Auto-thermal and Dry Reforming of Landfill Gas using a Rh/γAl_2O_3 Monolithic Catalyst

McKenzie Kohn[1], Marco Castaldi*[1], Robert Farrauto[2]

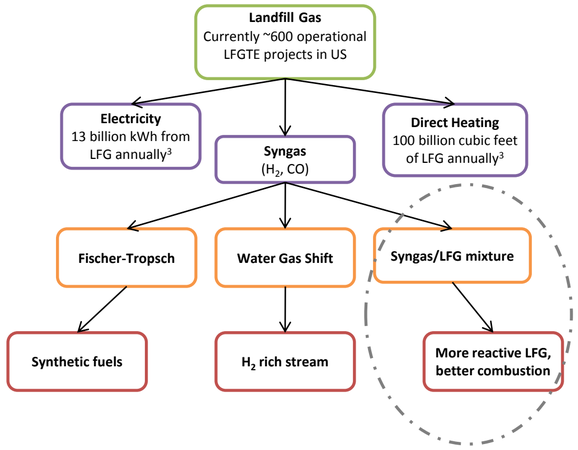
1. Earth and Environmental Engineering (HKSM), Columbia University, New York, NY 2. BASF Catalysts LLC, Iselin, NJ

Introduction

•In 2008, 413 million tons of municipal solid waste (MSW) was generated in the U.S.[1]
•64.5% of that MSW generated was landfilled[1]

Major LFG constituents	Approximate % volume
CH_4	45-55
CO_2	30-40
N_2	10-15
O_2	0-5
H_2	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
•LFG continues to be generated for 50 years after a landfill closes
•CH_4 has 25 times the GWP of CO_2[2]



Experimental Methods

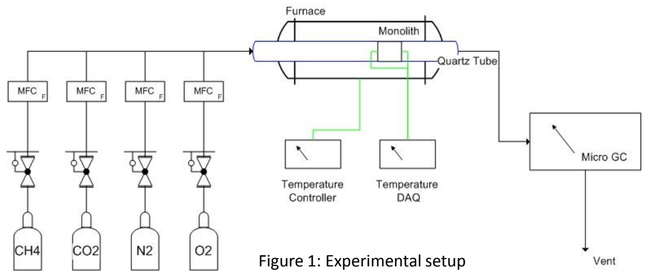


Figure 1: Experimental setup

Catalyst: 4% Rh/γ-Al_2O_3 wash coated cordierite monolith (400 cpsi)
Reactor Conditions: 8000 hr^{-1} GHSV, 1" quartz flow-through reactor
DR aging: 1.4:1 CH_4:CO_2 ratio mixture at 8000 hr^{-1} GHSV and 700°C for 24 hours
ATR: To determine the amount of O_2 needed for ATR, it was assumed that primarily methane combustion and dry reforming would occur, giving:

$1.3CH_4 + CO_2 + 0.6O_2 \rightarrow 2CO + 2H_2 + 0.3CO_2 + 0.6H_2O$
ΔH=0 kJ/mole

For a O_2:CH_4 ratio=0.46
• Because LFG can vary in composition from a 1:1 to 1.4:1 CH_4:CO_2 ratio, both of these extremes were tested

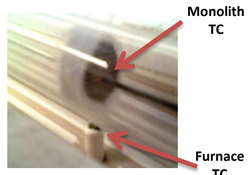


Figure 2: Monolithic catalyst

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

Experiment Type	Dry Reforming	Auto-thermal Reforming
1:1 CH_4:CO_2	8.3% CH_4, 8.3% CO_2, 83% N_2	8% CH_4, 8% CO_2, 83% N_2, 3.7% O_2 (Φ=4.3)
1.4:1 CH_4:CO_2	51% CH_4, 35% CO_2, 14% N_2	41% CH_4, 28% CO_2, 11% N_2, 19% O_2 (Φ=4.3)

Dry Reforming

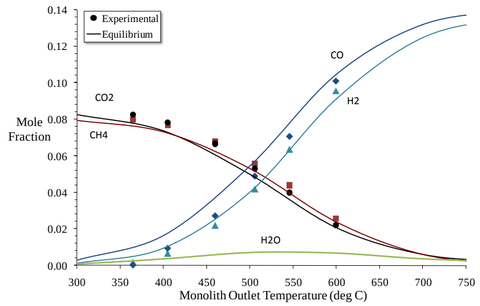


Figure 3: Dry reforming of a 1:1 CH_4:CO_2 mixture at 5000 hr^{-1} GHSV

•As the monolith temperature increases, CH_4 and CO_2 are more fully converted to CO and H2

•Conversion reaches equilibrium

Simplified dry reforming mechanism[4,5]
Stepwise dehydrogenation of CH_4: $CH_4 \rightarrow 2H_2 + C$
Oxidation of surface C: $O_2 + 2C \rightarrow 2CO$
•Therefore, the ability of the catalyst to capture and store oxygenated species is very important for catalyst activity

Possible surface carbon formation mechanisms

CO disproportionation:	$2CO \rightarrow CO_2 + C$	ΔH=-172 kJ/mole
CO reduction:	$CO + H_2 \rightarrow H_2O + C$	ΔH=-131 kJ/mole
CH_4 decomposition:	$CH_4 \rightarrow 2H_2 + C$	ΔH=75 kJ/mole

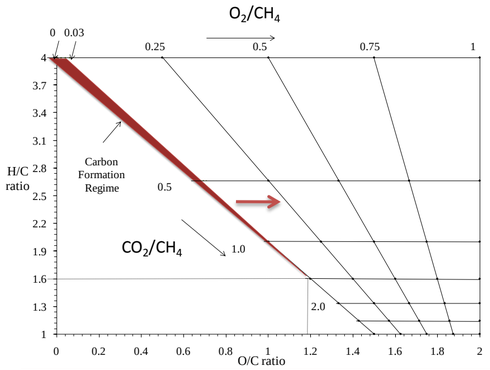


Figure 4: Thermodynamic carbon formation regime at 450°C and atmospheric pressure

