Reforming landfill gas to syngas

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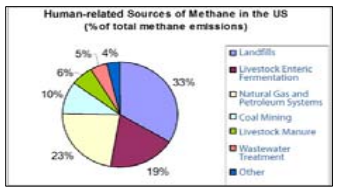
Abstract

A preliminary investigation into the dry reforming (synthesis gas production) of landfill gas (LFG), has begun using precious metal catalysts. Thermogravimetric analysis work was performed on the dry reforming reaction over 0.5% Pt/γ-Al2O3 catalysts. Variables such as reforming temperature, CO2 concentration, and the effect of pre-reduction have been studied. It was found that reforming at 900°C with pre-reduction gave the most H2 production for reactant gas concentrations similar to LFG. However, at this high temperature there was significant weight gain measured. EDX analysis and follow up oxidation tests confirmed that it was due to carbon deposition on the catalyst surface. Yet, this weight gain, up to 24% in some cases, did not coincide with a decrease in catalyst activity as was the case for the lower temperature tests. One possible mechanism for this is the onset on the carbon gasification (Boudouard) reaction at high temperatures. For increased CO2 concentrations, the activity of the catalyst at high temperatures was maintained (high production of syn gas) despite significant carbon deposition.

Background

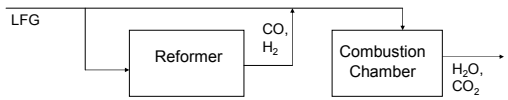


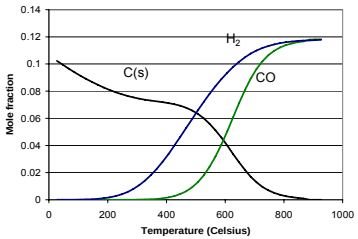
Methane reforming reactions

Steam reforming:	$CH_4 + H_2O \rightarrow CO + 3\,H_2$	$\Delta H = +226$ kJ/mol
Partial oxidation:	$CH_4 + \frac{1}{2}\,O_2 \rightarrow CO + 2\,H_2$	$\Delta H = -44$ kJ/mol
Dry reforming:	$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2$	$\Delta H = +261$ kJ/mol

Enhanced Combustion

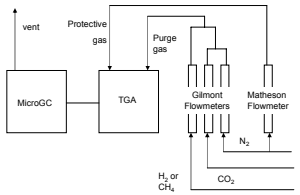
- Adding H2 to a hydrocarbon fuel
- Lower emissions of soot, NOx, hydrocarbons, and carbon monoxide
- Feed source is LFG with a fraction of it preprocessed (reformed into H2/CO)



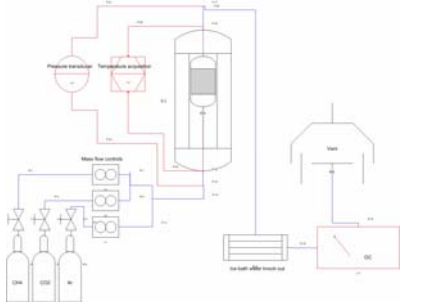


Calculation of equilibrium conversions for stoichiometric dry reforming reaction at atmospheric pressure.

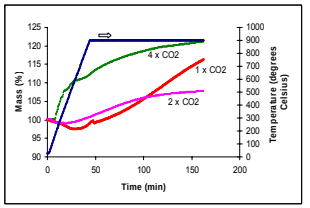
Experimental Methods



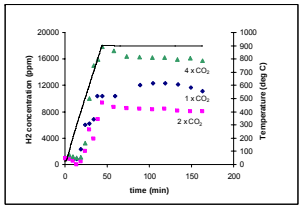
Schematic of TGA / MicroGC system for dry reforming.



Schematic of flow-through reactor system for dry reforming. Reactor consists of a ¾ inch ID quartz tube placed inside of a two stage furnace. Thermocouples are located at inlet and outlet of catalyst bed which is positioned in the constant-temperature regime of the furnace.



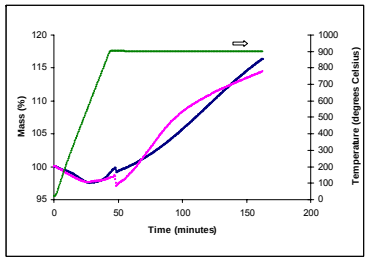
The effect of varying concentrations of CO2 with respect to carbon formation. Inlet gas streams consisting of CO2:CH4 ratios of 1, 2, and 4 were sent over pre-reduced 0.5% Pt/γ-Al2O3 catalysts, and mass percent gain was measured as a function of time and temperature.



