Auto-thermal and Dry Reforming of Landfill Gas using a Rh/yAl2O3 Monolithic Catalyst

McKenzie Kohn1, Marco Castaldi1, Robert Farrauto2

1. L. Earth and Environmental Engineering (HKSM), Columbia University, New York, NY

2. BASF Catalysts LLC, Iselin, NJ

Introduction

• In 2008, 413 million tons of municipal solid waste (MSW) was generated in the U.S.1
• Of that MSW generated was landfilled1

Major LFG constituents

Approximate % volume

CH4 45-55
CO2 30-40
N2 10-15
O2 0-5
H2 0-2

Landfill gas (LFG) is produced by the anaerobic decomposition of biomass in landfills.

• LFG has varying composition that can lead to low flame stability and more combustion emissions.
• FG continues to be generated for 50 years after a landfill closes.
• CH2 has 25 times the GWP of CO2.

Dry Reforming

Dry reforming is a large form of oil steam to combustion some of the fuel, producing heat in situ to drive concurrent endothermic reactions.

Relevant reactions:

- Methane combustion

O2 + CH4 → H2O + CO2

ΔH = -802 kJ/mole

- Methane partial oxidation

O2 + CH4 → CO + H2

ΔH = 61 kJ/mole

- Dry Reforming

H2O + CO → H2 + CO2

ΔH = 41 kJ/mole

- Water-Gas Shift

H2O + CO → H2 + CO2

ΔH = -41 kJ/mole

Dry reforming of a 1:1 CH4/CO2 mixture at 5000 h(2) GHSV:

• As the monolith temperature increases, CH2 and CO2 are more fully converted to CO and H2
• Conversion reaches equilibrium

Possible surface carbon formation mechanisms:

- CO disproportionation:

2CO → CO2 + CO

ΔH = 75 kJ/mole

• Carbon formation occurs when there are fewer oxidizing species.
• Carbon deposition during dry reforming of high CH2 LFG mixtures is possible
• Carbon deposition during ATR is less likely

Auto-thermal Reforming

Auto-thermal operation:

• The reactor operated auto-thermally without heat input from an external heat source for 17 hours.
• CH2 ignition was initiated by furnace heating, and then the furnace was turned off.

The monolith inlet temperature stabilized at 535°C and outlet temperature at 397°C.

The methane conversion remained stable at ~34%.

Table 1: Mole fractions of reactant gases for each experiment type

<table>
<thead>
<tr>
<th>Experiment Type</th>
<th>Dry Reforming</th>
<th>Auto-thermal Reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4 (0.10)</td>
<td>CH4 (0.10)</td>
<td>CH4 (0.10)</td>
</tr>
<tr>
<td>CH4 (0.15)</td>
<td>CH4 (0.15)</td>
<td>CH4 (0.15)</td>
</tr>
<tr>
<td>CH4 (0.20)</td>
<td>CH4 (0.20)</td>
<td>CH4 (0.20)</td>
</tr>
<tr>
<td>CH4 (0.25)</td>
<td>CH4 (0.25)</td>
<td>CH4 (0.25)</td>
</tr>
</tbody>
</table>

Figure 1: Experimental setup

Figure 2: Monolithic catalyst

Figure 3: Dry reforming of a 1:1 CH4/CO2 mixture at 5000 h(2) GHSV

Figure 4: Thermodynamic carbon formation regime at 450°C and atmospheric pressure

• Carbon formation occurs when there are fewer oxidizing species.
• Carbon deposition during dry reforming of high CH2 LFG mixtures is possible
• Carbon deposition during ATR is less likely

Figure 5: ATR: Introduction of small amounts of an oxidant into fuel stream to combat some of the fuel, producing heat in situ to drive concurrent endothermic reactions.

Figure 6: ATR experiment with an input mole ratio of CH4:CO2 = 1:0.46

Figure 7: Effect of monolith outlet temperature on H2/CO ratio and syngas production for 1:1 CH4/CO2 ratios

• Various H2/CO ratios achieved as a function of the monolith temperature
• Higher H2/CO ratios are achieved with ATR, but less syngas production than DR at high temperatures

Figure 8: Auto-thermal operation

• The Rh/yAl2O3 monolithic catalyst is a viable catalyst for dry reforming LFG mixtures with equal amounts of CH4 and CO2.
• Deactivation due to carbon formation is more likely for dry reforming than auto-thermal reforming.
• Sustained auto-thermal reforming was demonstrated on a laboratory scale.
• The H2/CO ratio of the syngas can be tuned as a function of the monolith temperature.

Conclusions

References


Acknowledgements

Special thank you to BASF and Columbia University for their generous support of this research.