ELSEVIER

Catalysis Today 71 (2001) 219–223

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Acetylene and hydrogen from pulsed plasma conversion of methane

Shuiliang Yao*, Akira Nakayama, Eiji Suzuki

Catalysis Science Laboratory, Research Institute of Innovative Technology for the Earth (RITE), 9-2 Kizugawadai, Kizu-cho, Soraku-gun, Kyoto 619-0292, Japan

Abstract

Recent progresses of methane conversion to acetylene and hydrogen using a high-frequency pulsed plasma (HFPP) were introduced. A comparison to conventional arc and partial oxidation processes was given. The HFPP process had the lowest methane consumption for power generation and acetylene and hydrogen productions and a relatively simple separation system for product purification, indicating that the HFPP process would have the lowest operating cost and investment. For the practical use of the HFPP process, a pulse power supply having an energy efficiency higher than 72% would be desired. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methane conversion; Acetylene; Pulsed plasma; High-frequency

1. Introduction

Over the past 20 years, the direct partial oxidation of methane to oxygenates has been remarkably focused [1–15]. However, Taylor et al. [16] pointed that product methanol should be stable over potential catalysts. We also found that even SiO_2, one of the most inert carriers, enables to oxidize methanol to formaldehyde, carbon mono and dioxides [17]. These findings suggested that the studies of the partial oxidation of methane over a catalyst have been confronted with almost insurmountable difficulties: to get a high selectivity of oxygenates with a high methane conversion over catalysts.

In such a situation, the interest of Research Institute of Innovative Technology for the Earth (RITE) in methane conversion to more valuable fuels and chemicals finally led to a study of acetylene and hydrogen productions using a plasma. The 10-year project was started in 1990 with the New Energy and Industrial Technology Development Organization (NEDO, Japan) as a financial sponsor. The plasma study began in the autumn of 1999. Table 1 summarizes RITE plasma studies, which illustrates the trajectory of our study. Most finally, a pulse power supply of a frequency up to 10 kPPS (kilo pulses per second) and a point-to-point (PTP) type of reactor were the optimum combination for acetylene and hydrogen productions.

The highly endothermic reaction of methane to acetylene (Eq. (1)) is favorable at high temperatures above 1500 K [30]. Two distinct processes of acetylene production from methane have been commercially developed [30–36]. One is the partial oxidation/combustion (POC) process developed by such as BASF and Du Pont. This process produces acetylene by burning feedstock with a supply of

---

* Corresponding author. Tel.: +81-774-75-2305;
fax: +81-774-75-2318.
E-mail address: yao@rite.or.jp (S. Yao).

0920-5861/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(01)00432-1

Table 1
RITE studies on plasma conversion of methane

	Specification	Reference
Non-plasma	Even SiO_2 can oxidize methanol	[17]
LFPP[a]	Relation of energy injection intensity to product selectivity	[18]
LFPP[a]	Methane to methanol, 47% methanol selectivity at 1.9% methane conversion	[19]
HFPP	Methane coupling and reforming with carbon dioxide to ethylene, hydrogen	[20]
HFPP	Methane to acetylene and hydrogen	[21,22]
HFPP	Methane to amorphous carbon nanoparticles	[23]
HFPP	An attemptable modeling of a single pulsed spark channel	[24]
HFPP	Analysis of the influence of pulse frequency on energy efficiency	[25]
HFPP	Development of a PTP reactor having a high energy efficiency	[26]
HFPP	Influence of the rise time of pulse voltage on methane conversion	[27]
HFPP	Economic evaluation	[28,29]

[a] Low-frequency pulsed plasma (240 PPS).

oxygen to provide the energy for the endothermic reaction. The other is an arc plasma. The arc process uses either DC or AC current, such as a typical process developed by Huels that employs a DC electric supply.

$$2CH_4 \leftrightarrow C_2H_2 + 3H_2, \qquad \Delta H^0 = 377\,\mathrm{kJ/mol},$$

$$\Delta G^0 = 311.3\,\mathrm{kJ/mol} \qquad (1)$$

In this study, we first demonstrated methane conversion using a high-frequency pulsed plasma (HFPP) process, and then compared our process to conventional arc and POC processes. The influence of the energy efficiency of the pulse power supply was discussed.

