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Extra pure hydrogen production through methane decomposition using nanosecond pulsed plasma and Pt–Re catalyst

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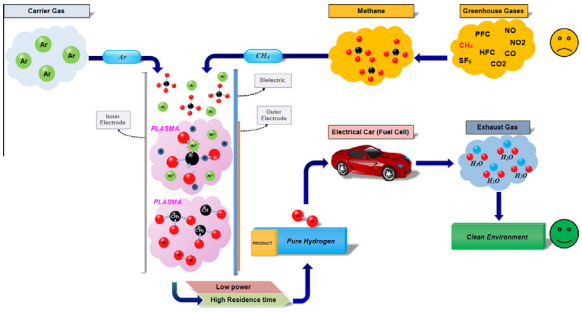
HIGHLIGHTS

- CH_4 conversion into extra pure H_2 is investigated in a pulsed DBD reactor.
- The absence of by products is highly appropriate for PEM fuel cells.
- The maximum energy efficiency of 26.08% is achieved for the plasma alone system.
- The maximum CH_4 conversion of 100% can be obtained at discharge power of 9 W.
- Performance of plasma alone, packed and catalytic plasma systems is compared.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, CH_4 conversion into H_2 via a nanosecond pulsed DBD plasma reactor has been studied experimentally. In order to maximize the energy efficiency, increase the input CH_4 flow rate and minimize the coke formation, some operating parameters including carrier gas flow, discharge power, CH_4 flow rate and concentration have been evaluated. In addition, performance of three types of plasma systems involving plasma alone, packed plasma and catalytic plasma systems is compared by filling the discharge zone with a commercial catalyst ($Pt–Re/Al_2O_3$) and glass packing particles. Extra pure H_2 production and maximum CH_4 conversion of 100% can be obtained using the packed plasma system at CH_4 flow rates of up to 20 ml/min, Ar flow rate of 50 ml/min and the average power consumption of nearly 9 W. However, the maximum energy efficiency of 26.08% is achieved for the plasma alone system at the CH_4 flow rate of 20 ml/min, Ar flow rate of 50 ml/min and the power consumption of approximately 4 W. It is interestingly understood that at the Ar flow rate of 50 ml/min and lowest discharge powers (below 10 W), not only very high energy efficiencies and CH_4 conversions are achievable, but also formation of undesirable by products including higher hydrocarbons, and formation of coke on the electrode surface can be inhibited dramatically. Moreover, in catalytic system, conversion of above 90% can be obtained even at CH_4 flow rates of up to 30 ml/min. The strong performance of the plasma system at such a high concentration of CH_4 in the feed flow (CH_4 = 30 ml/min and Ar = 50 ml/min) is of paramount importance in comparison with previous similar investigations.

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1. Introduction

Today, it is evidently noticed that public sensitivity regarding environmental issues has increased substantially in comparison with a recent past. Actually, due to the drastic exploitation and depletion of fossil fuels including oil and coal in addition to environmental issues such as global warming as a consequence of burning of these carbon-based fuels, enhancement of efficient fuel systems with least amount of noxious gas (NO_x, CO_x) emission has come into sharp focus [1–5].

CH_4 as the major constituent of the natural gas (75 wt% CH_4 [6]), which exists abundantly in reserves all around the world, has attracted noticeable attention owing to its specific properties. In fact, among all of the carbon-based fossil fuels, CH_4 consumption as a fuel produces the least amount of CO_2 [7]. In addition, CH_4 has the potential of reforming into environmentally friendly fuels such as H_2 which does not have any pollution when it is burnt except water vapor [5,8–12]. Hydrogen has long been regarded as a clean and promising alternative to fossil fuels, which can be utilized in fuel cell technology, internal combustion engines (ICE) or gas turbines [5,13–16].

UP to now, H_2 production through methane reforming has been usually accomplished by steam methane reforming (SMR), partial oxidation and auto-thermal reforming in conventional thermal reactors [17]. However, these processes not only require catalyst but also are carried out under high temperature, where rapid catalyst deactivation arises from coke deposition on the surface of the catalyst. Furthermore, these processes are usually accompanied by CO_2 emission into the environment. For example, for the steam methane reforming process, as far as it is shown in reaction (1), in order to decrease activation energy, usually catalyst is required (e.g., Ni/Al_2O_3) and the process is operated at temperature of 1100–1150 K [5,9,12,13,18–20]

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H = 206\ kJ\ mol^{-1} \tag{1}$$

