the aforementioned cold plasmas. This owes to the reasonable design of reactor configuration and the application of plasma mode used. In Fig. 6, the flow regions of feed gases are confined by the reactor configuration, which ensures all the feed gases through the plasma discharge zone. AC cold plasma jet of 20 kHz possesses higher electron density and higher plasma temperature than that of corona discharge and DBD. The high electron density directly gives rise to enhancement of the reforming reaction, and the high plasma

Fig. 12. Effects of Φ on conversions and selectivity by binode thermal plasma in Mode I. (a) Conversion of CH_4 and CO_2; (b) selectivity of H_2 and CO, $\Phi = F/P$, F is the total flux of CH_4 and CO_2 in m^3/h; P is the power on plasma reactor in kW. The experimental condition: CH_4/CO_2 of 4/6, input power of 20–32.4 kW, flow rates at 2.4–5 m^3/h.
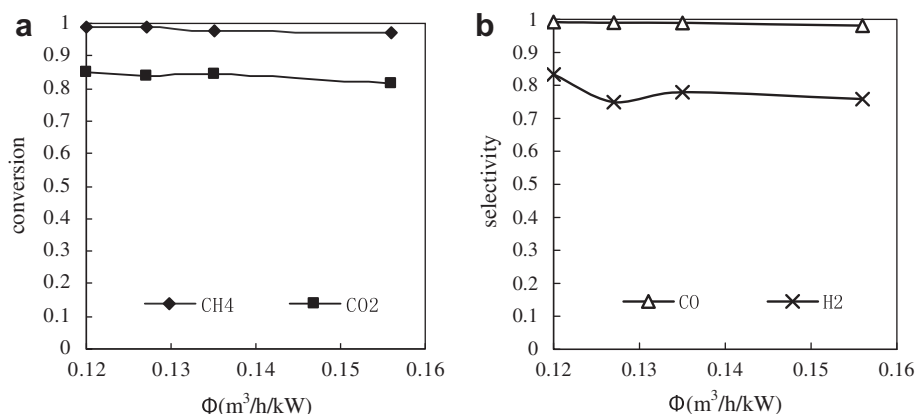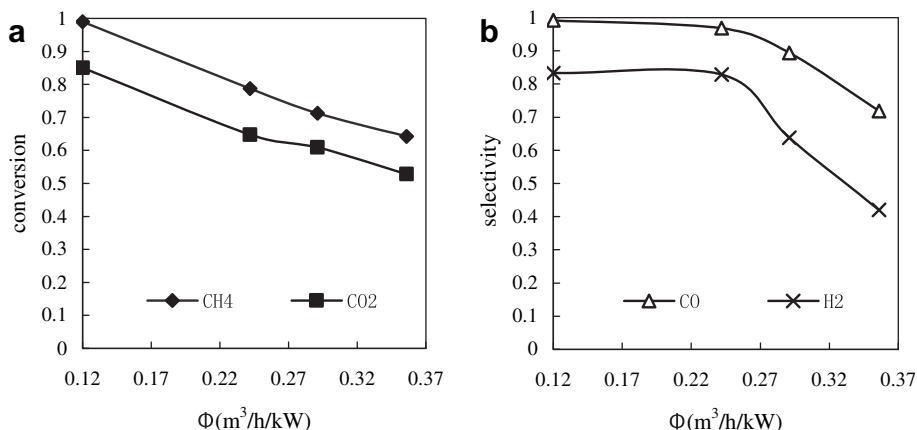
Fig. 13. Effects of Φ on conversions and selectivity by binode thermal plasma in Mode II. (a) Conversion of CH_4 and CO_2; (b) selectivity of H_2 and CO, The experimental condition: CH_4/CO_2 of 4/6, input power of 18–20 kW, flow rates at 2.4–6.4 m^3/h, and the flow rates of CH_4/CO_2 mixture introduced as the plasma-forming gas kept at 2.4 m^3/h.

temperature heats catalysts, directly results in enhancement of the synergistic effect of plasma and catalysts.

APGD seems to be a promising plasma form for CH_4–CO_2 reforming due to its high electron energy and electron density, as well as its proper plasma temperature. One of the major challenges is how to enlarge the process.

