Auto-thermal reforming of Landfill gas

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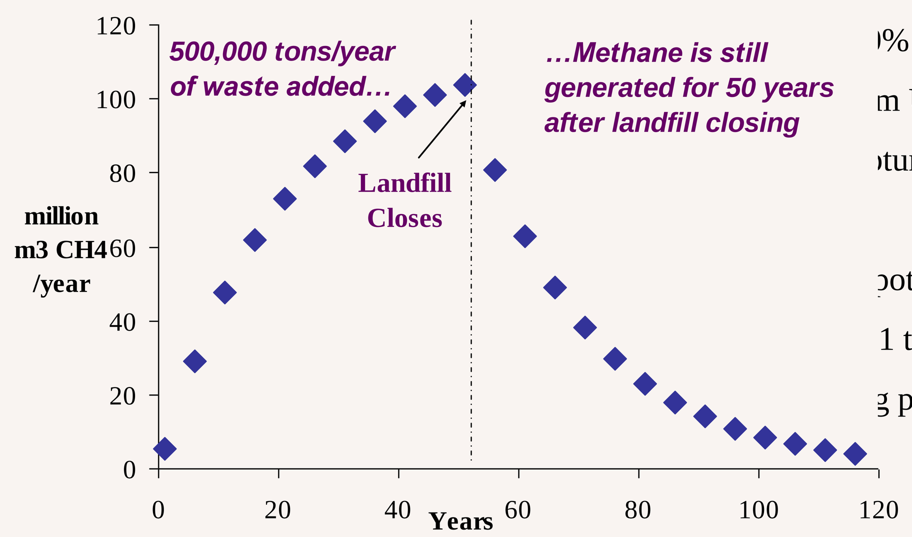
Introduction

Landfill gas is produced by the anaerobic decomposition of biomass in landfills via:

$$C_6H_{10}O_4 + 1.5\ H_2O \rightarrow 3.25\ CH_4 + 2.75\ CO_2$$



% of the methane m U.S. landfills is tured and utilized

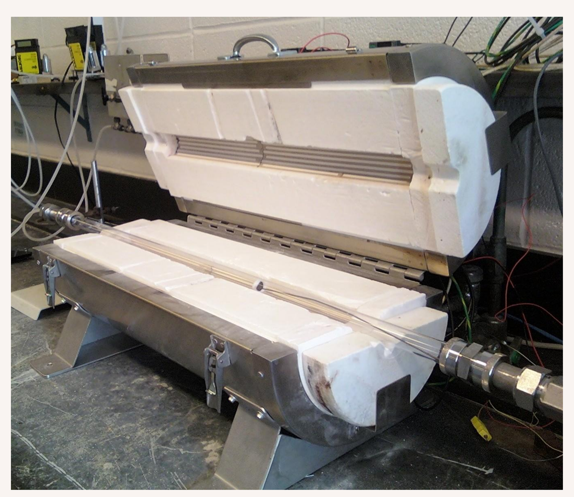
potent greenhouse 1 times the global potential of CO_2

Methane can be reformed with CO_2 to produce synthesis gas via reaction 1. Dry reforming can be made more economically and environmentally feasible using auto-thermal reforming, shown in reaction 2 (not balanced):

	① CH4 + CO2 → 2CO + 2H2	ΔH = 247 kJ/mol
	② CH4 + 2O2 → CO2 + 2H2O	ΔH = -802 kJ/mol
ATR	CH4 + CO2 + O2 → CO, H2, CO2, H2O	ΔH = 0 kJ/mol

Materials and methods

- •A 4% Rh/γAl$_2$O$_3$ monolith was used for all of the studies.
- •Outlet gas concentrations were measured using an Agilent QUAD gas chromatograph with Plot U and mole sieve columns.
- •Reaction rates were measured at temperatures from 400 to 800°C at 1 atm pressure.
- •ATR studies were performed by introducing varying amounts of oxygen into the reactor (from 0.1% to 5.3% of the feed stream.)



