Control of non-thermal effect in low current arc for fuel conversion

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Abstract: Arc plasma can provide both high energetic species to induce reactions by direct collisions called non-thermal effect and high thermal environment to activate reactions by thermal activation called thermal effect. This study introduced a novel method to enhance the non-thermal effect in arc plasma. The effect of control on non-thermal effect was verified in the methane dry reforming reaction. The experimental results indicated that the increase of non-thermal effect strongly accelerated C_2H_6 selectivity whereas that of other C_2 hydrocarbons almost remained unchanged. In comparison, the increase of thermal effect accelerated reaction pathway to further produce CO, resulting in increase of CO selectivity while all C_2 hydrocarbon selectivities were reduced. The study provided experimental evidence for the controllability and the influence of non-thermal effect in arc plasma on fuel conversion for the first time.

Keywords: Low current rotating arc, non-thermal effect, direct collisions, thermal effect, thermal activation, and dry reforming of methane

1. Introduction

It has been reported that arc plasma provides both high energetic species (e.g. electrons, ions, and excited species) and also a high thermal environment [1]. Therefore, arcs can activate reactions by direct collisions between highly energetic species and gas molecules called non-thermal effect or plasma chemistry and the thermal activation called thermal effect. However, the effective time scale of non-thermal effect is short affecting mostly in the early stage of the reaction. In comparison, the effective time scale of thermal effect is much longer affecting the overall reaction process. Because of that, the final products are mostly determined by thermal effect. Therefore, distinguishing non-thermal effect in arc plasma remains challenging. This study introduced a novel method to figure out the influences of non-thermal effect in the arc plasma on methane dry reforming by controlling Argon concentration mixed with the reactant (CH_4 and CO_2).

2. Experiment setup and calculation method

The experiment was carried out in the nozzle type rotating arc reactor constructed by a conical high voltage electrode made of copper covered by a cylindrical ground made of stainless steel, Fig. 1a. The gaseous reactant (i.e. CH_4 and CO_2) was mixed with Argon. The concentration of Argon was varied from 0 to 71.5 %. The total flowrate and CH_4/CO_2 ratio were fixed at 17.5 SLPM and 1/4, respectively. The electrical power was set 260 W. The arcs were adopted by an AC plasma power having low currents of several hundreds of mA and high voltage up to 12 kV. By virtue of the nozzle, arcs were stably anchoring between the high voltage electrode tip and the nozzle, resulting in stably elongated arcs, Fig. 1b.

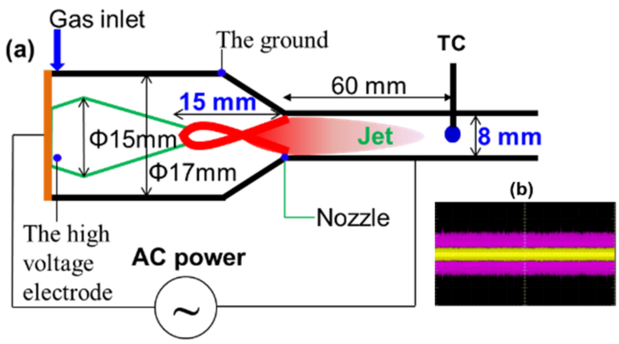

Fig. 1. (a) Experiment setup, (b) Oscillogram representing voltage and current characteristics of stably elongated arc discharge

N_2 was inserted into the downstream reactor to calculate the mass balance. The reactant conversion, product selectivity, and energy efficiency were calculated based on the equations below.

$$X_{CH_4} = \left(\frac{[C_{CH_4}]_{in} - \alpha\times[C_{CH_4}]_{out}}{[C_{CH_4}]_{in}}\right)\times 100\ (\%) \quad (1)$$

$$X_{CO_2} = \left(\frac{[C_{CO_2}]_{in} - \alpha\times[C_{CO_2}]_{out}}{[C_{CO_2}]_{in}}\right)\times 100\ (\%) \quad (2)$$

$$S_{H_2} = \left(\frac{\alpha\times[C_{H_2}]_{out}}{2\times[C_{CH_4}]_{in}\times X_{CH_4}}\right)\times 100\ (\%) \quad (3)$$