3.2.5. Gliding arc discharge

The principle of the gliding arc discharge was patented by Lesueur et al. in 1988 and was developed by Czernichowski et al. [30]. The reactor (Fig. 7) consists of two or more diverging metallic electrodes. When a high voltage is applied, a relatively low current-arc discharge is generated across the electrodes [61]. Gliding arc discharge is mainly distinguished by the arc flame. The discharge initially forms at the closest gap, the arc is then elongated and the arc root glides along the surface of electrodes by puff of the fast flow working gas, till extinguishes in plasma downstream. New discharges immediately reform at the initial spot repeatedly [15]. The gliding arc plasma can be either thermal or cold plasma depending on the discharge power and the gas flow rate [18].

The application of gliding arc discharge to CH_4–CO_2 reforming [61,62] has been increasing recently. Antonius Indarto et al. [62] studied CH_4–CO_2 reforming by gliding ac discharge with frequency of 20 kHz. At the total feed-gas flow rate of 1000 mL/min, the discharge power of 190 W and CH_4/CO_2 of 1:1, the conversions of CH_4 and CO_2 were about 40% and 31%, and the selectivity of H_2, CO and C_2H_2 was about 50%, 62% and 12%, respectively; the corresponding ECE and SE were 28% and 608 kJ/mol, respectively.

The ECE and SE of CH_4–CO_2 reforming by gliding arc discharge are better than that by corona discharge and DBD. However, the single pass conversion is lower, which seems due to its intrinsic characteristics that the discharge needs the puff of fast flow reactant gas to avoid arc overdeveloped.

Corona discharge and DBD are commonly used methods for CH_4–CO_2 reforming in early investigations, because they could be easily obtained and easy to handle in laboratory. However, the electron density in both plasmas is somewhat low, it is difficult to deal with high feed-gas flow rate with a reasonable conversion and ECE. APGD improves the ECE and SE of CH_4–CO_2 reforming, but the treatment capacity is still far from industrial requirement. However, the performance of APGD provides us the importance of the reasonable reactor configuration, high electron density and high plasma temperature, as well as ECE and SE performance targets for industrial-scale plasma reforming.

To obtain high energy conversion efficiency and large treatment capacity in CH_4–CO_2 reforming, the reasonable reactor configuration to ensure all the feed gases through the plasma discharge zone, and proper plasma mode with high electron density and high plasma temperature must be well-chosen. For this reason, CH_4–CO_2 reforming by thermal plasma is proposed.

3.3. CH_4–CO_2 reforming by thermal plasma

Thermal plasma, generated in the way of electric arc, is continuous and uniform plasma. Thermal plasma with features of relatively high enthalpy content, high temperature (temperature of
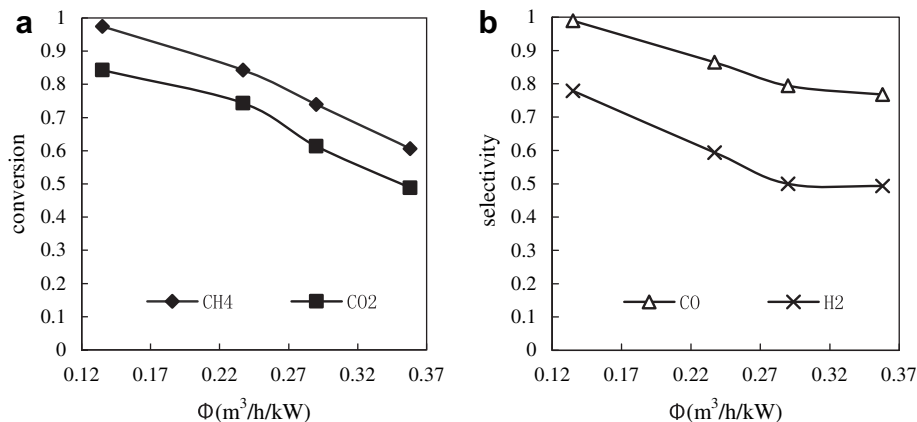

