Spring Technical Meeting
Eastern States Section of the Combustion Institute
March 8-11, 2018
Columbia, South Carolina

Plasma-Assisted Dry Methane Reforming for Syngas Production

Howard Pearlman[1], Matthew Giles[1], Chien-Hua Chen [1], Max Demydovych [1], Daniyal Kiani[2], Jonas Baltrusaitis[2]

[1]Research and Development, Advanced Cooling Technologies Inc., Lancaster, PA USA
[2]Department of Chemical and Biomolecular Engineer, Lehigh University, Bethlehem, PA USA

[*]Corresponding Author Email: howard.pearlman@1-act.com

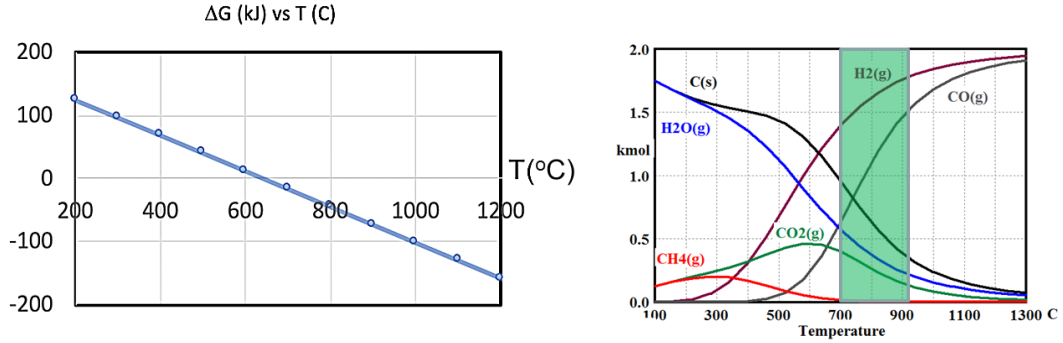
Abstract: Dry methane reforming (DMR) is a highly endothermic reaction ($CO_2+CH_4 \rightarrow 2CO+2H_2$; ΔH=247kJ/mol) that consumes two greenhouse gases (methane and carbon dioxide) and produces syngas. The syngas from DMR has an H_2/CO ratio in the range of 1-3, which is needed to produce different chemicals and liquid fuels including methanol, ethanol, acetyls (acetic acid), and formaldehyde, to name a few. This reaction is typically performed thermo-catalytically at 700-900°C with a nickel catalyst and suffers from coke formation that deactivates the catalysts. In our program, we developed a non-thermal, temperature-controlled dielectric barrier discharge (DBD) DMR reactor that can produce syngas at lower temperatures (as low as ambient temperature) and ambient pressure. In addition to its ability to operate at milder conditions, the plasma DMR reactor was found to excite CO_2 in the reactor and accelerate the rate of the reverse Boudouard reaction ($CO_2+C(s) \rightarrow 2CO$), which in turn reduces the rate of coke formation. Results have been obtained on conversion and selectivity as a function of: (1) electrical power input, (2) gap height, (3) reactor temperature, (4) dielectric material selection, and (5) nitrogen gas addition. Initial tests have also been performed using packed beds of dielectric beads and catalytic beads in the reactor volume. Conversion percentages of up to 78.1% and 89.9% were found for CO_2 and CH_4, respectively, at temperatures below 160°C using a CH_4/CO_2 ratio of 1 at the reactor inlet. These conversion values are comparable to those achieved using high temperature Ni-catalysts operating at 800°C. At present, the best energy efficiency achieved was 14.2%; promising approaches to increase the efficiency are needed and are being pursued.

Keywords: Nonthermal plasma, Syngas, Dry methane reforming

1. Introduction

Background on Traditional DMR: Dry methane reforming (DMR) involves the conversion of carbon dioxide (CO_2) and methane (CH_4) to hydrogen (H_2) and carbon monoxide (CO) (syngas). Without a catalyst, this reaction is favorable for temperatures in excess of about 700°C (Gibbs Free Energy calculation shown in Figure 1a) yet requires temperatures of 1,000-1,100°C to achieve high conversion (Figure 1b). To lower the required temperature, catalysts are used and operate in the range of 700-900°C [1,2], but are known to be susceptible to coking. This coking issue is largely attributed to the high rate of methane decomposition, forming C(s), compared to the slower rate of the reverse Boudouard reaction ($C(s) + CO_2(g) \rightarrow 2CO(g)$), which consumes the carbon. To address the issue, screening of catalysts has been a priority in the literature. Nickel and Nickel

alloys are generally used since they are less expensive than noble metals for industrial application yet suffer from coking.



