Auto-thermal and dry reforming of landfill gas over a Rh/γAl2O3 monolith catalyst

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1. Introduction

It is estimated that of the 413 million tons of municipal solid waste (MSW) generated per year in the United States, 64.5% is landfilled [1]. The biomass that makes up 67% of that municipal solid waste anaerobically decomposes in landfills to CH₄ and CO₂. A characteristic landfill gas (LFG) is composed of 45–55% CH₄, 30–40% CO₂, 10–15% N₂, 0–5% O₂, and other trace compounds, but the composition varies depending on the type of waste and the age of the landfill. Approximately 50–100 Nm³ of methane is generated per ton of MSW landfilled per year, and continues to be generated for at least 50 years after a landfill closes. Currently less than 10% of this is captured and used for energy [2]. This is likely to change as the demand for energy increases making complete and efficient utilization of LFG more important.

As of 2008 there were 565 LFG to energy conversion projects for both CH₄ conversion to H₂ and CO for both CH₄:CO₂ ratios without oxygen, but the catalyst has shown the ability to be regenerated in air. Auto-thermal tests, with and without external heat input, operating at an equivalence ratio of 4.3 (O₂:CH₄ = 0.46) and maintaining the CH₄:CO₂ ratio of either 1:1 or 1.4:1, did not show signs of carbon formation or deactivation. ATR experiments resulted in H₂:CO ratios between 1.0 and 2.0 that can be tuned depending on the monolith temperature, beneficial in the case of downstream Fischer–Tropsch processes. For the auto-thermal experiments, theoretical reaction extents were calculated based on experimental data and showed two primary regimes in catalyst operation: a CH₄ combustion and partial oxidation regime, and reforming and water–gas shift regime.

**Keywords:**
Auto-thermal reforming
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**A B S T R A C T**

Auto-thermal and dry reforming of methane and carbon dioxide mixtures was investigated experimentally at temperatures between 300 °C and 800 °C at atmospheric pressures using a Rh/γAl₂O₃ monolith catalyst. CH₄:CO₂ ratios of 1:1 and 1.4:1 were tested. The Rh catalyst reached equilibrium conversions of CH₄ and CO₂ to H₂ and CO for both CH₄:CO₂ ratios. Equilibrium analysis shows that carbon formation is likely for dry reforming but not for auto-thermal reforming. Experimentally, carbon formation was seen after long-term exposure to 1.4:1 CH₄:CO₂ ratios without oxygen, but the catalyst has shown the ability to be regenerated in air. Auto-thermal tests, with and without external heat input, operating at an equivalence ratio of 4.3 (O₂:CH₄ = 0.46) and maintaining the CH₄:CO₂ ratio of either 1:1 or 1.4:1, did not show signs of carbon formation or deactivation. ATR experiments resulted in H₂:CO ratios between 1.0 and 2.0 that can be tuned depending on the monolith temperature, beneficial in the case of downstream Fischer–Tropsch processes. For the auto-thermal experiments, theoretical reaction extents were calculated based on experimental data and showed two primary regimes in catalyst operation: a CH₄ combustion and partial oxidation regime, and reforming and water–gas shift regime.