2. Introduction and evaluation of the HFPP process

The HFPP process produces a lot of pulsed spark discharge channels at a rate of one discharge channel over a pulse discharge duration (less than 200 ns) [21]. The temperature of the gas in the discharge channels is elevated to a high level within several ten nanoseconds by plasma heating and then cooled by the gas outside the discharge channels. Methane conversion to acetylene and hydrogen occurs mainly in the pulsed spark discharge channels having a high temperature enhanced by the plasma heating [24].

The HFPP process for methane conversion to acetylene and hydrogen productions is shown in Fig. 1, in which the separation system is simply added. Fresh

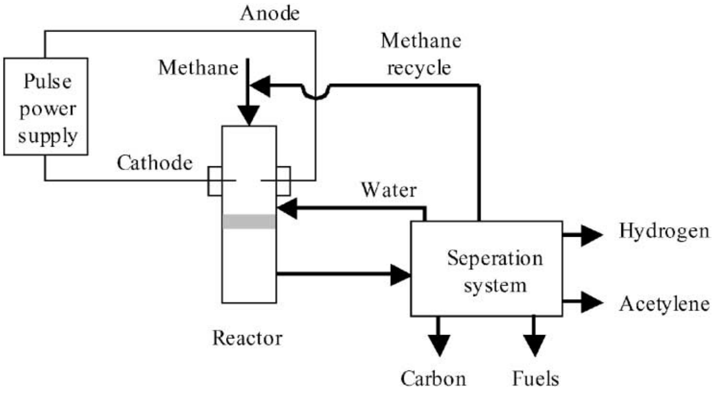

Fig. 1. A future process for acetylene and hydrogen productions using the HFPP of methane.

and recycled methane is supplied to a PTP plasma reactor. The product effluent is then quenched with water. Water can also be used to dissolve out acetylene [32]. Amorphous carbon nanoparticles can be removed before or after water quenching. The other separation and purification of reaction products can be similar with those used in the arc process. Here, we used the result that has been described in detail elsewhere [26] to demonstrate the HFPP process. As shown in Fig. 1, the outer and inner diameters and length of the PTP reactor are 15, 12, and 800 mm, respectively. Two stainless steel electrodes with sharp-pointed discharge terminals (SUS 304, $\Phi 1.5$ and 200 mm length) of 5 mm gap distance are set in the central part of the reactor. Methane (99.9995%) is supplied into the upper part of the vertically installed reactor at a flow rate of 300 ml/min at atmospheric pressure. In order to avoid an extreme increase in the temperature of the reactant gas in the reactor, about 50 min resting time is used after a 2–3 min discharge operation. As a result, methane conversion is 39.0% at 8132 PPS (energy injection rate: 32 W). Detailed figures are given in Tables 2 and 3. There, carbon and other liquid products are not included into the calculation, since they cannot be quantified right now.

For convenience of comparison, related figures of conventional arc (Huels) and POC (BASF) processes are also listed in Tables 2 and 3. On the behaviors of methane conversion conditions, the arc process uses the highest reaction temperature, since gas temperature in an arc column is about 18 000 K [30], implying that it is a hard operation condition. Furthermore, a high reaction temperature suggested that a large amount of water is required for quenching of the products from the plasma reactor. The temperature of the background gas in the PTP reactor using the HFPP process can be as low as a room temperature, although the channel temperature is possibly at a level of about 3000 K [24]. The low background temperature profits process operation and investigation.

Table 2
Comparison of acetylene production with conventional arc and POC processes

Process	Arc [34]	POC [30]	HFPP [26]
Reaction temperature (K)	∼18 000	∼2000	Bulk: ∼room, channel: ∼3000
Raw materials for 1 ton acetylene production			
Methane (ton)	2.9	4.03	1.48
Oxygen (95%) (ton)		5.2	
Total input (ton)	2.9	9.23	1.48
Conversion (%)			
Methane	82.4	91.2	39.0
Oxygen		∼100	
Product selectivity (%)			
Acetylene	51.5	35.0	83.2
Ethylene	23.7	0.65	3.78
Carbon monoxide		56.5	
Carbon	17.9	2.61	–
Others	6.9	5.89	13.0
Acetylene yield (%)	42.4	31.9	32.4
Product concentration (mol%)			
Acetylene	14.8	8.1	14.6
Hydrogen	54.9	55.3	48.2
Hydrogen/acetylene	3.7	6.8	3.3
Hydrogen/carbon monoxide		2.1	
Main final by-products	Hydrogen, carbon black, ethylene	Off-gas (hydrogen/carbon monoxide)	Hydrogen, amorphous carbon nanoparticles