(a) (b)

Figure 1: HSC thermodynamic equilibrium calculations showing (a) DMR is favorable for temperatures of about 700°C and higher where Gibbs Free Energy (ΔG) is less than zero, (b) High H_2 and CO yields are thermodynamically achieved at high temperature.

Background on Non-Thermal Plasma and Plasma-Catalytic DMR: Plasma-assisted combustion and reforming produces ionized and excited species that enable chemical pathways otherwise not available [3-5]. For dry methane reforming, plasma energy can be used to dissociate methane into a methyl radical and hydrogen atom; the activation threshold for this reaction is 4.5eV. Likewise, carbon dioxide can be dissociated into carbon monoxide and atomic oxygen, though this requires substantially more energy to perform via direct electronic excitation dissociation (11eV). As such, researchers have also considered a less energy intensive route for CO_2 splitting using stepwise vibrational excitation [5]. Catalysts have also been added to nonthermal plasma reactors with the intent to benefit from synergistic couplings between the plasma and the catalyst. It should be mentioned that nonthermal plasma with and without catalysts has been shown to produce syngas from CH_4 and CO_2. Interestingly, conversion to syngas can occur at cold temperatures (ambient to a few hundred degree C), below that for which traditional catalysts have any activity. Moreover, when nonthermal plasma is combined with catalysts, conversion and syngas yield have been shown to increase beyond that otherwise achieved with catalysts alone even accounting for any temperature increase of the catalyst due to the plasma.

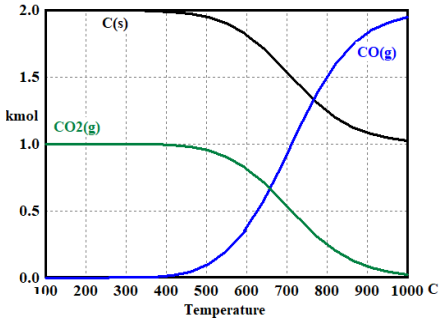


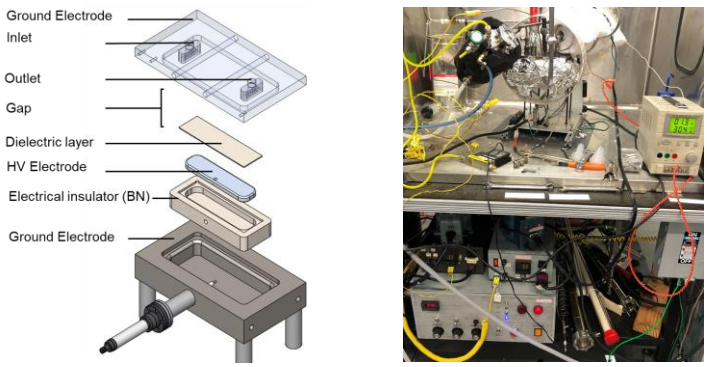
Figure 2: Thermodynamic equilibrium calculation showing the reverse Boudouard reaction requires high temperatures for high conversion.

Objective of this study: Our two objectives here are: (1) to evaluate the effect of flow and plasma properties on the conversion of CO_2 and CH_4 and the selectivity for syngas using a dielectric barrier discharge (DBD) plasma reactor and a DBD packed bed reactor containing dielectric beads or catalytic particles and (2) to evaluate whether non-thermal plasma can accelerate the rate of the

reverse Boudouard reaction (i.e., increase the rate of reaction of C(s) with CO_2 to form CO) and thus reduce the rate of coke formation in plasma DMR. The idea here is that excited states of CO_2 can enable the reverse Boudouard reaction to occur at lower temperatures than the 600-800^oC that would otherwise be required based on thermodynamic equilibrium calculations (see Figure 2). This was suggested by [6] who interestingly showed that coke formed on a conventional 12wt%Ni-Al_2O_3 catalyst at 550^oC, yet no coke was observed when a DBD plasma was applied.