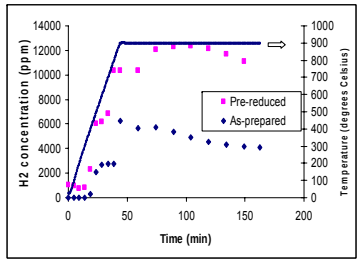
The effect of varying concentrations of CO2 with respect to H2 production. Inlet gas streams consisting of CO2:CH4 ratios of 1, 2, and 4 were sent over pre-reduced 0.5% Pt/γ-Al2O3 catalysts, and H2 concentration was measured as a function of time and temperature.

Results

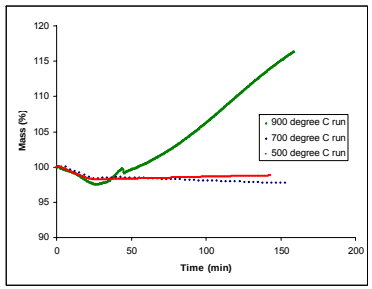
TGA / MicroGC results



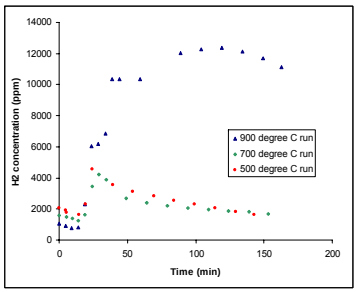
Comparison of mass percent gain for pre-reduced and non-pre-reduced 0.5% Pt/γ-Al2O3 catalysts. Mass percent gain and temperature is shown as a function of time for an inlet stream of 7ml CH4, 7ml CO2, and 90ml N2.



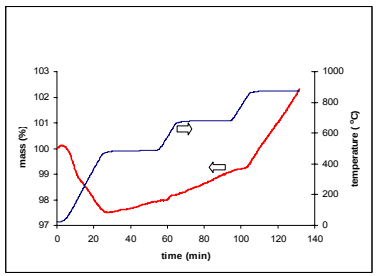
H2 conversion using pre-reduced and non-pre-reduced 0.5% Pt/γ-Al2O3 samples. Conversion is shown as a function of time and temperature for an inlet stream of 7ml CH4, 7ml CO2, and 90ml N2.



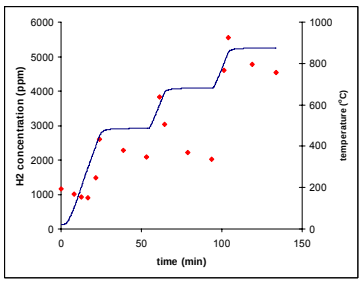
The effects of varying temperatures on mass percent growth during dry reforming runs. Runs were performed on pre-reduced 0.5% Pt/γ-Al2O3 samples with inlet stream of 7ml CH4, 7ml CO2, and 90ml N2.



H2 conversion as a function of time for varying temperatures. Runs were performed on pre-reduced 0.5% Pt/γ-Al2O3 samples with inlet stream of 7ml CH4, 7ml CO2, and 90ml N2.



The effects of ramping and stabilizing temperatures on mass percent growth during dry reforming runs. Runs were performed on pre-reduced 0.5% Pt/γ-Al2O3 samples with inlet stream of 7ml CH4, 7ml CO2, and 90ml N2.



The effects of ramping and stabilizing temperatures on H2 production during dry reforming runs. Runs were performed on pre-reduced 0.5% Pt/γ-Al2O3 samples with inlet stream of 7ml CH4, 7ml CO2, and 90ml N2.

EDX results

Run Description	Species	Weight %
DR Temp = 900 No Reduction Industrial Grade gases	**C**	**24.1**
	O	Not measured
	Al	71.7
	Pt	4
DR Temp = 900 No Reduction UHP gases	**C**	**18.86**
	O	7.80
	Al	66.04
	Pt	7.30
DR Temp = 900 Reduction Temp = 1000 Industrial Grade gases	**C**	**16.60**
	O	12.06
	Al	66.89
	Pt	4.45
DR Temp = 900 Reduction Temp = 900 Industrial Grade gases	**C**	**22.46**
	O	11.81
	Al	61.19
	Pt	4.53
DR Temp = 900 Reduction Temp = 900 Industrial Grade gases	**C**	**27.82**
	O	13.05
	Al	57.31
	Pt	4.16
DR Temp = 700 Reduction Temp = 700 Industrial Grade gases	**C**	**9.94**
	O	13.66
	Al	72.81
	Pt	3.59
DR Temp = 500 Reduction Temp = 500 Industrial Grade gases	**C**	**3.82**
	O	14.32
	Al	74.03
	Pt	7.83

Conclusions

- Higher temperatures yields higher mass gains
- Higher temperatures yields more H_2/CO
- No real significant change in BET
- EDX results show correct trends in terms of C
  - –Verified by subsequent burn-off experiments
- Kinetic parameters calculated
  - –Model development
  - –Estimation of Durability – long term deactivation
- Flow reactor experimentation beginning
  - –Space velocity, new catalyst formulations, durability, addition of inlet oxygen, long term deactivation
- No appreciable performance on Au / Al_2O_3