Plasma-assisted production of hydrogen from hydrocarbons*

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Abstract: This paper is dedicated to the discussion of possible plasma applications for hydrogen-rich gas production from hydrocarbons. Different types of plasma, both thermal and nonequilibrium ones, are under consideration. A special attention is devoted to experimental and theoretical results on hydrocarbon conversion in nonequilibrium plasma of pulse microwave discharge. A comparison of plasma methods and conventional catalytic technology is presented as well.

INTRODUCTION

Currently, industrial demand for hydrogen and hydrogen-rich gas is continuously growing. This is related first of all with hydrogen energy concept development in energy production and transportation. Conventional catalytic technology, essentially in the case of small- and moderate-scale portable applications, has certain problems because of relatively low specific productivity, high metal capacity, and equipment size. Even thermal plasma, being very high energy density media, is giving an attractive alternative for hydrogen and syngas production. In this approach, plasma replaces catalysis and accelerates chemical reactions mainly because of high temperature effect. The advantages of plasma chemical methods are extremely high specific productivity of apparatus, low investment, and operation costs. However, relatively high electric energy consumption applies certain restrictions on possible applications of thermal plasma approach. Nonthermal plasma can accelerate chemical reactions at the low temperature as well owing to active species generation by fast electrons. If active species, generated by nonthermal plasma, are capable of promoting many cycles of chemical transformation then high specific productivity of plasma can be combined with low energy consumption of traditional catalysts. That is why this so-called plasma catalysis approach has generated permanent, strong interest in recent decades. Some hydrocarbon (HC) conversion processes and, in particular, methane decomposition into hydrogen and carbon black, are endothermic reactions, and to cover process enthalpy and to shift chemical equilibrium to hydrogen and carbon, reagents should be heated in any case. Nevertheless, the temperature level required to shift chemical equilibrium is relatively low (600–1000 K), and one can use for the process relatively low potential heat while plasma will be applied only as a catalytic agent for active species generation.

THERMAL PLASMA APPLICATION FOR HYDROGEN PRODUCTION

One of the main problems of hydrocarbon conversion processes, from a chemical point of view, is kinetic limitation. Low rates of processes (see Fig. 1) give the only possibility for application of con-
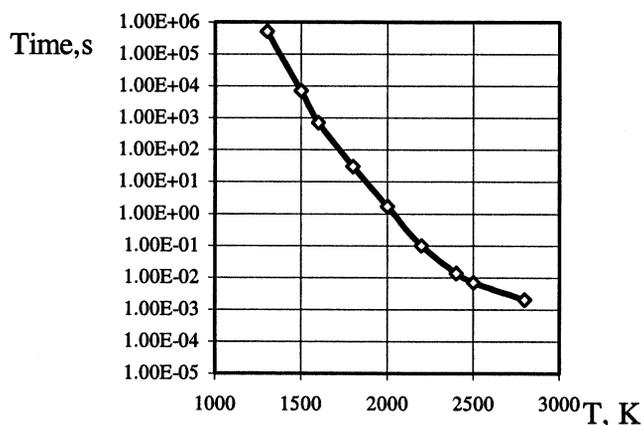

Fig. 1 Characteristic time of methane-steam conversion as a function of temperature.

ventional thermal technology: using special high-priced catalysts to attain reasonably high specific productivity and suitable equipment size. However, in any case, large equipment size and metal capacity characterize this technology. The necessity to heat the catalyst to the high working temperature leads also to the problem of "cold-start" restricting mobile applications.

Thermal plasma can essentially improve situation. Plasma is a high-density source of energy, which can cover process enthalpy and provide optimal temperature range to eliminate kinetic limitations. Hydrocarbon conversion in thermal plasma [1,2] demonstrates a high specific productivity of thermal plasma. This approach gives small installation size, providing reasonable values of energy cost of hydrogen production in comparison with catalytic technology.

Table 1 presents some types of processes that are now investigated intensively.

