

## Greenhouse Gas Dry Reforming to Syn-Gas

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### Introduction

According to the EPA Landfill Methane Outreach Program [1] landfills generate about 26% of the U.S. methane emissions from landfill gas (LFG), which is typically 50% CH<sub>4</sub> and 50% CO<sub>2</sub>. Since land filling will continue to be used in the foreseeable future, it makes sense to design landfills that capture the maximum possible amount of methane for use in generating power. However, because of the low heating value of LFG, most engines need to be modified considerably and once modified, they require a consistent composition of the fuel. LFG variation leads to higher pollutant emissions, such as NO<sub>x</sub>, CO and unburned hydrocarbons (UHC) and emissions waiver are often required before LFG thermal energy projects are permitted. One solution to this issue is to reform a portion of the LFG to produce synthesis gas which can be mixed with the remaining un-processed LFG to yield a more reactive mixture to enhance the combustion performance.

To understand the operating regimes of such a reforming reactor, a series of tests were done on a Rh-containing monolith reactor. The tests focused on reacting CO<sub>2</sub> and CH<sub>4</sub> to generate synthesis gas (i.e. dry reforming). Specific issues were investigated such as carbon formation (coke) and its effect on deactivation of the catalyst along with performance variations for a range of CH<sub>4</sub> to CO<sub>2</sub> ratios and operating temperature. In addition, catalyst activity was tested and determined to be stable during the time on stream for testing. Effluent species concentrations were measured versus varying reactor temperatures from 550 – 590°C and space velocities from 7,600 – 16,000 hr<sup>-1</sup>. Reactant gas mixtures consisted of 0.08 atm CH<sub>4</sub>, CO<sub>2</sub> partial pressures from 0.08 – 0.25 atm, and a balance of argon totaling 1 atm total pressure.

### Experimental

Experiments were performed at atmosphere pressure using a quartz flow-through reactor loaded with a Rh/γAl<sub>2</sub>O<sub>3</sub> washcoated monolith (400 cpsi) obtained from BASF Catalysts (formerly Engelhard Corp). The monolith had a bulk density of 0.44 g/cm<sup>3</sup> and precious metal loading of 150 grams/ft<sup>3</sup>. The quartz tubular reactor was placed in a two-stage furnace, and the temperature was controlled via two Variac voltage transformers. K-type thermocouples were inserted at the inlet and outlet of the catalyst bed, and temperature readings were acquired with an Omega OMB-DAQ-54 data acquisition system. The mass flow rate of each inlet gas into the reactor was controlled with Aalborg GFC17 mass flow controllers, which were fed from gas cylinders of UHP CH<sub>4</sub>, CO<sub>2</sub>, and argon. The outlet flow from the catalytic reactor coupled to an on-line Agilent 3000 Micro GC instrument to analyze the species concentrations in the outlet stream.

### Results and Discussion

The investigation revealed a few interesting results in terms of rate of CO production compared to H<sub>2</sub> production at various CO<sub>2</sub> partial pressures. Figure 1 shows that the rate of H<sub>2</sub> production levels off while the CO production rate continues to increase as the CO<sub>2</sub> partial pressure increases.

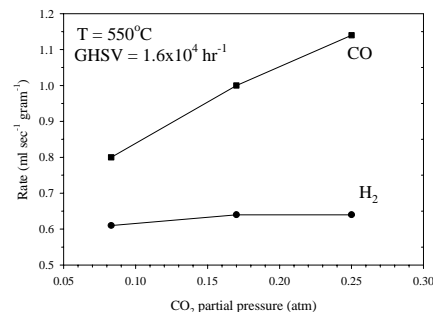


Figure 1. Rate of CO and H<sub>2</sub> production versus inlet CO<sub>2</sub> partial

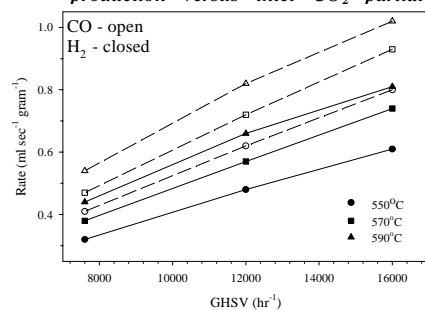


Figure 2. Rate of CO and H<sub>2</sub> production versus operating temperature and GHSV

temperatures and CO<sub>2</sub> to CH<sub>4</sub> ratios. This was confirmed by returning to a baseline condition periodically during the testing and comparing reaction rates.

### Significance

Unlike current base metal formulations, such as Ni, the Rh formulation tested had stable activity for extended time on stream and there appears to be no sign of carbon formation. Further confirmation is in progress in terms of long term deactivation studies and TGA/DTA studies to quantify if any carbon deposition is occurring. If carbon is found to be depositing, regeneration techniques will be explored. These findings highlight the fact that while increased CO<sub>2</sub> concentration in LFG may reduce H<sub>2</sub> production rates, overall reforming is still occurring, thus yielding a more reactive mixture. If hydrogen production is the objective, these results give insight into the dominant reaction paths under various conditions. If a reactive mixture is the objective, these findings suggest as long as operating temperatures are sufficiently high, significant reforming will occur via CO and WGS reactions.

### References

1 Themelis, N.J. Waste Management World, June 2006

This is likely due to the increased CO<sub>2</sub> partial pressure activating the reverse water gas shift reaction (RWGS) at the higher CO<sub>2</sub> levels. While the WGS reaction is likely always in equilibrium, it is not until the high levels of CO<sub>2</sub> in the feed that it begins to compete with the forward and reforming reaction, thus reducing the H<sub>2</sub> generation rate while enhancing the CO production rate.

A second result is the comparison of the reaction rates at three different space velocities and operating temperatures shown in Figure 2. As the space velocity is increased for a given temperature, the difference between reaction rates between CO and H<sub>2</sub> production become more pronounced. This effect is also evidenced for an increase in temperature at any given space velocity. This effect is a combination between equilibrium constraints at the low GHSV of 7,600 hr<sup>-1</sup> versus more kinetic competition at the higher GHSV of 16,000 hr<sup>-1</sup>.

During the investigation a single Rh-containing monolith was used for all testing to gain insight into potential deactivation. The results indicate the activity of the catalyst was stable over a wide range of space velocities, operating