

NOVEL TECHNIQUE FOR THE PRODUCTION OF HYDROGEN USING PLASMA REACTORS

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ABSTRACT

Natural gas is one of the major sources of hydrogen via steam reforming. Alternate routes for the conversion of methane to more valuable products, such as higher hydrocarbons and hydrogen, have also drawn a lot of interest from researchers. Plasma reactors have been found to be an effective technique for the activation of methane at low temperatures. Cold plasmas can be generated by pulse streamer discharges (corona discharges) or by micro-discharges on the dielectric surface (silent discharges). The electron discharges are capable of exciting and decomposing the feed gas molecules. The corona reactor consists of dc current, a point to plane geometry, and zeolite catalyst in the reaction zone. The feed gases consist of methane, hydrogen, and oxygen. Methane conversion and hydrogen selectivities of 55% and 75%, respectively, have been found over X zeolite, and 20% and 70%, respectively, at high throughputs over Y zeolite with residence times on the order of seconds. Power consumption as low as 20 eV/converted CH₄ molecule has been achieved.

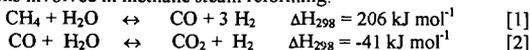
INTRODUCTION

With large increases in proven natural gas reserves worldwide, it can be expected that natural gas will play an increasingly important role in energy and chemicals supplies in the 21st century. The production of hydrogen from natural gas has also received more attention. Catalytic steam or CO₂ reforming of methane, the principal component of natural gas, is the principal process for the hydrogen production. About 50% of all hydrogen is produced from natural gas, and 40% of this is produced by steam reforming (1). A recent review by Armor (2) presents an excellent summary of the issues of hydrogen production by both conventional and potential technologies. While hydrogen production from fossil sources produce CO₂, methane has a significantly lower CO₂ impact than other fossil sources, see Table 1.

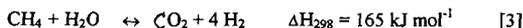
Table 1. CO₂ co-production with fossil hydrogen sources (3).

CO ₂ /H ₂	Hydrogen Source Technology
0.25	Methane steam reforming
0.31	Pentane steam reforming
0.33	Partial oxidation of methane
0.59	Partial oxidation of heavy oil
1.0	Partial oxidation of coal

Hydrogen is an important feedstock for the synthesis of ammonia, methanol, hydrochloric acid and so on. Hydrogen should become the ultimate non-polluting fuel, although it appears that it will be produced initially from fossil sources, and methane is the best source. There are two reversible reactions involved in methane steam reforming:



The overall reaction is:



Methane steam reforming is thermodynamically favorable at high temperatures (the operating temperature is usually higher than 800°C) and low pressure. An intensive energy input is required due to the high temperature operation, and the endothermic nature of the reaction requires extremely large heat fluxes. While this is the primary commercial process, the

constraints make the process relatively expensive and economically attractive only on a very large scale (a characteristic of all processes which operate at extreme temperatures due in significant part to the over-riding need to maximize energy efficiency).

To drive these reactions at much lower gas temperatures, a cold or non-equilibrium plasma can be used (4). The cold plasma is characterized by high electron temperatures and low bulk gas temperatures (as low as room temperature). Therefore, gas heating is not a significant energy sink with cold plasmas. For an electrically driven system, the energy converted to heat should be minimized since this is a relatively inefficient heating method. Additionally, the advantage of small thermal masses and small temperature gradients directly impact the economy of scale of the process. While the low temperature system may not significantly increase efficiency with increases in scale size, it may potentially operate economically at much smaller scales than for high temperature systems. We have previously reported the methane conversion to higher hydrocarbons via corona discharge (5,6) and plasma catalytic conversion (7-9). We have found that the corona discharge is an efficient and effective technique for the low gas temperature (as low as 40°C) methane conversion.

These systems exhibit non-equilibrium behavior, allowing production of substantial yields of C₂ hydrocarbons at very low temperatures. Hydrogen is a substantial co-product formed from both methane coupling and product dehydrogenation. Water is formed in only small quantities. Oxidative conditions, in both the dc system and also in ac systems, also produce substantial hydrogen yields with significant CO formation. CO₂ formation can vary, but generally CO₂ is a minor product. C₂ products may still be formed, but in lower quantities. Work to this point in time has focused on the production of hydrocarbon or oxygenate products and not on maximization of hydrogen production.

