

Towards conversion of landfill gas to high-value liquid hydrocarbons in a combined reforming-FTS process

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Introduction

Landfill gas (LFG) is a potential environmental contaminant due to the high methane concentrations in this biogas. Municipal solid waste facilities currently either flare (lose energy content) or convert to compressed natural gas or generate electricity. In this project, as shown in Figure 1, we propose the two-step conversion of LFG to middle distillate products. Steam is added to the LFG to aid in boosting the H₂:CO ratio from typically 1:1 ratio from dry reforming to the 2:1 ratio needed for CO hydrogenation. Our preliminary techno-economic evaluation demonstrates that this process is feasible. Encouraged by these results, we are currently assessing the integration of these two catalytic systems before moving onto real LFG.

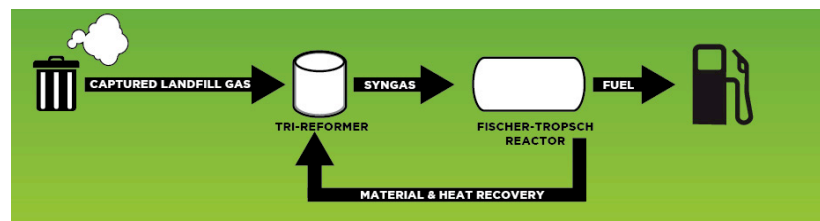


Figure 1. Process for conversion of landfill gas (LFG) to high-value liquid fuels.

Materials and Methods

Reforming catalyst were of the Ni/Mg/(Ce,Zr)O₂ form with the support prepared by co-precipitation and the metal added by incipient wetness. The catalysts were characterized by XRD, XPS, TPR, SEM/EDS, and BET SA before and after use. LFG conversion experiments were performed with simulated feeds and catalytic activity and selectivity were assessed using temperature-programmed and isothermal conditions.

The FTS catalyst is based on Co/SiO₂ and prepared by impregnation in a way such that the Co penetration depth into the silica pellets is controlled. The catalysts were characterized by H₂ chemisorption, TPR, XPS, and BET SA. Catalyst testing was performed in a fixed bed reactor under typical FTS conditions. GC/MS was used for product identification and quantification.

Results and Discussion

A Ni/Mg/(Ce,Zr)O₂ system was selected for the tri-reforming catalyst. Initially, the catalyst formulation was optimized with a feed of CH₄:CO₂:O₂:H₂O of 1:1:0.1:0.1, which closely resembles typical LFG. The catalyst with a Ce:Zr ratio of 0.6:0.4 demonstrated the

highest H₂ yield and characterization studies correlated well with reducibility and oxygen mobility. Furthermore, at least 8% wt Ni and 4% wt Mg were needed to minimize coke formation. The optimal formulation to maximize H₂ yield was 8Ni/8Mg/(Ce_{0.6}Zr_{0.4})O₂. For steady-state conversion at T=800°C, a small amount of O₂ (CH₄:O₂ = 1:0.2) was further added to the feed to reach a H₂:CO ratio of 2:1 and minimize coke formation rates to ~6 x 10⁻⁴ g/g/h. A further increase the steam or oxygen amount did not lead to lower coke formation rates and the CO₂ conversion substantially decreased [1].

Simultaneously, our team has developed an egg-shell Cobalt catalyst that can synthesize diesel and jet fuel from syngas in a highly selective manner via Fischer-Tropsch Synthesis [2-4]. The solution parameters used during the catalyst synthesis were used to achieve an eggshell catalyst with controlled Co penetration (see Figure 2, left). This catalyst has been used to convert synthetic syngas and syngas derived from pine chips to middle distillate products (see Figure 2, center and right).



Figure 2. (left) Optical photograph of a cut egg-shell catalyst showing the dark ring of cobalt catalyst on the periphery of a silica particle; (center) Sample of liquid hydrocarbon fuel produced using an egg-shell catalyst; (right) GC analysis of fuel produced showing selectivity towards middle distillate products.

Significance

LFG conversion to high-value liquid hydrocarbon fuels is proposed in a two-step process. A Ni/Mg/(Ce,Zr)O₂ catalyst is able to convert simulated LFG to syngas with a H₂:CO ratio of 2:1 without appreciable coke formation. An eggshell Co-based catalyst provides syngas conversion to middle distillate products in high yield.

References

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