$$S_{CO} = \left(\frac{\alpha\times[C_{CO}]_{out}}{[C_{CH_4}]_{in}\times X_{CH_4} + [C_{CO_2}]_{in}\times X_{CO_2}}\right)\times 100\ (\%) \quad (4)$$

$$S_{C_2H_y} = \left(\frac{\alpha\times\left(2\times[C_{C_2H_y}]_{out}\right)}{[C_{CH_4}]_{in}\times X_{CH_4} + [C_{CO_2}]_{in}\times X_{CO_2}}\right)\times 100\ (\%) \quad (5)$$

$$\mathrm{SEI} = \frac{\text{Plasma power}}{F_{total}}\ (\mathrm{kJ/L}) \quad (6)$$

$$\mu = \frac{\alpha\times\left([C_{CO}]_{out}\times \mathrm{LHV_{CO}} + [C_{H_2}]_{out}\times \mathrm{LHV_{H_2}}\right)}{[C_{CH_4}]_{in}\times X_{CH_4}\times \mathrm{LHV_{CH4}} + \mathrm{SEI}\times\left([C_{CH_4}]_{in} + [C_{CO_2}]_{in}\right)}\ (\%) \quad (7)$$

α correction factor (gas expansion) $\frac{[C_{N_2}]_{in}}{[C_{N_2}]_{out}}$.

$[C]_{in}$ is concentration without plasma application while $[C]_{out}$ is concentration with plasma application.

F_{total} is total flowrate.

LHV is low heating value.

3. Experiment results and discussion

3.1. Method to track the increase of non-thermal effect

Previous studies have reported that major hydrocarbon produced by methane activation or dry reforming of methane in DBD plasma is C_2H_6. Selectivity of C_2H_6 is much higher than that of C_2H_4 and C_2H_2 (i.e. SEL(C_2H_6) >SEL(C_2H_4) >SEL(C_2H_2)) [2,3]. This indicated that reaction path driven by non-thermal effect mostly results in C_2H_6 among C_2 hydrocarbon species. In contrast, the major hydrocarbon produced by methane activation in arc plasma is C_2H_2. The selectivity of C_2H_6 is smaller than that of C_2H_4, and both are much smaller than that of C_2H_2 (i.e. SEL(C_2H_2) >SEL(C_2H_4) >SEL(C_2H_6) [4,5] as illustrated in Fig. 2. Based on the results as background, we can track the change of C_2H_6 selectivity to study the change of non-thermal effect in arc plasma.

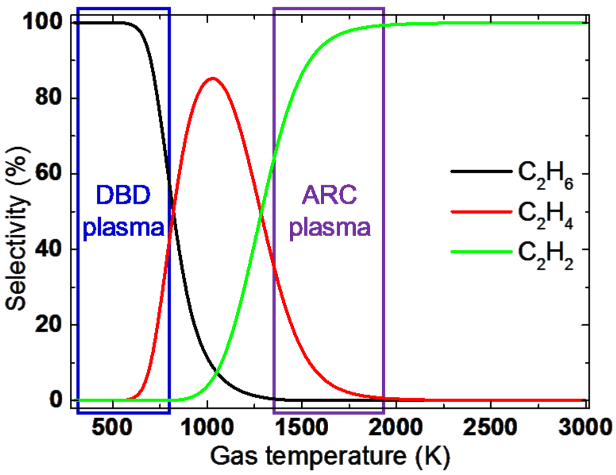

Fig. 2. Changes of C_2 hydrocarbons corresponding to different gas temperatures of methane activation without oxidant, calculated from the equilibrium condition.

3.2. Increase of Argon excitation density

Optical emission spectroscopy can verify the increases of Argon excitation and ionization concentration according to the increase of Argon concentration. For example, a clear increase of density of Argon excitation (i.e. $2p^5(^2P^0_{1/2})4s$ and $2p^5(^2P^0_{1/2})4p$) according to the increase of Argon concentration from 0% to 71.42% was found at the wavelength of 750.39 nm, Fig. 3.