Table 1

Processs	ΔH, eV	Heat supply DQ, eV	H_{comb}, eV	Process temperature T,K
Pyrolysis				
$CH_4=C+2H_2$	0.9	0.39	−8	1000–1100
$C_3H_8=3C+4H_2$	1.3	0.9	−20.4	1000–1100
$C_8H_{16}=8C+8H_2$	12.5	3.9	−51	1000–1100
Steam reforming				
$C+H_2O=CO+H_2$	1.3	0.43	−3.9	900–1000
$CH_4+H_2O=CO+3H_3$	2.2	0.56	−8	1000–1100
$C_3H_8+3H_2O=3CO+7H_2$	5.4	0.79	−20.4	1000–1100
$C_8H_{16}+8H_2O=8CO+16H_2$	12.5	3.9	−51	1000–1150
$CH_3OH+H_2O=CO_2+3H_2$	0.7	0.33	−6.7	500–600
Partial oxidation				
$C+1/2\ O_2=CO$	−1.1	0.16	−3.9	
$CH_4+1/2\ O_2=CO+2H_2$	−0.2	0.34	−8	1100–1500
$C_3H_8+1.5\ O_2=3CO+4\ H_2$	−2.1	0.45	−20.4	1100–1600
$C_8H_{16}+4O_2=4CO+8H_2$	−9.9	3.9	−51	1100–1900

An optimal regime of hydrocarbon conversion is determined by two main factors: energy consumption and conversion degree (see example of methane-steam conversion in Fig. 2). Now two types of processes—steam reforming and partial oxidation—are regarded as an effective source of hydrogen. Water vapor reacts in steam-reforming process with fuel, forming carbon monoxide, dioxide, hydrogen, and water. This process is endothermic, so energy must be supplied for this reaction. Partial oxidation is fuel reaction with oxygen with formation of carbon monoxide and hydrogen. One process is exothermic and hence does not demand energy supply. One can see that each process type has some advantages and disadvantages. From one side, the steam reforming provides a high hydrogen output when from other side partial oxidation leaves essential energy quantity.
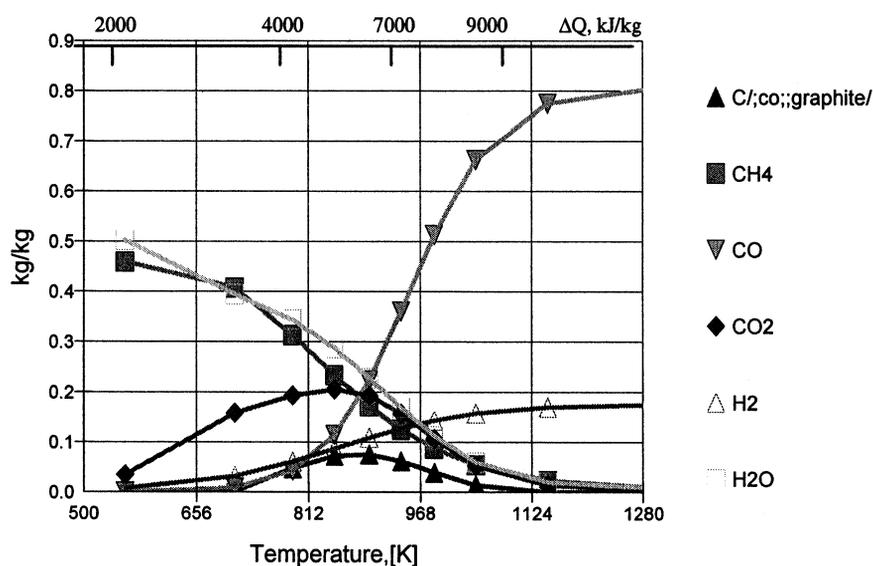

Fig. 2 Equilibrium composition of methane-steam conversion vs. process temperature and energy input (initial temperature 300 K).

Let us note that accurate control of steam and oxygen content give the possibility of autothermal reforming process organization, when exothermic oxidation supplies energy for endothermic reaction. Generally, processing schemes include a water-shift reaction. This reaction plays an important role in the process of hydrogen generation for fuel-cell application. One process optimal temperature is about 400 °C and demands chronium-promoted iron oxide catalyst.