EXPERIMENTAL

The experimental apparatus will be essentially the same as has been previously described (5-9). The reactor is a quartz tube or quartz lined stainless tube. The reactor is heated (when needed) by a cylindrical furnace placed around the reactor. An Omega K-type thermocouple is attached to the outside wall of the reactor to monitor and control the gas reaction temperature. The temperature measured in this way has been calibrated against the internal temperature, and has been discussed elsewhere (5,6). When a low gas temperature is employed for the gas discharge reactions, the reactor is cooled outside by flowing room air. For the low temperature reactions (less than 100°C), the gas discharge is usually initiated at room temperature. Then the gas will be self-heated by the plasma. The gas temperature can be controlled by adjusting the flow rate of the flowing room air outside the reactor. The flow rates of feed gases methane, hydrogen, oxygen and helium are regulated by mass flow controllers (Porter Instrument Co. model 201). The gas from the reactor flows through a condenser to remove condensable liquid and is then analyzed by the chromatograph. A CARLE series 400 AGC (EG&G) was used for the detection of products. In some cases, a MKS mass spectrometer is used for on line analysis and for temperature programmed oxidation of carbon deposited on catalytic materials. Recovered liquids are analyzed off-line using a Varian GC with appropriate columns.

In the present reactor design, the plasma is generated in a gap between two stainless steel electrodes as diagrammed in Figure 1. The upper electrode, which may be a wire (generally dc) or a circular plate (generally ac) is centered axially within the reactor tube, while the lower electrode is a circular plate with holes for gas to flow through and positioned perpendicular to the reactor axis and a fixed distance below the top electrode. Catalyst beds (when used) are generally placed on the lower electrode, but placement below the lower electrode, outside of the discharge zone, is possible. The dc corona discharge is created using a high voltage power supply (Model 210-50R, Bertan Associates Inc.). The lower plate electrode is always held at a potential of zero volts (i.e., grounded). The ac power source consists of a primary AC power supply, transformer, wave generator, and an energy analyzer. An Elgar Model 251B power source supplies the primary AC power. A Wavetek Model 182A wave generator sends a sinusoidal wave signal at the selected frequency to the primary power supply. A midpoint grounded Magnetec Jefferson high voltage transformer supplies the secondary power to the reactor system. The secondary voltage is generally varied from 3.75 to 8.75 kV. An Elcontrol Microvip MK 1.2 energy analyzer measures primary power usage. The catalysts which will be used in some experiments is a NaY or NaX zeolite in a powder form (<80 mesh). The preparation and characterization of these zeolites has been discussed elsewhere (4-6). Other materials may be tried as well.

RESULTS

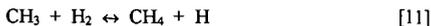
The previous investigations on oxidative conversion of methane by gas discharges in the absence (5,10) and/or presence (6-9) of heterogeneous catalysts have confirmed that cold plasma methane conversion proceeds via a free radical mechanism, where the formation of methyl radicals is the rate-controlling step. The oxygen used under those conditions will induce significant oxidation of methane and hydrocarbon products to produce carbon oxides (mostly carbon monoxide). The selectivity of higher hydrocarbons is thereby reduced. Methyl radicals also may be generated from reaction of methane with hydrogen radicals (10):



Hydrogen radicals are produced relatively easily within cold plasmas (11). One may supply hydrogen instead of oxygen for initiating higher hydrocarbon formation. It can be expected that a 100% selectivity of higher hydrocarbons will be achieved from methane and hydrogen plasma reactions except for possible carbon formation. In general, methyl radical formation is thought to be responsible for the initiation of radical reactions leading to higher hydrocarbon production. The methyl radical also can be formed by reaction of methane with other radicals (e.g., CH_3 , O, OH, and so on). In addition to the formation from radical reactions (e.g., reaction [8]), methyl radicals can be produced by electron-methane collisions (10). The hydrogen radical may also be an essential ingredient for the removal of undesired carbon deposition, which has a negative effect on gas discharges:



However, it has also been found that hydrogen appears to inhibit methane conversion in a discharge in the absence of a catalyst (12). The reason for this inhibition by hydrogen may be explained by the following reaction (5):



The inhibition was also observed during the plasma catalytic methane conversion over NaY zeolite.