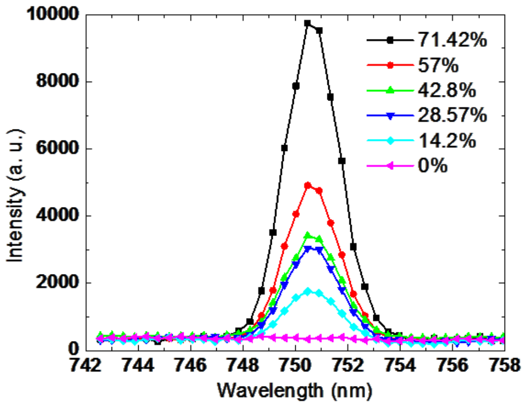

Fig. 3. Optical emission spectra of Argon excitation at different Argon inlet concentration

3.3. Product analysis

Syngas (H_2 and CO) was the main product of methane dry reforming reaction, which remained unchanged, 48% in H_2 selectivity and 90% in CO selectivity because of fixed CH_4/CO_2 ratio of 1/4. C_2H_2 was the main hydrocarbon in the product. Selectivity of C_2H_2 was about three times higher than that of C_2H_4 and six times higher than that of C_2H_6, which was consistent with results reported in the previous publications [4,5].

However, it was found that the selectivity of C_2H_6 was strongly increased by increase of Argon concentration whereas that of C_2H_4 and C_2H_2 nearly remained unchanged, Fig. 4. This trend was totally different to the previous publications. For example, at a given electric power, gas temperature can be enhanced by arc length elongation, resulting in reductions of all C_2 hydrocarbon selectivities against increase in CO selectivity [4]. The effect of increased electric power on C_2 hydrocarbons was another example. Increase of electric power enhanced both gas temperature and electron density, resulting in increases in both thermal effect and plasma chemistry (non-thermal effect). However, the increase of thermal effect was relatively bigger than that of plasma chemistry. Therefore, selectivity of all C_2 hydrocarbons slightly reduced against minor increase of CO selectivity, which was reported in previous publications [4,5]. These comparisons indicated that non-thermal effect was enhanced by increase of Argon concentration, resulting in significant increase of C_2H_6 selectivity and negligible changes of other C_2 selectivities.

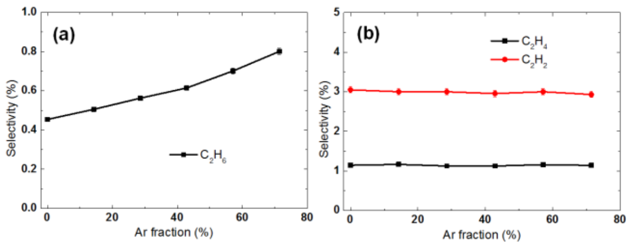

Fig. 4. (a) C_2H_6 selectivity, (b) C_2H_4 and C_2H_2 selectivity corresponding to different Argon concentrations

An analysis of the kinetics of methane decomposition with oxidant induced by plasma was needed to have a full understanding on the influence of non-thermal effect.

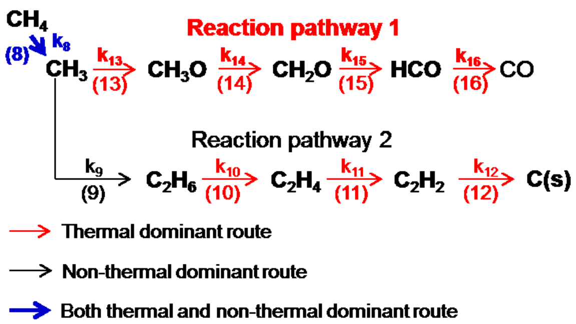

Fig. 5. Kinetics of methane decomposition with oxidant

There are two main reaction pathways for methane decomposition coupled with oxidant: Reaction pathway 1 to produce CO mainly is controlled by thermal effect, while reaction pathways 2 to produce C_2 hydrocarbons is mainly driven by non-thermal effect because reaction (9) from CH_3 radical to C_2H_6 (Eqn. (9)) triggering reaction pathway 2 is driven by non-thermal effect, Fig. 5. The reaction pathways 1 is the dominant path of methane dry reforming because syngas is the major product.