Taking into account the above drawbacks of conventional H_2 production methods, finding a solution for efficient H_2 production from CH_4 with less CO_2 emission and coke deposition has attracted investigators' attention in recent decades. Direct CH_4 conversion, especially via non-thermal plasmas (NTPs), can be regarded as an attractive candidate to overcome shortcomings of conventional processes. Since in direct CH_4 pyrolysis processes, CH_4 molecules are dominantly converted to carbon and H_2, the separation processes in order to separate H_2 from other gaseous by products such as CO_2 can be eliminated, which is particularly in favor of fuel cell systems [2,18,19,21–29]. In addition, owing to non-equilibrium properties of NTPs, these reactors are appropriate for reactions in which low equilibrium conversion of the feed gas can be achieved at high temperatures [6,30–33]. In fact, the NTP is known as a promising low temperature pathway for gas phase reactions, in particular for non-oxidative conversion of CH_4 into other valuable products such as H_2 and higher hydrocarbons [6,34–40]. In NTPs, thermal activation and electron collisions are the two probable mechanisms of reactions; however, the second mechanism is dominant [41]. Consequently, the majority of the electrical energy, which is transferred to the reactor, is consumed to rise temperature of electrons instead of increasing the gas bulk temperature, which subsequently leads to generation of a huge number of reactive species, causing chemical reactions at room temperature and atmospheric pressure [10,18,42,43]. Furthermore, NTPs have the advantage of being in small scale, and also low maintenance cost in comparison with that of thermal-catalytic methods and the arc [11,44].

Among NTPs, dielectric barrier discharge (DBD) is one of the most popular plasma reactors which has been investigated exclusively for methane decomposition processes [2,5,8,9,14,38,40,45,46]. Actually, specific characteristics of DBD plasma reactors including ease of use, low cost, less possibility of arcs and sparks owing to presence of the dielectric material and its brighter horizon at industrial scales, has made this kind of NTP attractive for CH_4 reforming processes [8,9,46–51].

In dealing with such situation, among different types of power supplies (i.e., AC, DC, microwave, pulse [52]) which are applied to provide the required electrical energy in plasma reactors, using pulse power supplies can exhibit better results. According to literature, energy efficiency of the plasma chemical reactions can be modified by a factor of 4 when rectangular pulses are utilized instead of sinusoidal voltages [45]. However, this kind of power supply has not been used extensively owing to high manufacturing cost as a consequence of its difficulties [52,53].

It must be pointed out that in order to boost the performance of the pulse system, the pulse width of the power supply is of paramount importance and must be take into account. Indeed, narrower pulse width (i.e., microsecond and nanosecond scale) is in favor of breaking bonds of feed molecules rather than heating the gas bulk and surrounding materials [54,55].

This fact is evident in previous research on CH_4 decomposition via DBD plasma reactors. In this case, in 2014, Nishida et al. [5] used pulse generator with the pulse width in the microsecond scale for efficient H_2 production. However, it was stated that to enhance process efficiency, using narrower pulse width should be further developed, and it was still lacking in their investigation.

Considering the purpose of pure H_2 production from methane decomposition in addition to promoting energy efficiency of the process, previous studies have been accompanied by some lack of capabilities. For instance, formation of undesirable by products such as higher hydrocarbons may occur by the radical polymerization [56]. Moreover, low H_2 production rate as a consequence of low CH_4 conversion for high CH_4 flow rates is another drawback of the current studies, which is a challenge for further development of the process at an industrial scale. It is undoubtedly obvious from the previous investigations that reaching CH_4 conversion of higher than 90% and pure H_2 production at high CH_4 flow rates is still lacking and must be studied more exclusively.

In addition, coke formation on the inner electrode surface of the DBD plasma reactor is another serious problem in carbon-containing plasma chemical processes. In fact, existence of coke can cause a reduction in the number of discharge streamers and energetic electrons, leading to lower CH_4 conversion [52]. Moreover, coke formation leads to deterioration of the plasma discharge, thereby causing a decline in the reaction rate. Thus, it is crucial to prevent solid carbon deposition in order to make the plasma discharge long-lasting and stable [57].

It is stated that presence of steam can inhibit the coke formation distinguishably [57]; however, it is a serious challenge in methane decomposition processes yet, especially in the cases in which pure methane is fed into the reactor as the feed gas, and this is evident even in new studies on methane decomposition processes [5,8,18,45].

In our previous studies, we have focused on H_2 production through heavy hydrocarbon cracking by using a DBD plasma reactor with nanosecond pulse power supply [15,58–61]. Recently, we have focused on evaluation of operating parameters including external electrode length, applied voltage and pulse repetition frequency on H_2 production from methane decomposition via the mentioned DBD plasma reactor [62]. Now, for further enhancement of our previous work, other operating parameters involving the carrier gas (Ar) and input CH_4 flow rates, and also effects of a commercial catalyst and glass packing on plasma performance have been analyzed. Moreover, all of the previous methane decom-