Table 3
Methane demand for electric power generation and acetylene and hydrogen productions

Process	Arc [34]	POC [30]	HFPP [26]
Raw material (as methane) (ton/ton-acetylene)	2.9	4.03	1.48
Discharge electric power (kkWh/ton-acetylene)	9.8		10.35
Processing electric power (kkWh/ton-acetylene)	2.3	0.35	2.3[a]
Total electric power (kkWh/ton-acetylene)	12.1	0.35	12.65
Methane for power generation (ton/ton-acetylene[b])	1.81	0.05	1.90
Total methane consumption (ton/ton-acetylene)	4.71	4.08	3.38

[a] Assumed as the same as arc.

[b] Calculated on 0.15 kg-methane/kWh-electric power.

Using the HFPP process, acetylene selectivity is the highest and acetylene concentration in products from the reactor is at a same level as arc but higher than that using the POC process. These implied that the separation system using HFPP or arc would be simpler than the POC process.

The main by-products of HFPP, arc, and POC processes are hydrogen and amorphous carbon nanoparticles, ethylene, hydrogen, and carbon black, and carbon and synthesis gas, respectively. The HFPP process is potentially and economically favorable due to the high additional value of amorphous carbon nanoparticles that are possibly a good material for lithium batteries [37].

Arc and HFPP processes need a power generator that can be established in a gas field, in which natural gas is required. Similarly, an air separation plant must be stationed near the main POC process area. In order to evaluate the general economic, here, the methane consumption in each process is used. This methane consumption includes the amounts of methane required for electric power generation and for acetylene and hydrogen productions. The figures in Table 3 show that HFPP process holds the lowest methane consumption.

The main problem of the HFPP process is the energy efficiency of the pulse power supply. We estimated the methane consumption as a function of energy efficiency (Fig. 2). Our HFPP process has a potential if the energy efficiency of the pulse power supply is higher than 72%, which still requires many efforts to make such a pulse power supply although a pulse power supply having an energy efficiency higher than 80% is achievable [38,39].

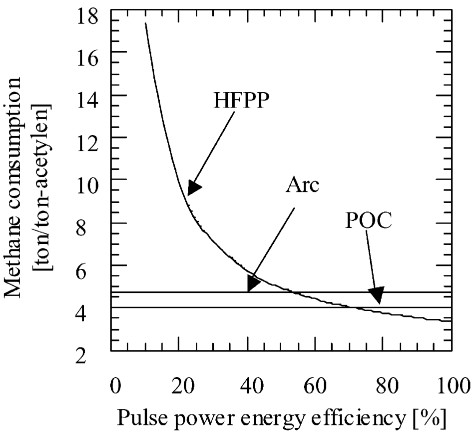

Fig. 2. Methane demand in arc [34], POC [30], and HFPP [26] processes as a function of energy efficiency of a pulse power supply.

3. Conclusion

The HFPP process has the potential for methane conversion to acetylene and hydrogen. The general figures such as methane and energy consumption are superior to the conventional arc and POC processes. It is important to develop a pulse power supply having an energy efficiency higher than 72%. Since acetylene is a raw material of engineering resins of balanced properties such as polybutylene terephthalate and a raw material of a good solvent terahydrofuran, the demand of acetylene and hydrogen as a clean energy source is expected for a good future [40].

Acknowledgements

The financial support from the New Energy and Industrial Technology Development Organization (NEDO, Japan) is gratefully acknowledged.

