

# Auto-thermal Reforming of Landfill Gas for Synthesis Gas Generation

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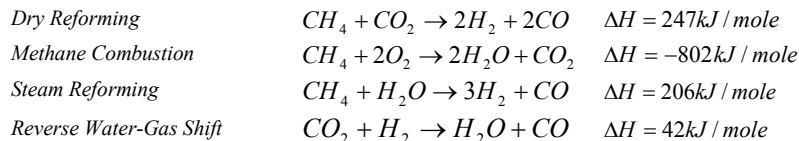
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## Introduction

The demand for clean energy is becoming increasingly pronounced. Many projects are being developed that utilize energy sources that have multiple benefits, such as carbon neutral and conversion of waste to useful products. Landfill gas (LFG) (primarily composed of CH<sub>4</sub>, CO<sub>2</sub>) has those characteristics and is more aggressively being pursued as a distributed fuel source. LFG is produced by the anaerobic digestion of biomass in landfills at a rate of seven trillion m<sup>3</sup>/year<sup>1</sup>, and has an energy content of approximately 17,800 BTU/m<sup>3</sup>. There are currently 450 LFG energy conversion projects that directly generate power<sup>2</sup>, with more being considered to produce liquid fuels. Yet, due to the low heating value and inconsistent composition, the fuel has flame stability problems and when combusted can produce more emissions, such as NO<sub>x</sub>, CO, and unburned hydrocarbons compared to high quality fuels. In addition, the variable composition makes it difficult to develop a process that yields consistent fuels. One solution is to catalytically reform the LFG to syngas to produce more robust combustion or a more consistent feedstock for liquid fuel production.

Dry reforming is a very endothermic reaction and has a high propensity for coke production. This research investigates the viability of a Rh/γ-Al<sub>2</sub>O<sub>3</sub> catalyst to reform LFG, and explores auto-thermal reforming (ATR) as a way to eliminate the need for external heat transfer by generating it internally in a monolithic reactor. ATR is the process of combusting some fuel with air or O<sub>2</sub> to provide heat for concurrent endothermic reforming reactions. The following reactions are relevant in this research:



## Materials and Methods

Experiments were performed at atmospheric pressure using a quartz flow-through reactor and a Rh/γ-Al<sub>2</sub>O<sub>3</sub> washcoated cordierite monolith (400 cpsi) obtained from BASF Catalysts. The monolith had a bulk density of 0.44 g/cm<sup>3</sup> and precious metal loading of 1.2 g/in<sup>3</sup>. A two-stage furnace was controlled with Omega temperature controllers. K-type thermocouples were inserted into a channel of the monolith and the furnace. Temperature readings were acquired with an Omega OMB-DAQ-55 data acquisition system. The mass flow rate of each inlet gas into the reactor was controlled with Aalborg GFC17 mass flow controllers that were fed from gas cylinders of UHP CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub> and Zero grade O<sub>2</sub>. The outlet flow from the catalytic reactor was coupled to an on-line Agilent QUAD Micro GC instrument to analyze the species concentrations in the outlet stream.

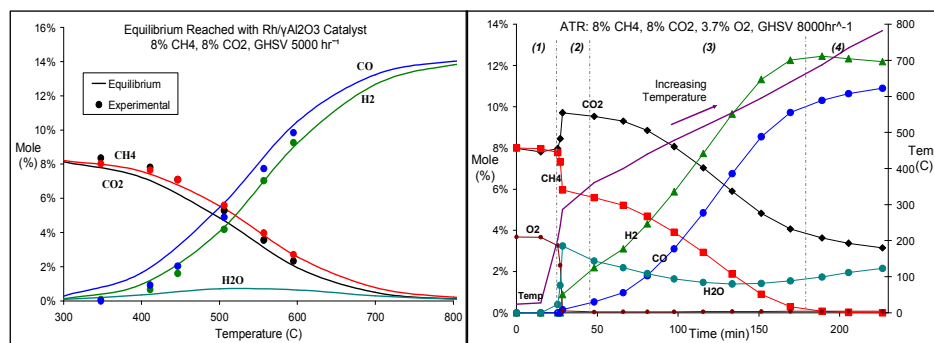


Figure 1: Dry reforming at equilibrium

Figure 2: ATR reaction regions

## Results and Discussion

The Rh/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was effective in promoting equilibrium conversion of CH<sub>4</sub> and CO<sub>2</sub> to H<sub>2</sub> and CO while resisting coke deposition, as seen in figure 1. As shown in figure 2, with ATR, the CH<sub>4</sub> is fully consumed and as temperature increases, H<sub>2</sub>/CO ratio decreases. Region 1 in figure 2 shows the rapid combustion of CH<sub>4</sub> and O<sub>2</sub>, in which CO<sub>2</sub> and H<sub>2</sub>O are produced. Also in this region, the monolith temperature rapidly increases to 75°C above the inlet gas temperature (furnace temperature). Immediately following the combustion, higher temperatures and the presence of water generated from the reaction allow for steam reforming, producing H<sub>2</sub>/CO ratios of approximately 3. As the furnace temperature is further increased, in region 3, CO<sub>2</sub> and CH<sub>4</sub> are consumed at approximately 1:1 ratios, and the H<sub>2</sub>/CO ratio decreases to 1.2, characteristic of dry reforming. In region 4, as temperature is further increased, reverse water gas shift occurs, consuming H<sub>2</sub> and CO<sub>2</sub>, decreasing the H<sub>2</sub>/CO ratio further to 1.1.

This understanding of the ATR reaction sequence has been extended to undiluted LFG mixes composed of approximately 1.5:1 CH<sub>4</sub>:CO<sub>2</sub> ratios. Reforming LFG without employing the ATR concept produces H<sub>2</sub>/CO ratios around 0.7 and does not fully utilize all of the CH<sub>4</sub> present because the reactions are limited by sub-stoichiometric amounts of CO<sub>2</sub>. ATR results in approximately 58% methane conversion at 575°C, compared to 22% in dry reforming at the same temperature. Auto-thermal reforming of LFG provides a H<sub>2</sub>/CO ratio from 1-3, depending on the temperature and time of O<sub>2</sub> introduction into the stream, making it a desirable technology for chemical or fuel synthesis.

## Significance

This research presents a viable catalyst and process for utilizing LFG cleanly and more efficiently using a precious metal monolith supported catalyst, for a variety of different applications such as synthesis gas for fuel cells, electricity, direct heating, or Fischer Tropsch gas to liquids technology without coke formation. The ATR process requires O<sub>2</sub> or air, and results in lower energy input by the user, a cleaner burning fuel, and full conversion of CH<sub>4</sub> and CO<sub>2</sub>, known greenhouse gases.

## References

1. Themelis, N. and Ulloa, P. *Renewable Energy* 32(2007):1243-1257
2. U.S. Environmental Protection Agency Landfill Methane Outreach Program. An Overview of Landfill Gas Energy in the United States (2008)