An increase of gas temperature enhanced reaction rates of all reactions except reaction (9), resulting in an increase of methane conversion to CO following reaction pathway 1 with a negligible change of reaction pathway 2 because the increase of gas temperature has insignificant influence on CH_3 conversion to C_2H_6. As a result, increase of thermal effect enhanced CO selectivity against the reduction of all C_2 selectivity reported by Dinh et al. [4].

However, the mechanism of non-thermal effect inducing reactions is completely different to that of thermal effect. Fig. 5 indicated that increase of non-thermal effect strongly enhanced reaction (8) and (9) to further produce C_2H_6, resulting in increase of C_2H_6 selectivity whereas it had negligible influence on remained reactions (i.e. reactions (10)─(16)).

Increase of non-thermal effect had also influences on other species, but these influences were much smaller than that on C_2H_6. In addition, although C_2H_6 selectivity was nearly doubled (from 0.45% up 0.8%), the actual increased amount was only 0.35 % that was too small compared the selectivity of C_2H_4, C_2H_2 or CO. Therefore, we did not detect clear changes of C_2H_4, $C_2H_{2,}$ and CO selectivity according to the increase of Argon concentration.

In addition to the increase of non-thermal effect, change of gas temperature by the increase of Argon concentration can also be a possible reason for the strong increase of C_2H_6 selectivity. A lower gas temperature can be a favorite environment to further produce C_2H_6 species than C_2H_4 and C_2H_2. However, measurement of gas temperature refused this possibility. A further Argon dilution increased gas temperature (i.e. the downstream gas temperature increased from 460^{o}C to 600^{o}C corresponding to the increase of Argon concentration from 0% to 71.5%, Fig. 6) that provided an environment for a further dehydrogenation of C_2H_6. Meanwhile, the experimental results reported a double increase of C_2H_6 selectivity. This indicated that the increase in plasma chemistry to further activate reactions was the unique reason for the significant increase of C_2H_6 selectivity corresponding to Argon concentration increase.

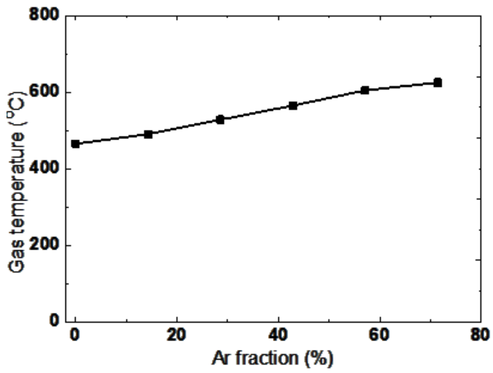

Fig. 6. The downstream gas temperature corresponding to different Argon concentrations

Take all into account, although C_2H_6 selectivity was small (from 0.45% to 0.8%) due to the inherent characteristics of dry reforming of methane in arc plasma, a nearly double increase of C_2H_6 selectivity and unchanged C_2H_4 and C_2H_2 selectivities indicated that the non-thermal effect was enhanced by addition of Argon. This provided a chemical base for controllability and influences of non-thermal effect on the fuel conversion process in arc plasma.

3.4. Conversion and energy efficiency

The experimental results showed that the conversions of reactants were enhanced by the increase of Argon concentration at a given electrical power of 260 W. This was reasonable because the actually fed mole of reactant was reduced. For example, an increase of Argon concentration from 0 % to 71.2 % corresponding to a decrease of reactant concentration from 100 % down to 28.5 % resulted in increases of conversions from 25 % to 55 % to CH_4 and 12 % to 27 % to CO_2, respectively, Fig. 7a.