References

[1] T.J. Hall, J.S.J. Hargreaves, G.J. Hutchings, R.W. Joyner, S.H. Taylor, Fuel Process. Technol. 42 (1995) 151.
[2] T. Kobayashi, N. Guilhaume, J. Miki, N. Kitamura, M. Haruta, Catal. Today 32 (1996) 171.
[3] O.V. Krylov, Catal. Today 18 (1993) 209.
[4] G.E. Keller, M.M. Bhasin, J. Catal. 73 (1982) 9.
[5] J.L. Matherne, G. Culp, in: AIChE Annual Meeting, Chicago, Paper No. 59f, 1990.
[6] L.L. Lee, A.M. Aitani, Fuel Sci. Int. 9 (1991) 137.
[7] S.C. Tsang, J.B. Claridge, M.L.H. Green, Catal. Today 23 (1995) 3.
[8] R.G. Mallinson, C.M. Sliepcevich, S. Rusek, Am. Chem. Soc., Div. Fuel Chem. 32 (1987) 266.
[9] S.L. Suib, R.P. Zerger, J. Catal. 139 (1993) 383.
[10] L.M. Zhou, B. Xue, U. Kogelshatz, B. Eliasson, Energy and Fuels 12 (1998) 1191.
[11] C.G. Liu, A. Marafee, B.J. Hill, G.H. Xu, R. Mallinson, L. Lobban, Ind. Eng. Chem. Res. 35 (1996) 3295.
[12] D.W. Larkin, T.A. Caldwell, L.L. Lobban, R.G. Mallinson, Energy and Fuels 12 (4) (1998) 740.
[13] M. Okumoto, K. Takashima, S. Katsura, A. Mizuno, Therm. Sci. Eng. 7 (1999) 23.
[14] N.D. Spencer, C.J. Pereira, AIChE J. 33 (1987) 1808.
[15] J. Happel, L. Kramer, Ind. Eng. Chem. 59 (1967) 39.
[16] S.H. Taylor, J.S.J. Hargreaves, G.J. Hutchings, R.W. Joyner, in: M.M. Bhasin, D.W. Slocum (Eds.), Methane and Alkane Conversion Chemistry, Plenum Press, New York, 1995, p. 339.
[17] S.L. Yao, F. Ouyang, K.S. Tabata, E. Suzuki, Appl. Catal. A 198 (1999) 43.
[18] S.L. Yao, F. Ouyang, A. Nakayama, E. Suzuki, Trans. Mater. Res. Soc. Jpn. 25 (1) (2000) 373.
[19] S.L. Yao, T. Takemoto, F. Ouyang, A. Nakayama, E. Suzuki, A. Mizuno, M. Okumoto, Energy and Fuels 14 (2) (2000) 459.
[20] S.L. Yao, F. Ouyang, A. Nakayama, E. Suzuki, M. Okumoto, A. Mizuno, Energy and Fuels 14 (4) (2000) 910.
[21] S.L. Yao, A. Nakayama, E. Suzuki, AIChE J. 47 (2) (2001) 419.
[22] S.L. Yao, A. Nakayama, E. Suzuki, AIChE J. 47 (2) (2001) 413.
[23] S.L. Yao, E. Suzuki, A. Nakayama, Thin Solid Films 390 (2001) 165.
[24] S.L. Yao, E. Suzuki, A. Nakayama, Plasma Chem. Plasma Process., in press.
[25] S.L. Yao, E. Suzuki, A. Nakayama, in: Proceedings of the 220th ACS National Meeting on Catalysis and Plasma Technology, Washington, DC, August 20–24, 2000.
[26] S.L. Yao, E. Suzuki, N. Meng, A. Nakayama, Plasma Chem. Plasma Process., in press.
[27] S.L. Yao, E. Suzuki, N. Meng, A. Nakayama, AIChE 2001 Spring National Meeting, Topical Conference on Natural Gas Utilization, Houston, TX, April 22–26, 2001.
[28] S.L. Yao, A. Nakayama, E. Suzuki, in: Proceedings of the Fifth International Conference on Greenhouse Gas Control Technology, Australia, August 13–16, 2000.
[29] E. Suzuki, S.L. Yao, A. Nakayama, Ecol. Ind. 5 (2000) 19.
[30] T.P. Forbath, B.J. Gaffney, Petrol. Refiner 33 (1954) 160.
[31] H.W. Leutner, C.S. Stokes, Ind. Eng. Chem. 53 (5) (1961) 341.
[32] E.H. Curtis, Chem. Proc. Eng. 44 (10) (1963) 579.
[33] J. Happel, L. Kramer, Ind. Eng. Chem. 59 (1) (1967) 39.
[34] H. Gladish, Hydrocarbon Process. Petrol. Refiner 41 (6) (1962) 159.
[35] P.P.A. Tesner, Brit. Chem. Eng. 3 (1958) 72.
[36] W.B. Howard, B.H. Wood, E.J. Kaltenbacher, Chem. Eng. Prog. 57 (11) (1961) 50.
[37] NEDO Report, PR-9604, 1996.
[38] L. Civitano, NATO ASI Ser. G 34 (1993) 103.
[39] M. Rivaletto, P. Pignolet, Eur. Phys. J.: Appl. Phys. 3 (1998) 159.
[40] H. Ohno, Syokubai 42 (1) (2000) 46.