Fig. 14. Effects of Φ on conversions and selectivity by binode thermal plasma in Mode II. (a) Conversion of CH_4 and CO_2; (b) selectivity of H_2 and CO, The experimental condition: CH_4/CO_2 of 4/6, input power of 22.5–25.625 kW, flow rates at 3–8 m^3/h, and the flow rates of CH_4/CO_2 mixture introduced as the plasma-forming gas kept at 3 m^3/h.
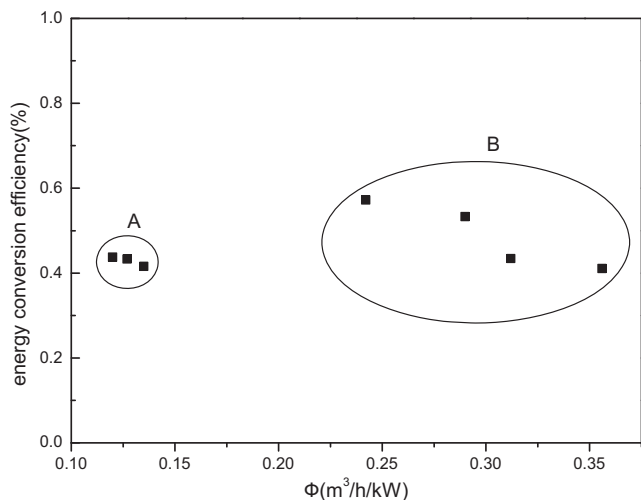
Fig. 15. Effects of Φ on energy conversion efficiency by binode thermal plasma. The experimental condition: CH_4/CO_2 of 4/6, input power of 18–32.4 kW, flow rates at 2.4–8 m³/h.

heavy particle and electron is 0.5–1 eV) and high electron density (10^{19}–10^{20} m^{-3}), has obviously thermal effect and chemical effect. It covers a wide range of applications and has been applied in industry [63].

There are several types of thermal plasma devices: direct current (DC) arc torch, alternating current (AC) arc torch, radio-frequency (RF) inductively coupled torch and high-frequency capacitive torch. The DC arc torch is used widely (Fig. 8 [63]). Commonly, a DC arc torch consists of a thoriated tungsten (2–3% ThO_2) rod or button type cathode and one or more water-cooled copper anodes which are separated by insulating materials. The arc is established between the electrodes by a special trigger and pushed through the nozzle resulting in a high temperature flame. The power of the torch controlled by changing the input voltage or current can reach 10^2–10^7 W [64]. Since thermal plasma is a source of high temperature and chemically active species, it is potential for CH_4–CO_2 reforming.

Lan et al. [65] studied CH_4–CO_2 reforming by single-anode hydrogen thermal plasma jet. The operating power reached 8.5 kW and feed-gas flow rate 2.17×10^4 mL/min (1.3 m³/h), both were much higher than that of cold plasmas. At CH_4/CO_2 of 4/6, the conversions of methane and carbon dioxide were 87.98% and 84.34%, respectively;

the selectivity of CO and H_2 was 82.27% and 43.48%, respectively; and the ECE and SE were 36% and 520 kJ/mol, respectively.

Tao et al. [66] studied CH_4–CO_2 reforming by single-anode nitrogen thermal plasma jet with and without catalysts. As shown in Fig. 9, nitrogen gas was served as discharge gas to form high temperature jet injected into the tube reactor; hydrogen was used to reduce the catalysts. The catalysts were located at appropriate place in the reactor to be heated by the plasma jet. The mixture of methane and carbon dioxide were led to converge vertically with the plasma jet at the top of the reactor, in which feed gases were mixed with the plasma jet and the reforming reaction took place at the same time. In catalysts bed, the remained feed gases were further converted. The experimental results were shown in Fig. 10. For example, the conversions of CH_4 and CO_2 were high to 92.32% and 82.19%, and the selectivity of CO and H_2 were also high to 90.05% and 75.43%, respectively, at the conditions of total flow rate 3.33×10^4 mL/min (2.0 m³/h), the molar ratio of CH_4/CO_2 4/6, and the plasma power 9.6 kW Fig. 10 showed that there was a synergistic effect in the reaction by plasma with catalyst, by which the conversion and selectivity were 10–20% higher than those by plasma only. Meanwhile, the ECE and SE reached 54% and 290 kJ/mol, respectively.

Comparing with that by cold plasmas, CH_4–CO_2 reforming by single-anode thermal plasma exhibits the significant advantages like large treatment capacity, little by-product, relatively high energy conversion efficiency, which is closer to industrial application. Furthermore, in above experiments, the feed gases were injected only into the plasma jet, not into the discharge region between the anode and the cathode. If the feed gases are introduced into the discharge region as plasma-forming gas directly, the treatment capacity and the energy conversion efficiency could be raised further. To verify the idea, a binode thermal plasma generator is applied to CH_4–CO_2 reforming [67].

The binode thermal plasma generator consists of a club-shaped cathode and two columnar anodes which are separated by insulating materials. After the discharge is first ignited between the cathode and the first anode, the ionized gas is puffed to the second anode where the DC power supply is applied. Then the discharge channel is established between the cathode and the second anode, and the binode plasma jet is formed.