2. Methods / Experimental

Two laboratory-scale DBD reactors (flat plate and cylindrical) were developed. The reactors had a high voltage electrode surrounded by a dielectric layer, a small gap (adjustable 0.3-1.1mm), and a ground electrode. Most tests were done using a flat plate design, shown schematically in Figure 3a. For this reactor, Kovar was used for the high voltage electrode since it has a low coefficient of thermal expansion. The dielectrics tested included alumina (Al_2O_3), boron nitride (BN), and aluminum nitride (AlN). Reactants were metered and delivered using mass flow controllers. The reformate was sampled using a syringe and analyzed using an SRI gas chromatograph. Species quantified include methane (CH_4), carbon dioxide (CO_2), hydrogen (H_2), carbon monoxide (CO), oxygen (O_2), and nitrogen (N_2). For generating the discharge, a Plasma Technics DAT210 high voltage inverter (providing up to 500W with a 7.5kV transformer operating at 16-17kHz) was used. The inverter was controlled using PlasmaView software from Plasma Technics. Figure 3b is a picture of the hardware.



(a) (b)

Figure 3: (a) Flat plate DBD reactor having a centrally located high voltage Kovar electrode housed in a boron nitride insulator with a flat dielectric layer adjacent to the high voltage electrode. The gap is adjustable (0.3-1.1mm) and can be filled with dielectric or catalyst particles, (b) the actual hardware setup.

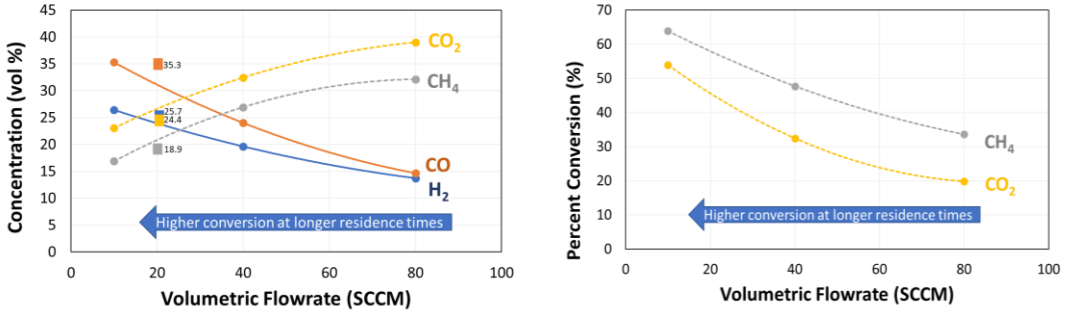
Regarding operating parameters, experiments were performed for flowrates ranging from 10sccm to 120sccm with premixed CH_4-CO_2 compositions having CH_4/CO_2 ratio ≤ 1. The pressure in all tests was atmospheric and the temperature of the reactor ranged from ambient (20^oC) to as high as 720^oC (determined by a thermocouple embedded in the ground electrode very close to the gap in which the plasma discharge occurred).

3. Results and Discussion

Results showing the effect of flow residence time, electrical power input, and gap spacing are briefly summarized here. Also, the effect of low-temperature CO_2 plasma on coke removal has also been demonstrated.

Effect of Flow Residence Time

Lower flowrates (corresponding to increased residence time) result in higher conversion of CH_4 and CO_2 (Figure 4). Representative CH_4, CO_2, H_2 and CO concentrations in the reformate are plotted as a function of volumetric flowrate in Figure 4a for the same CH_4/CO_2 ratio (=1), electrical power (nominal 100W), and gas temperatures < 100°C; in Figure 4b, the corresponding percent conversions of CH_4 and CO_2 are also plotted. As shown, the conversion increased from 33.6% to 63.9% for CH_4 as flowrate decreased from 80sccm to 10sccm. Similarly, CO_2 conversion increased from 19.8% to 53.9% over the same flowrate range. This corresponds to an approximate doubling of conversion for both reactants over the range of flowrates considered. These results can be explained by a higher probability of electron impact dissociation reactions at longer residence times, which promotes conversion of the reactants. Moreover, the ratio of the power input (which is fixed in these tests) to the volumetric flowrate increases as flowrate decreases. This means that the energy input per unit volume increases as flowrate decreases (residence time increases) and therefore higher conversions are achieved.