The effects of hydrogen in the feed on methane conversion, Figure 2, and product selectivities, Figure 3, shows that the C_2 yield is higher than that achieved with plasma oxidative conversion of methane (7,8). The oxygen concentration is held constant at 2.5% while the ratio of methane and hydrogen is changed to achieve different partial pressures. It is also shown that the C_2 yield and methane conversion do not change significantly with the increasing hydrogen feed concentration. Most of the C_2 product is acetylene (more than 85%). Hydrogen yield is reduced and higher CO selectivity is observed with increasing hydrogen feed concentration in the presence of oxygen. This suggests that CO formation is not favored under conditions of higher hydrogen yield, and the higher hydrogen feed concentrations enhance CO formation.

Small amounts of oxygen added to the feed improve C_2 hydrocarbon production. The oxygen enrichment, Figure 4, in the gas feed reduces the C_2 selectivity but causes significant increases in methane conversion that more than offsets the loss of selectivities up to a maximum at about 2 percent oxygen. However, with very small amounts of oxygen, carbon deposition can cause deactivation of the reactions, Figure 4. The reason for the increase in the methane conversion with increasing oxygen partial pressure is that other active species are generated in addition to hydrogen radicals when oxygen is present in CH_4/H_2 plasmas. These new active species include O, oxygen anion and OH radicals. All of these strongly abstract hydrogen from methane. Hydrogen yield under the influence of added oxygen generally increases with increased oxygen in the feed.

Recent results from one experiment with a methane and oxygen (4/1) mixture and no diluent has shown that hydrogen, acetylene and CO are the major products in the dc system with catalyst. These results are shown in Figure 5.

CONCLUSIONS

Substantial hydrogen production has been observed as a by-product to methane conversion in low temperature plasmas. Various configurations and operating conditions have been used, including ac and dc power, with and without catalysts, under oxidative and non-oxidative conditions and at elevated pressures. The ability of a low temperature, and elevated pressure, process to efficiently produce hydrogen from methane holds significant promise for providing substantial increases in hydrogen utilization on shorter time frames and, perhaps most significantly, on smaller scales than may be achievable with thermal systems.

REFERENCES

1. Barbieri, G., and Di Maio, F.P., *Ind. Eng. Chem. Res.* **36**, 2121(1997).
2. Armor, J. N., *Applied Catalysis A: General*, **176**, 159(1999).
3. Scholz, W. H., *Gas Sep. Purif.*, **7**, 131 (1993).
4. Venugopalan, M., and Veprek, S., in "Topic in Current Chemistry: Plasma Chemistry IV." (Boschke, F.L. Ed.), p.1, Springer-Verlag, New York, 1983.
5. Liu, C-J., Marafee, A., Hill, B., Xu, G.-H., Mallinson, R., and Lobban, L., *Ind. Eng. Chem. Res.* **35**, 3295(1996).
6. Marafee, A., Liu, C-J., Hill, B., Xu, G-H., Mallinson, R., and Lobban, L., *Ind. Eng. Chem. Res.*, **36**, 632(1997).
7. Marafee, A., Liu, C., Xu, G., Mallinson, R. and Lobban, L., *Applied Catalysis A: General*, **164**, 21 (1997).
8. Liu, C-J, Mallinson, R. G. and L. L. Lobban, *Journal of Catalysis*, **179**, 326(1998).
9. Lobban, L., Liu, C.-J., and Mallinson, R., *Applied Catalysis A: General*, **178**, 17(1999).
10. Oumghar, A., Legrand, J.C., Diamy, A.M., and Turillon, N., *Plasma Chem. and Plasma Proc.* **15**, 87 (1995).
11. Hollahan, J.R., and Bell, A.T., "Techniques and Applications of Plasma Chemistry", John Wiley & Sons, New York, 1974.
12. Meshkova, G.I. and Eremin, E.N., *Russ. J. Phys. Chem.* **44**, 255(1970).

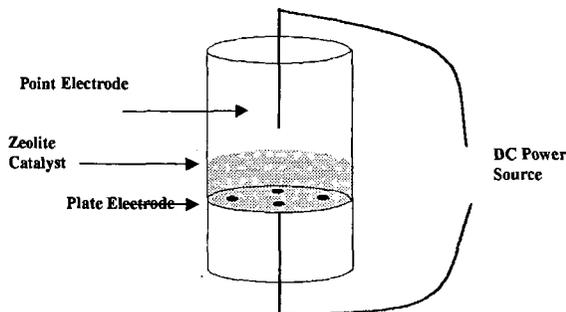


Figure 1. Point-plate dc Reactor Configuration with Catalyst Bed.