Reported results [3] give energy cost about 13 MJ/kg H_2 (0.27 eV/mol) for catalytic partial steam oxidation, 100 MJ/kg H_2 (2.1 eV/mol) for partial steam oxidation and 130 MJ/kg H_2 (2.7 eV/mol). Recent results [1] show that energy cost can be decreased to 7 MJ/kg H_2 (0.15 eV per hydrogen molecule) in the case of methane partial oxidation process. However, this value of energy cost requires improved thermal management (heat recuperation) and is still higher with respect to that in the case of conventional catalytic process.

HYDROGEN PRODUCTION BY NONEQUILIBRIUM PLASMA

The perspectives of further energy cost reduction are related to nonequilibrium chemistry. Nonequilibrium chemistry can appears in two aspects. The first one can be attained in arc discharges via fast mixing of plasma jet and reactants to quench radicals and other active species generated by

plasma in high temperature zone. Another concept of plasma-assisted chemical processes for hydrocarbons conversion, which can lead to further energy cost reduction is the concept of nonthermal plasma. In this case, plasma is a source of active species generated at relatively low reagents temperature. The catalytic character of nonthermal plasma was pointed out in several experiments carried out in various nonequilibrium discharges: methane decomposition and higher hydrocarbons conversion in pulse and continuous microwave discharges [4], hydrocarbons conversion in Glidarc [5], and in pulse corona discharge. HC conversion in Gliding Arc shows good-looking results: 3 kWh/nm^3 syngas (2.5 eV/mol) for steam reforming, 0.11 kWh/nm^3 of syngas (0.09 eV/mol) for partial oxidation in oxygen, 0.3 kWh/nm^3 (0.25 eV/mol) for steam-oxygen conversion and 0.98 kWh/nm^3 (0.82 eV/mol) for air-steam conversion in the presence of Ni catalyst. Experimental results of methane conversion in pulse corona discharge indicate the catalytical character of plasma activity when the energy cost of hydrogen is reduced up to 1.5 eV/mol in the process of methane decomposition [6] and 0.3 eV/mol in the process of conversion of CH_4/CO_2 mixture [7].

New results of HC conversion were obtained in combine pulse microwave discharge [4]. In these experiments, HC were preheated up to relatively low temperature (about 700–1000 K) in a conventional heat exchanger at the first stage and passed after that through nonequilibrium pulse microwave discharge at the next stage. Although the temperature level required to eliminate kinetic limitations was relatively low, it was discovered that plasma gives an essential increase of hydrogen output. The small addition of microwave energy (up to 10 % of thermal energy input) results in a significant increase of conversion degree, sharp decrease of H_2 energy cost (see Table 2, Fig. 3).

Table 2 HC conversion in pulse microwave discharge.

Process	Plasma energy fraction	Conversion degree increase	H_2 plasma energy cost
Methane decomposition	5 %	7 % $\rightarrow$ 18 %	0.1 eV/mol
Ethane decomposition	5 %	19 % $\rightarrow$ 26 %	0.25 eV/mol
Ethanol decomposition	5 %	23 % $\rightarrow$ 62 %	0.1 eV/mol
Methane-steam conversion	5 %	10 % $\rightarrow$ 16 %	0.35 eV/mol
Ethanol-steam conversion	1 %	41 % $\rightarrow$ 58 %	~0.1 eV/mol
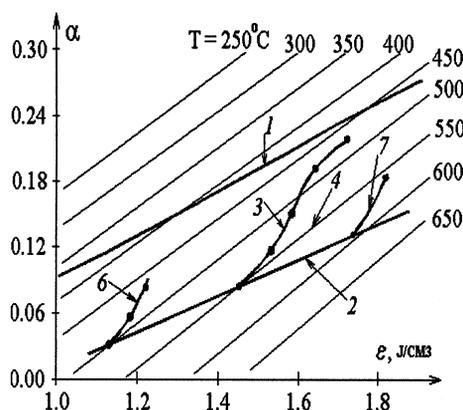
Fig. 3 Plasma catalysis process of methane conversion: α: conversion degree; ε: energy input; T: gas temperature; 1: equilibrium calculation; 2: experiment with gas heating only; 3,5,7: experiment with adding the discharge; 4: isothermal curve.