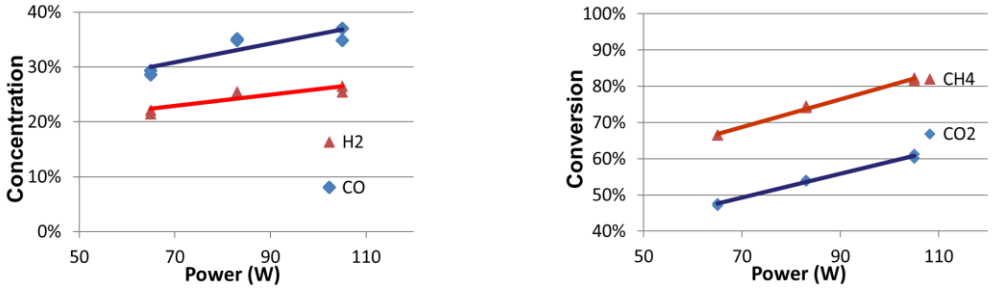


(a) (b)

Figure 4: Decreasing flowrate increases the residence time and increases CH_4 and CO_2 conversions, CH_4/CO_2=1.0, Power=90-106W, Al_2O_3 dielectric, No catalyst, 1.1mm gap (ground electrode to dielectric). Gas inlet temperature=21°C, Exit temperature=22-95°C, except square data points where T_{in}=24°C, T_{out}=500°C.

Effect of Electrical Power Input

Increasing the electrical power increased the H_2 and CO yields and CH_4 and CO_2 conversions, as shown in Figures 5a,b, for otherwise identical conditions. These trends are expected since higher power corresponds to higher energy input to the reactor, which increases the electron density and therefore increases the probability of electron impact reactions that promote DMR.



(a) (b)

Figure 5: Increasing electrical power increases the H_2 and CO yields and CH_4 and CO_2 conversions, Parameters: CH_4/CO_2 = 1, Q=10sccm, Gap = 0.37mm, Reactor temperature = 151-162°C, Al_2O_3 dielectric, No catalyst.

Effect of Gap Spacing

Reducing the gap distance increases the electrical field strength (defined as the voltage divided by the gap distance), which in turn increases the electron temperature. Higher electron temperature enhances electron impact reactions and therefore leads to higher CH_4 and CO_2 conversions. Figure 6 is a plot of power input needed to achieve nearly fixed conversions of 74.0-80.1% for CH_4 and 49.1-59.7% CO_2 and shows that when the gap was reduced from 1.17mm to 0.37mm, the energy required to maintain nearly the same conversion decreased by 28%; further reducing the gap however resulted in diminishing benefits since coke formation increased at gaps smaller than 0.37mm. This is thought to be due to the very high electron temperature in small gaps that leads to an increase in methane decomposition to carbon. This is known to be a high energy process.

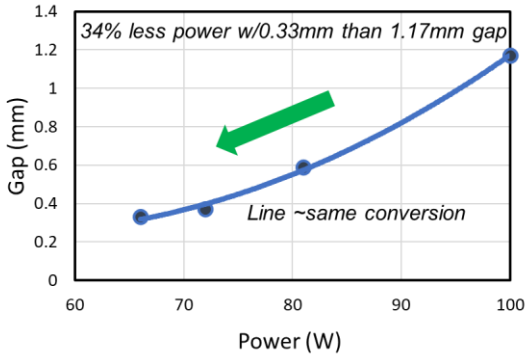
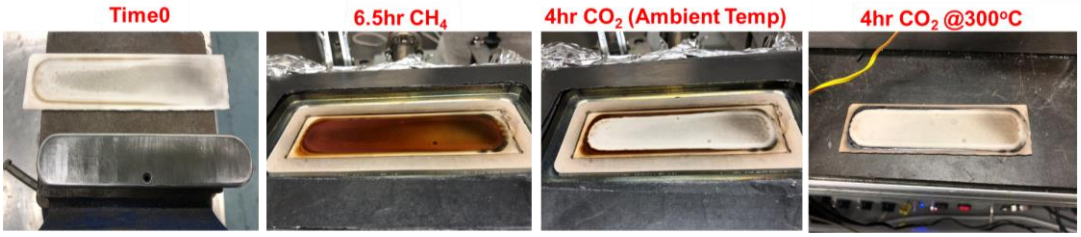


Figure 6: Decreasing the gap distance decreases the power needed to maintain nearly same conversion of CH_4 and CO_2 at otherwise identical conditions. $CH_4/CO_2=1$, $Q_{total}=10$ sccm.