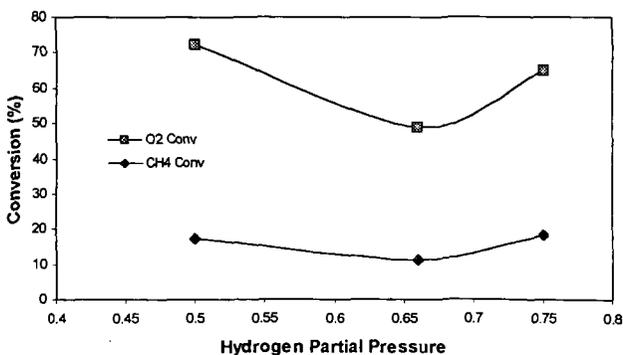


Figure 2. Methane Conversion at varying hydrogen partial pressures with constant oxygen concentration (2.5%) and balance methane, dc power over NaY Zeolite at 2 Bar.

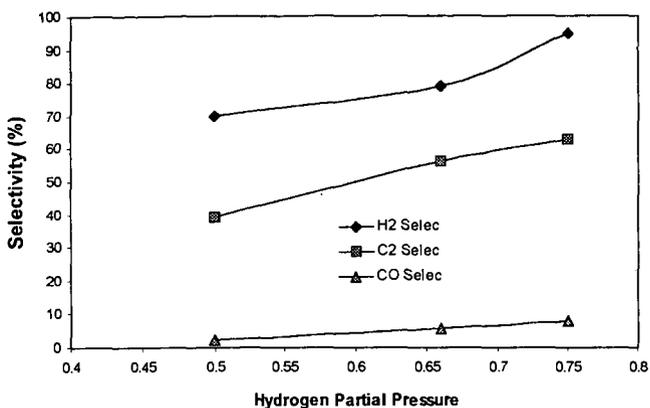


Figure 3. Product Selectivities at varying hydrogen partial pressures, dc Power over NaY Zeolite at 2 Bar.

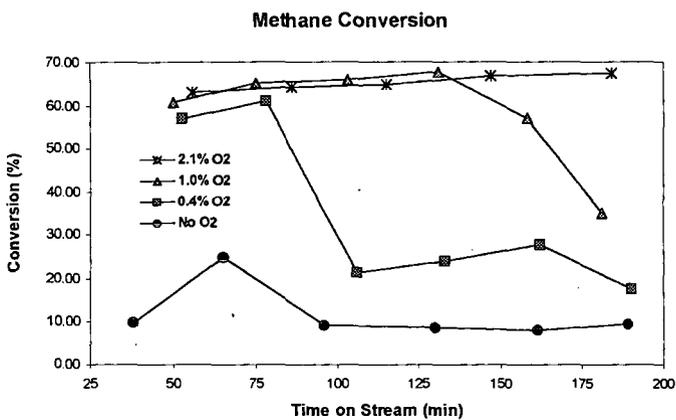


Figure 4. Methane Conversion vs. Reaction Time for Different O₂ Amounts.

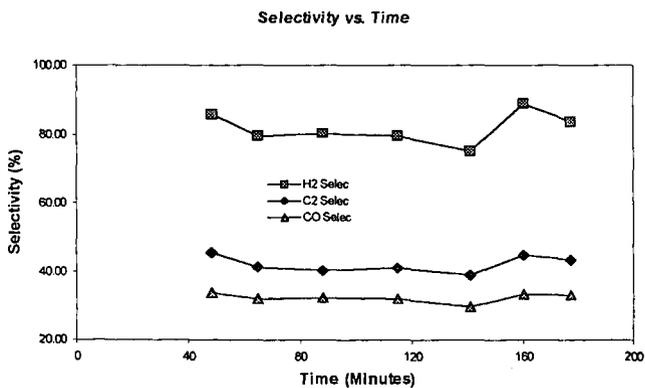


Figure 5. Product Selectivities for CH₄/O₂ = 4/1