Experimental study was conducted in a binode thermal plasma generator in two modes (Fig. 11). One was to introduce feed gases (CH_4 and CO_2) only into the discharge region from gas inlet II as plasma-forming gas (mode I); the other was to introduce them

Table 1
Comparison of conversions and specific energy with different plasmas.

Plasma form	Feed flux (mL/min)	CH_4/CO_2	P (W)	Conversion (%)		Selectivity (%)					H_2/CO	SE (kJ/mol)	ECE (%)	Ref.
				CH_4	CO_2	CO	H_2	C_2H_2	C_2H_4	Coke				
Corona discharge	43	1/1	46.3	62.4	47.8	66.8	70	15.8	1.5	−	1.2	1798	13	23
DC corona discharge	60	1/2	63	94.1	77.9	97.1	69.4	−	−	2.39	0.6	1134	21	25
Corona discharge + zeolite	25	1/1	8.4	56.3	22.8	9.1	−	15.0	1.9	−	2.1	4022	4	26
DBD	150	2/1	500	64.3	55.4	33.3	−	1.2	1.2	−	1.7	8124	3	39
DBD	20	1/1	107.4	72.8	44.4	∼82	∼70	−	−	−	1.0	7289	4	43
DBD + Ni/Al_2O_3	30	1/1	130	55.71	33.48	60.9	51.92	10.12		−	1.0	10 385	3	44
Microwave discharge	200	3/2	60	70.8	68.8	75	−	17.8	4.1	−	1.5	307	47	50
Glow discharge	120	1/1	23	61	50	∼63	∼77.5	∼15	∼9	∼8	1.4	313	44	57
Cold plasma jet	0.83×10^4	4/6	770	45.68	34.03	85.41	78.11	/	/	14.59	0.8	202	63	59
Cold plasma jet + Ni/Al_2O_3	0.83×10^4	4/6	770	60.06	40.35	96.79	96.87	/	/	3.21	1.0	134	80	59
Gliding arc discharge	1000	1/1	190	∼40.00	∼31.00	∼62	∼50	∼12	−	−	0.9	608	28	62
Single-anode thermal plasma (H_2)	2.17×10^4	4/6	8.5×10^3	87.98	84.34	82.27	43.48	/	/	17.66	0.4	520	36	65
Single-anode thermal plasma (N_2)	3×10^4	4/6	9.6×10^3	89.82	80.14	88.37	68.60	/	/	11.63	0.7	348	48	66
Single-anode thermal plasma (N_2) + Ni/Al_2O_3	3.33×10^4	4/6	9.6×10^3	92.32	82.19	90.15	75.43	/	/	9.85	0.7	290	54	66
Binode thermal plasma	7.33×10^4	4/6	1.8×10^4	78.71	64.80	96.79	82.85	/	/	3.21	0.8	274	57	67

simultaneously into the discharge region from gas inlet II and the exit of jet from gas inlet III (mode II). A constant current power supply was applied in the experiments. The operating voltage significantly increases with the increasing flow rate of CH_4 and CO_2 introduced as the plasma-forming gas, so did the discharge power. However, the discharge power was not affected when CH_4 and CO_2 were introduced into the plasma jet from gas inlet III. For convenience, define $\Phi = F/P$ to scale the plasma treatment capacity [67]. Where, F was the total flux of CH_4 and CO_2 in m^3/h; P was the power on plasma reactor in kW. Apparently, Φ implied the average energy acting on each molecule. The larger Φ was, the lower the acting energy was.

As shown in Figs. 12–15, mode I brought about higher conversion and selectivity but appreciably lower energy conversion efficiency, while mode II brought about higher energy conversion efficiency but somewhat lower conversion and selectivity. Under the experimental conditions of CH_4/CO_2 of 4/6, input power of 18 kW and total feed flux of 7.33×10^4 mL/min (4.4 m^3/h) in mode II, it was confirmed that the conversions of CH_4 and CO_2 were 78.71% and 64.80%, the selectivity of CO and H_2 was 96.79% and 82.85%, respectively, and ECE achieved a maximum of 57%; SE achieved a minimum of 274 kJ/mol.

A comparison for reforming performances by different plasmas is given in Table 1. Thermal plasma process shows higher conversions and selectivity, larger treatment capacity, as well as considerable energy conversion efficiency (ECE) and specific energy (SE). It may be appropriate to scale up to industrial application.