Moreover, one can see (Fig. 3) that the gas temperature decreases during chemical reaction, indicating the nonthermal character of the plasma effect.

To explain the experimental results, the following possible mechanisms of the plasma effect on CH_4 decomposition were taken into account: thermal acceleration related with local overheating onto microwave streamer channels; radical acceleration provided by possible chain reactions of methane radicals such as CH_3, H, CH_2 generated by plasma from matrix gas; autocatalytic methane decomposition on the surface of carbon black particles generated in plasma zone; ion acceleration aroused by ion-molecular chain reaction of methane decomposition.

An estimation of thermal acceleration mechanism was made supposing that complete thermal energy recuperation took place under experimental conditions, which is certainly an assessment from aloft. Figure 4 shows a dependence of methane conversion degree on plasma energy input for this case. One can see that this mechanism cannot explain experimental results obtained. The same conclusion was made about radical acceleration mechanism. Kinetic modeling of the plasma effect based on radical mechanism of CH_4 decomposition has shown that radical chain, which might be initiated by plasma via radical production, would have too small a chain length to explain the measured value of methane decomposition energy cost. Autocatalytic methane decomposition has been rejected as well because of a too-low (a discrepancy was more than several orders of magnitude) value of surface methane decomposition rate constant to explain the process characteristic time under experimental conditions. The most probable candidate to explain the catalytic effect of pulse microwave plasma on methane dissociation is supposed to be ion-molecular Winchester mechanism. This mechanism is characterized by low activation energy and high reaction rate, and is considered now as the most probable mechanism of the new phase generation in SiH_4 plasma. This mechanism can be described as: (1) initiation $CH_4 + e = CH_3^+ + H$, (2) cluster growth reactions $CH_3^+ + CH_4 = C_2H_5^+ + H_2$, $C_nH_{2n+1}^+ + CH_4 = [C_{n+1}H_{2n+5}^+]^*$, $[C_{n+1}H_{2n+5}^+]^* = C_{n+1}H_{2n+3}^+ + H_2$, and (3) chain termination $C_nH_{2n+1}^+ + e = C_nH_{2n} + H$. *Ab initio* calculations of rate parameters of the above-described process permits us to make kinetics analysis. It was shown that this mechanism might explain experimental results both from the point of view of process energetic and process kinetics. Figure 4 presents the theoretical dependence of methane conversion on plasma energy input. The reasonable agreement between experimental and theoretical results is an argument in favor of the ion-molecular mechanism.
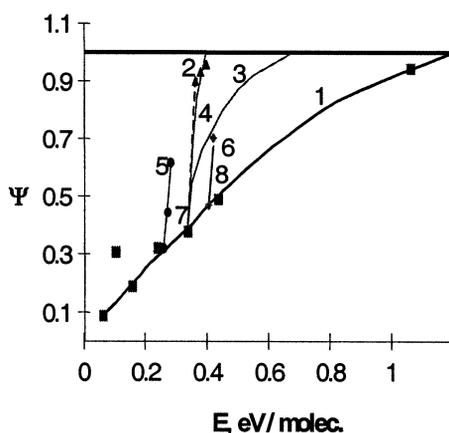

Fig. 4 The dependence of relative (with respect to equilibrium one) methane conversion degree on specific energy input. 1: experimental results in pure thermal case; 2, 5, 6: experimental results illustrating the effect of plasma catalysis. Initial gas temperature in the discharge is 550 °C, 450 °C, 650 °C respectively; 3: the upper limit for isothermal decomposition; 4, 7, 8: theoretical curves for ion-cluster chain mechanism.

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