•Carbon formation occurs when there are fewer oxidizing species
•Carbon deposition during dry reforming of high CH4 LFG mixtures is possible
•Carbon deposition during ATR is less likely

Auto-thermal Reforming

ATR: Introduction of small amounts of an oxidant into fuel stream to combust some of the fuel, producing heat in situ to drive concurrent endothermic reactions
Relevant reactions:

Methane Combustion	$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$	ΔH=-802 kJ/mole
Methane Partial Oxidation	$CH_4 + ½O_2 \rightarrow 2H_2 + CO$	ΔH=-36 kJ/mole
Dry Reforming	$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	ΔH=247 kJ/mole
Steam Reforming	$CH_4 + H_2O \rightarrow 3H_2 + CO$	ΔH=206 kJ/mole
Water-Gas Shift	$H_2O + CO \rightarrow CO_2 + H_2$	ΔH=-42 kJ/mole

ATR $CH_4 + CO_2 + O_2 \rightarrow H_2, CO, H_2O, CO_2$ **ΔH=0 kJ/mole**

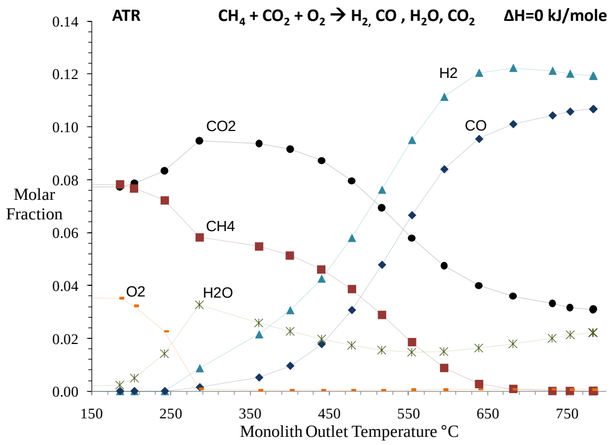
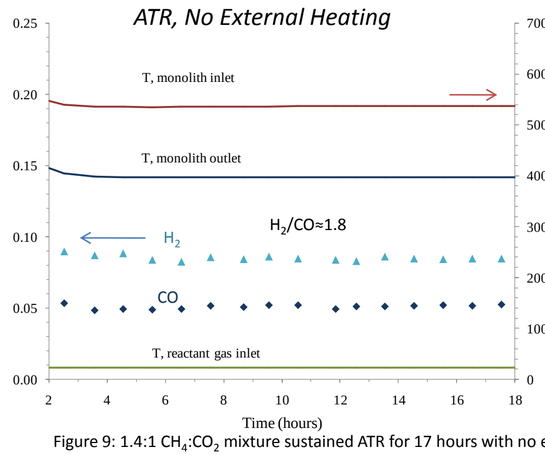


Figure 6: ATR experiment with an input mole ratio of 1:1:0.46 CH_4:CO_2:O_2

Auto-thermal operation



•The reactor operated auto-thermally **without heat input from an external heat source** for 17 hours

•CH_4 ignition was initiated by furnace heating, and then the furnace was turned off.

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

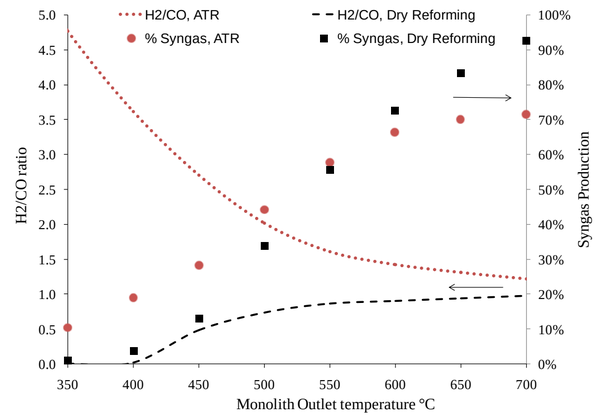
•Methane conversion remained stable at ~34%

Figure 9: 1.4:1 CH_4:CO_2 mixture sustained ATR for 17 hours with no external heating

Figure 7: Effect of monolith outlet temperature on H_2:CO ratio and syngas production for 1:1 CH_4:CO_2 ratios

•Various H_2:CO ratios achieved as a function of the monolith temperature

•Higher H_2/CO ratios are achieved with ATR, but less syngas production than DR at high temperatures



Conclusions

•The Rh/γ-Al_2O_3 monolithic catalyst is a viable catalyst for dry reforming LFG mixtures with equal amounts of CH_4 and CO_2.

•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 H_2/CO ratio of the syngas can be tuned as a function of the monolith temperature.

References

1. Arsova, Ljupka, van Haaren, Rob, Goldstein, Nora, Kaufman, Scott M. and Themelis, Nickolas J. "The State of Garbage in America." BioCycle Vol 49 No 12(2008) 22
2. IPCC, 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment. Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp.
3. Environmental Protection Agency, Landfill Methane Outreach Program, May 2010
4. Rostrup-Nielsen, J.R. "Production of synthesis gas." Catalysis Today. 18(1993):305-324.
5. Wei, Junmei, Enrique Iglesia. "Isotopic and kinetic assessment of the mechanism of reactions of CH_4 with CO_2 or H_2O to form synthesis gas and carbon on nickel catalysts." Journal of Catalysis. 224(2004): 370-383.

Acknowledgements

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