4. Understanding of reforming by plasma process

Generally, the reaction of CH_4–CO_2 reforming by plasma may be very complex. However, it can be simply understood as follows:

$$CH_4 \xrightarrow{e^* \text{ or pyrolysis}} C + 2H_2 \tag{7}$$

$$CO_2 \xrightarrow{e^* \text{ or pyrolysis}} CO + O \tag{8}$$

$$C + O \rightarrow CO \tag{9}$$

$$H_2 + O \rightarrow H_2O \tag{10}$$

Eqs. (7) and (8) are highly endothermic reactions, induced by energetic electrons impact or thermo-chemical pyrolysis. Eqs. (9) and (10) are radical reactions, which occur without activation barrier.

There are two mechanisms in the conversion of CH_4 and CO_2 by energetic electrons impact. One is direct dissociation, the molecules of CH_4 or CO_2 are collided by electrons with kinetic energy higher than dissociation energy threshold of groud-state molecule. It can be expressed as.

$$AB \xrightarrow{e^*} A + B \tag{11}$$

The other is vibrational excitation, for most non-electronegative molecules (N_2, H_2, CO, CH_4, CO_2, etc.), vibrational excitation by electron-impact occurs via the formation of an intermediate state [68–71], which then stimulates chemical conversions in the reactions. It can be expressed as

$$A + BC(v) \rightarrow AB + C \tag{12}$$

It is the vibrational excitation that is most effective in conversion of CH_4 or CO_2 because the energy required for electron in this case is lower than that in direct dissociation. For the plasma with

electron temperature of 1–3 eV, the number of electrons to induce vibrational excitation is much more than that to induce direct dissociation, the bulk of discharge energy input can be localized on preferred chemical process channels by vibrational excitation [68,72].

It is known that the ionization degree of cold plasma is much lower than that of thermal plasma. Besides electrons, free radicals and ions, there are still many molecules in the plasma. The ionization degree is also proportional to the input power. The higher the input power is, the higher ionization degree will be achieved. And then, more radicals but fewer molecules can be formed. As a result, the conversions of CH_4 and CO_2 will be higher. The APGD plasma jet and thermal plasma have the highest ionization degree and appropriate electron temperature, as well as proper gas temperature in all plasmas introduced above, therefore, CH_4–CO_2 reforming by them shows better energy conversion efficiency and specific energy. Comparing them, thermal plasma possesses much larger treatment capacity, considerable energy conversion efficiency and specific energy as well, it is not difficult to obtain thermal plasma equipments with large power of thousands kilowatt, the only thing to do is increase its energy conversion efficiency further. This can be done by improving the thermal plasma generator, more reasonable reactor design and operation, as well as an optimal synergy of plasma with catalysts and heat recovery of the process.

5. Conclusion

CH_4–CO_2 reforming by different plasmas is reviewed in this paper. For achieving high conversions and high energy conversion efficiency by plasma process, three key factors have to be taken into account. They are electron density, plasma temperature and reactor configuration. Corona discharge and DBD are non-uniform plasmas with low electron density and limited reaction volume which restrict the treatment capacity. Microwave discharge is a uniform discharge with high plasma temperature and large discharge space, but the equipment is more complicated and expensive which restricts its industrial application. Gliding arc discharge and APGD possess high electron energy and electron density, as well as proper plasma temperature, but the reactor is difficult to enlarge, the treatment capacity of both plasmas is still far from industrial requirements. Thermal plasma is an efficient technology for CH_4–CO_2 reforming to synthesis gas because of its high specific enthalpy content, high temperature, high electron density, large treatment capacity, easy to enlarge and relatively high energy conversion efficiency. For raising the energy conversion efficiency of thermal plasma process further, the feed gases introduced into the discharge region and the synergistic effect of plasma with catalysts should be taken into consideration in future work.

Nomenclature

n_i	the moles of i component (mol)
$n_{CH_4}^{\cdot}$	the moles of methane converted (mol)
x_i	conversion of i component
S_i	selectivity of i component

F   the total fluxes of CH_4 and CO_2 (m^3/h)
P   the input power of plasma (kW)
$\Phi = F/P$ the plasma treatment capacity ($m^3/h/kW$)
LHV   the lower heating value of substance (kJ/mol)
SE   specific energy (kJ/mol)
ECE   energy conversion efficiency
DBD   dielectric barrier discharge
APGD   atmospheric pressure glow discharge

References

[1] Rostrup-Nielsen JR. New aspects of syngas production and use. Catalysis Today 2000;63(2–4):159–64.

[2] Wender I. Reactions of synthesis gas. Fuel Processing Technology 1996;48(3):189–297.

[3] Wilhelm DJ, Simbeck DR, Karp AD, Dickenson RL. Syngas production for gas-to-liquids applications: technologies, issues and outlook. Fuel Processing Technology 2001;71(1–3):139–48.