Effect of CO_2 Plasma on Decoking

A major problem for dry methane reforming is formation of coke which occurs over a broad range of temperatures, as shown in the thermodynamic equilibrium calculation (Figure 1b). Coke then deactivates catalysts by limiting access to active surfaces and metal particles. Encouraged by the work of Kameshina et al. [6], we started to explore decoking with the use of a DBD CO_2 plasma. Again, the thought is that if the rate of this reaction can be increased at low temperatures with plasma, the rate of C(s) depletion can be more competitive with the rate of C(s) production from CH_4 decomposition (primary carbon formation step) and help alleviate the coking problem in DMR. Our process was to initially flow pure methane (CH_4) through the DBD reactor for a period of 6.5 hours (coking up the reactor) after which the CH_4 flow was turned off and CO_2 turned on for a period of 4 hours. Results from tests performed at ambient temperature and 300°C are shown in Figure 7 showing the coke produced by decomposition of CH_4 was effectively removed with the CO_2 plasma, even at ambient temperature.



(a) (b) (c) (d)

Figure 7: Images showing (a) the Al_2O_3 dielectric layer and high voltage electrode at the start of the test, (b) the dielectric layer after 6.5 hours of CH_4 flow (coked surface), (c) the dielectric after CO_2 plasma for 4 hours at ambient temperature and (d) with CO_2 plasma at 300°C.

Energy Efficiency of the Plasma DMR Process: The energy efficiency is important since it determines the electricity required for conversion. Defining the efficiency (η) based on DMR reaction enthalpy, the highest efficiency achieved using our DBD plasma reactor is 14.2%. Here, η is a measure of how efficiently the plasma process performs compared to the standard reaction enthalpy referenced to the specific energy input (SEI) where SEI is the plasma power input divided by the gas flowrate. SEI is important and known to be a main factor in the determining the conversion and the energy efficiency of plasma reforming. More detailed calculations will be given in the presentation.

4. Conclusions

Nonthermal plasma-based DMR offers an alternative way to produce syngas at temperatures below that for which catalysts are active and further has the potential to increase conversion and selectivity beyond that achieved with catalysts alone. In our work, we have achieved conversion percents as high as 78.1% CO_2 and 89.9% CH_4 at low temperatures (ambient to 150-160^{o}C) using a unity CH_4/CO_2 ratio reactant mixture even without the use of catalysts. In addition, the effect of the flowrate, gap, and electrical power have also been considered. The use of a packed bed of dielectric or catalytic beads in the plasma zone was also tested. Conversion percents were clearly higher with the use of packed bed. The beads serve to locally increase the electric field and associated electron temperature in the regions around the contact points between beads, which contributes to higher dissociation rates and thus higher conversion. Regarding decoking, the use of a DBD CO_2 plasma was also shown to be an effective way to remove carbon.

Acknowledgements

The authors appreciate financial support from DOE Office of Science under contract DE-SC0019664. Special thanks are also extended to our Program Manager, Sai Gollakota, at NETL.

5. References

1. Aramouni, N. A. K.; Touma, J. G., Tarboush, B. A., Zeaiter, J., Ahmad, M. N. Catalyst design for dry reforming of methane: Analysis review. Renew. Sustain. Energy Rev. 2018, 82 (2017), 2570–2585.
2. Zhu, J, Peng, X., Yao, L., Shen, J., Tong, D., Hu, C. The promoting effect of La, Mg, Co and Zn on the activity and stability of Ni/SiO_2 catalyst for CO_2 reforming of methane, International Journal of Hydrogen Energy 36 (2011) 7094–7104.
3. Mehta, P., Barboun, P., Go, D., Hicks, J., Schneider, W. Catalysts enabled by plasma activation of strong chemical bonds: A Review, ACS Energy Letters, 4 (2019) 1115-1133.
4. Eliasson, B., Liu, C.-J., Kogelschatz, U. Direct conversion of methane and carbon dioxide to higher hydrocarbons using catalytic dielectric barrier discharges with zeolites, Ind. Eng. Chem. Res. 2000, 39 (2000) 1221-1227.
5. Snoeckx, R., Bogaerts, A. Plasma Technology – A Novel Solution for CO_2 Conversion?, Chem. Soc. Rev. 46 (2017) 5805.
6. Kameshima, S., Tamura, K., Ishibashi, Y., Nozaki, T. Coking characteristics of dry methane reforming by DBD-catalyst hybrid reaction with cyclic operation, International Journal of Plasma Environmental Science and Technology 9 (1) (2015).