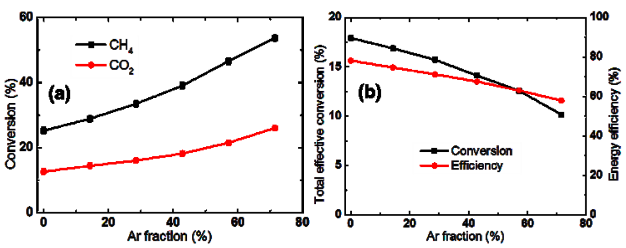

Fig. 7. (a) The conversions of reactants, (b) the total effective conversion and energy efficiency

Effective conversion can be a good parameter for absolute amount of converted reactant, which was calculated by multiplication of conversion and reactant concentration). Fig. 7b showed that the total effective conversion was reduced against the addition of Argon. Therefore, the presence of Argon reduced the absolute amount of converted reactant, lowering the efficiency of energy usage.

Further addition of Argon increased the proportion of energy used for heating up the discharge gas resulting in waste of energy for reactant conversion leading to lower conversions. Argon addition can enhance the density of excited and ionized Argon and can also increase the density of electron to activate reactants by direct collisions further. But for the effectiveness by high energy species was limited in number, in the total, the overall energy efficiency of process was reduced by further increase of Argon concentration.

3.5. Reaction mechanism by non-thermal effect

Further addition of Argon can enhance the density of vibrational, excited, and ionized Argon by following reactions, Eqns. (17)─(19), [3].

$$Ar + e \rightarrow Ar\,(Vi) + e \quad (17)$$
$$Ar + e \rightarrow Ar^* + e \qquad E_{th} = 11.55\ eV \quad (18)$$
$$Ar + e \rightarrow Ar^+ + 2e \qquad E_{th} = 15.8\ eV \quad (19)$$

Argon addition can increase the reactant conversion by increasing direct collisions (i.e. Eqns. (20)─(23)), [3]. CO_2 dissociation induced by direct collisions was expressed in Eqns. (20)─(21).

$$Ar^+ + CO_2 \rightarrow Ar^+ + CO + O \quad (20)$$
$$Ar^* + CO_2 \rightarrow Ar + CO + O \quad (21)$$

CH_4 dissociation induced by direct collisions was expressed in Eqns. (22)─(23).

$$Ar^* + CH_4 \rightarrow CH_3 + H + Ar \quad (22)$$
$$Ar^+ + CH_4 \rightarrow CH_3 + H + Ar^+ \quad (23)$$

Secondly, Argon addition can also increase electron density or electron temperature that is efficient to further dissociate reactants by reactions expressed in Eqns. (24) and (25). However, at a given electrical power, further increase of Argon concentration increased RMS-current while reducing RMS voltage (Fig. 8) that can result in higher electron density but lower electron temperature. Therefore, the increase of reactions induced by electron direct collisions was not clear.

$$e + CO_2 \rightarrow CO + O + e \quad (24)$$
$$e + CH_4 \rightarrow CH_3 + H + e \quad (25)$$

With the above discussions and the experimental results, the influence of non-thermal effect or plasma chemistry in arc plasma on the dry reforming of methane was clarified. Though the absolute amount was not large, non-thermal effect had distinguishable effect on the fuel reforming process, determining the selectivity of C_2H_6.

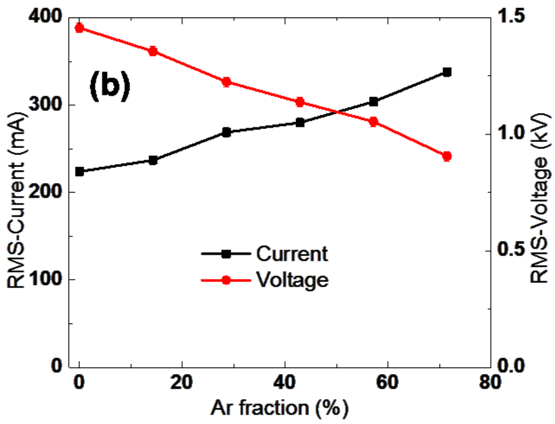

Fig. 8. The current-voltage characteristics corresponding to increase of argon concentration

4. Conclusion

This study provided experimental evidence on the existence, controllability and the influence of the non-thermal effect in the low current arc technology. Although the thermal effect can be a dominant contribution of arc plasma driving the final product, the contribution of non-thermal was undeniable. The result can be a guide to make warm plasma process where non-thermal effect is not negligible in arc process

5. References

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