[4] Teuner S. Make CO from CO_2. Hydrocarbon Processing 1985;64:106.

[5] Teuner S. A new process to oxo-feed. Hydrocarbon Processing 1987;66:52.

[6] Udengarrd NR, Hansen JHB, Hanson DC. Oil Gas Journal 1992;90:225.

[7] Edwards JH. Potential sources of CO_2 and the options for its large-scale utilization mow and in the future. Catalysis Today 1995;23(1):59–66.

[8] Haghighi M, Sun Z, Wu J, Bromly J, Wee HL, Ng E, et al. On the reaction mechanism of CO_2 reforming of methane over a bed of coal char. Proceedings of the Combustion Institute 2007;31(2):1983–90.

[9] Bradford MCJ, Vannice MA. CO_2 reforming of CH_4. Catalysis Reviews-Science and Engineering 1999;41(1):1–42.

[10] Fischer F, Tropsch H. The composition of products obtained by the petroleum synthesis. Brennst Chemistry 1928;39(3).

[11] Ashcroft AT, Cheetham AK, Green MLH, Vernon PDF. Partial oxidation of methane to synthesis gas using carbon dioxide. Nature 1991;352:225–6.

[12] Huang A, Xia G, Wang J, Suib SL, Hayashi Y, Matsumoto H. CO_2 reforming of CH_4 by atmospheric pressure ac discharge plasmas. Journal of Catalysis 2000;189(2):349–59.

[13] Sekiguchi H, Mori Y. Steam plasma reforming using microwave discharge. Thin Solid Films 2003;435(1–2):44–8.

[14] Paulmier T, Fulcheri L. Use of non-thermal plasma for hydrocarbon reforming. Chemical Engineering Journal 2005;106(1):59–71.

[15] Fridman A, Nester S, Kennedy LA, Saveliev A, Mutaf-Yardimci O. Gliding arc gas discharge. Progress in Energy and Combustion Science 1998;25(2):211–31.

[16] Czernichowski A. Electrically assisted conversion of carbon dioxide into synthesis gas. Greenhouse Gas Control Technologies; 1999:439.

[17] Bossel U. Well-to-wheel studies, heating values, and the energy conservation principle. Proceedings of Fuel Cell Forum; 2003.

[18] Fridman A. Plasma chemistry. New York: Cambridge University Press; 2008.

[19] Langmuir I. Oscillations in ionized gases. Proceedings of the National Academy of Sciences 1928;14:627–37.

[20] Goossens M. An introduction to plasma astrophysics and magnetohydrodynamics. Netherlands: Kluwer Academic Publishers; 2003.

[21] Schütze A, Jeong JY, Babayan SE, Park J, Selwyn GS, Hicks RF. The atmospheric-pressure plasma jet: a review and comparison to other plasma sources. IEEE Transaction on Plasma Science 1998;26(6):1685–93.

[22] Fridman A, Chirokov A, Gutsol A. Non-thermal atmospheric pressure discharges. Journal of Physics D Applied Physics 2005;38(2):1–24.

[23] Yang Y. Methane conversion and reforming by nonthermal plasma on pins. Industrial and Engineering Chemistry Research 2002;41(24):5918–26.

[24] Dai B, Zhang XL, Gong WM, He R. Study on the methane coupling under pulse corona plasma by using CO_2 as oxidant. Plasma Science & Technology 2000;2(6):577–80.

[25] Li M, Xu G, Tian Y, Chen L, Fu H. Carbon dioxide reforming of methane using DC corona discharge plasma reaction. Journal of Physical Chemistry A 2004;108(10):1687–93.

[26] Liu C, Mallinson R, Lobban L. Comparative investigations on plasma catalytic methane conversion to higher hydrocarbons over zeolites. Applied Catalysis A General 1999;178(1):17–27.

[27] Zhang X, Dai B, Zhu A, Gong W, Liu C. The simultaneous activation of methane and carbon dioxide to C2 hydrocarbons under pulse corona plasma over $La_2O_3/\gamma-Al_2O_3$ catalyst. Catalysis Today 2002;178(3–4):223–7.

[28] Kogelschatz U, Eliasson B, Egli W. From ozone generators to flat television screens: history and future potential of dielectric-barrier discharges. Pure and Applied Chemistry 1999;71(10):1819–28.

[29] Kogelschatz U. Dielectric-barrier discharges: their history, discharge physics, and industrial applications. Plasma Chemistry and Plasma Processing 2003;23(1):1–46.

[30] Moreau M, Orange N, Feuilloley MGJ. Non-thermal plasma technologies: new tools for bio-decontamination. Biotechnology Advances 2008;26(6):610–7.

[31] Dong L, He Y, Yin Z, Chai Z. Hexagon and stripe patterns in dielectric barrier streamer discharge. Plasma Sources Science and Technology 2004;13(1):164–5.

[32] Liu C, Xu G, Wang T. Non-thermal plasma approaches in CO2 utilization. Fuel Processing Technology 1999;58(2–3):119–34.

[33] Istadi NASAmin. Co-generation of synthesis gas and C2+ hydrocarbons from methane and carbon dioxide in a hybrid catalytic-plasma reactor: a review. Fuel 2006;85(5–6):577–92.

[34] Park J, Henins I, Herrmann HW, Selwyn GS, Jeong JY, Hicks RF, et al. An atmospheric plasma source. Applied Physics Letters 2000;76(3):288–90.

[35] Eliasson B, Kogelschatz U. Modeling and application of silent discharge plasmas. IEEE Transaction on Plasma Science 1991;19(2):309–23.

[36] Gesser HD, Hunter NR, Probawono D. The CO_2 reforming of natural gas in a silent discharge reactor. Plasma Chemistry Plasma Process 1998;18(2):241–5.

[37] Li Y, Xu G, Liu C, Elisson B, Xue B. Co-generation of syngas and higher hydrocarbons from CO_2 and CH_4 using dielectric-barrier discharge: effect of electrode material. Energy Fuels 2001;15(2):299–302.

[38] Zou JJ, Li Y, Zhang YP, Liu CJ. Product distribution of conversions of methane and carbon dioxide using dielectric barrier discharge. Acta Physico –Chimica Sinica 2002;18(8):759–63.

[39] Jiang T, Li M, Li Y, Xu G, Liu C, Eliasson B, et al. Comparative investigation on the conversion of greenhouse gases using dielectric barrier discharge and corona discharge. Journal of Tianjin University 2002;35(1):19–22.

[40] Zhang Y, Li Y, Wang Y, Liu C, Eliasson B. Plasma methane conversion in the presence of carbon dioxide using dielectric-barrier discharge. Fuel Processing Technology 2003;83:101–9.

[41] Bai M, Zhu X, Bai M, Zhan K, Wang N. Study on methane and carbon dioxide conversion using DBD at atmospheric pressure. Transactions of Beijing Institute of Technology 2005;25:217–21.

[42] Goujard V, Tatibouët JM, Batiot-Dupeyrat C. Use of a non-thermal plasma for the production of synthesis gas from biogas. Applied Catalysis A: General 2009;353(2):228–35.

[43] Wang Q, Yan BH, Jin Y, Cheng Y. Investigation of dry reforming of methane in a dielectric barrier discharge reactor. Plasma Chemistry Plasma Process 2009;29(3):217–28.

[44] Song HK, Choi JW, Yue SH, Lee H, Na BK. Synthesis gas production via dielectric barrier discharge over $Ni/\gamma-Al_2O_3$ catalyst. Catalysis Today 2004;89(1–2):27–33.

[45] Zhang AJ, Zhu AM, Guo J, Xu Y, Shi C. Conversion of greenhouse gases into syngas via combined effects of discharge activation and catalysis. Chemical Engineering Journal 2009, available online and in press.

[46] Jiang T, Li Y, Liu C, Xu G, Eliasson B, Xue B. Plasma methane conversion using dielectric-barrier discharges with zeolite A. Catalysis Today 2002;72(3–4):229–35.

[47] Eliasson B, Liu C, Kogelschatz U. Direct conversion of methane and carbon dioxide to higher hydrocarbons using catalytic dielectric-barrier discharges with zeolites. Industrial and Engineering Chemistry Research 2000;39(5):1221–7.

[48] Lee H, Song HK, Min BR. Heating effect of plasma catalytic reaction on the CH_4 reforming of CO_2 over $Ni/\gamma-Al_2O_3$ catalyst in dielectric-barrier discharge reactor. Chemistry Letters 2006;35(6):646–7.

[49] Fidalgo B, Dominguez A, Pis JJ, Menéndez JA. Microwave-assisted dry reforming of methane. International Journal of Hydrogen Energy 2008;33(16):4337–44.

[50] Zhang JQ, Yang YJ, Zhang JS, Liu Q. Study on the conversion of CH_4 and CO_2 using a pulsed microwave plasma under atmospheric pressure. Acta Chimica Sinica 2002;60(11):1973–80.

[51] Cho W, Ju WS, Lee SH, Baek YS, Kim YC. Investigation of synthesis gas production from natural gas and CO_2 by microwave plasma technology, studies in surface science and catalysis carbon dioxide utilization for global sustainability. Proceedings of 7th International Conference on Carbon Dioxide Utilization 2004;153:205–8.

[52] Li X, Tang C, Dai X, Yin Y. Study of atmospheric pressure abnormal glow discharge. Plasma Science & Technology 2008;10(2):185–8.

[53] Duten X, Packan D, Yu L, Laux CO, Kruger CH. DC and pulsed glow discharge in atmospheric pressure air and nitrogen. IEEE Transactions on Plasma Science 2000;30(1):178–9.

[54] Mohamed AAH, Block R, Schoenbach KH. Direct current glow discharge in atmospheric air. IEEE Transactions on Plasma Science 2000;30(1):182–3.

[55] Li X, Tao X, Yin Y. An atmospheric-pressure glow-discharge plasma jet and its application. IEEE Transactions on Plasma Science 2009;37(6):759–63.

[56] Li D, Li X, Bai M, Tao X, Shang S, Dai X, et al. CO_2 reforming of CH4 by atmospheric pressure glow discharge plasma: a high conversion ability. International Journal of Hydrogen Energy 2009;34(1):308–13.

[57] Ghorbanzadeh AM, Lotfalipour R, Rezaei S. Carbon dioxide reforming of methane at near room temperature in low energy pulsed plasma. International Journal of Hydrogen Energy 2009;34(1):293–8.

[58] Chen Q, Dai W, Tao X, Yu H, Dai X, Yin Y. CO_2 reforming of CH_4 by atmospheric pressure abnormal glow plasma. Plasma Science & Technology 2006;8(2):181–4.

[59] Long H, Shang S, Tao X, Yin Y, Dai X. CO_2 reforming of CH_4 by combination of cold plasma jet and $Ni/\gamma-Al_2O_3$ catalyst. International Journal of Hydrogen Energy 2008;33(20):5510–5.

[60] Koinuma H, Ohkubo H, Hashimoto T, Inomata K, Shiraishi T, Miyagana A, et al. Development and application of a micro beam plasma generator. Applied Physics Letters 1992;60(7):816–7.

[61] Bo Z, Yan J, Li X, Chi Y, Cen K. Plasma assisted dry methane reforming using gliding arc gas discharge: effect of feed gases proportion. International Journal of Hydrogen Energy 2009;33(20):5545–53.

[62] Indarto A, Choi JW, Lee H, Song HK. Effect of additive gases on methane conversion using gliding ac discharge. Energy 2006;31:2986–95.

[63] Fauchais P, Vardelle A. Thermal plasmas. IEEE Transactions on Plasma Science 1997;25(6):1258—80.

[64] Boulos MI, Fauchais P, Pfender E. Thermal plasmas: fundamentals and applications, vol. 1. New York: Plenum Press; 1994.

[65] Lan T, Ran Y, Long H, Wang Y, Yin Y. Experimental study on syngas production by carbon dioxide reforming of methane by plasma jet. Natural Gas Industry 2007;27(5):129—32.

[66] Tao X, Qi F, Yin Y, Dai X. CO_2 reforming of CH_4 by combination of thermal plasma and catalyst. International Journal of Hydrogen Energy 2008;33 (4):1262—5.

[67] Tao X, Bai M, Wu Q, Huang Z, Yin Y, Dai X. CO_2 reforming of CH_4 by binode thermal plasma. International Journal of Hydrogen Energy 2009;34(23):9373—8.

[68] Fridman AA, Rusanov VD. Theoretical basis of non-equilibrium near atmospheric pressure plasma chemistry. Pure and Applied Chemistry 1994;66 (6):1267—74.

[69] Schulz GJ. Vibrational excitation of N_2, CO, and H_2 by electron impact. Physical Review A 1964;135(4A):988—94.

[70] Phelps AV. Rotational and vibrational excitation of molecules by low-energy electrons. Review of Modern Physics 1968;40(2):399—410.

[71] Henry RJW, Chang ES. Rotational-vibrational excitation of H_2 by slow electrons. Review of Modern Physics 1972;5(1):276—84.

[72] Rusanov VD, Fridman AA, Sholin GV. The physics of a chemically active plasma with nonequilibrium vibrational excitation of molecules. Soviet Physics Uspekhi 1981;24(6):447—74.