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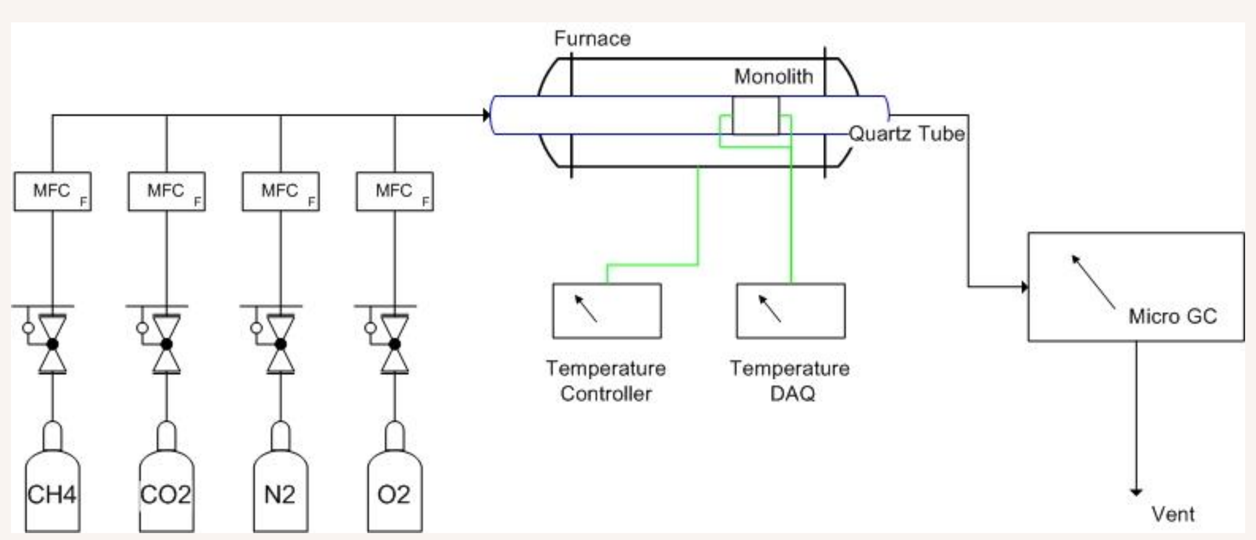


Figure 1. Schematic of Dry Reforming Setup

Results

1. Rh/γAl$_2$O$_3$ catalyst approaches equilibrium

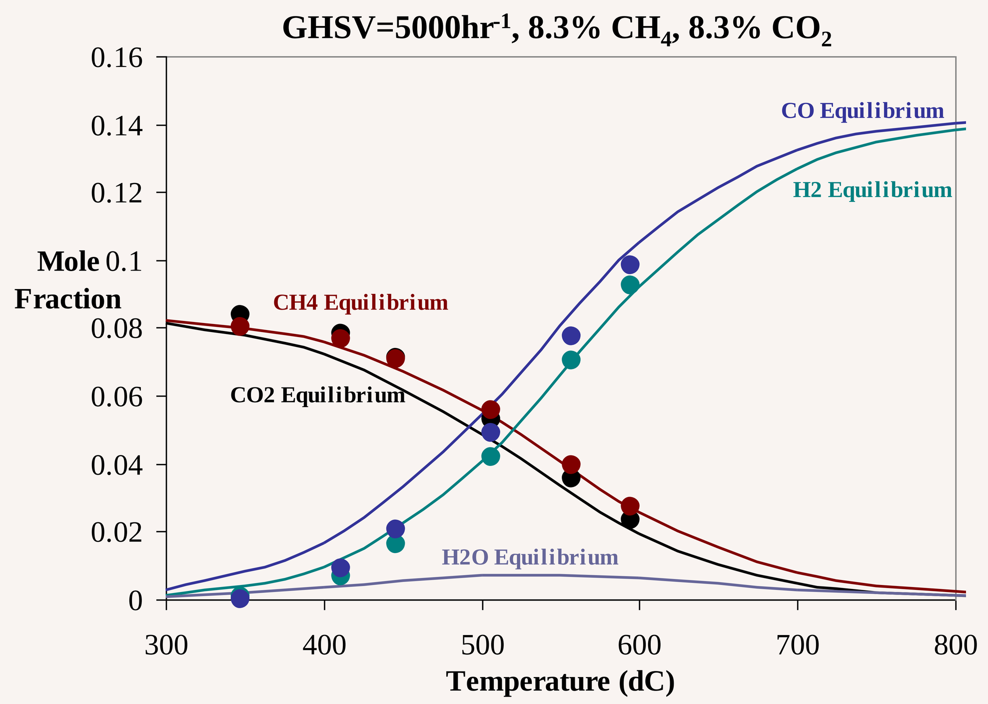


Figure 2. Experimental approach to equilibrium

2. Reaction order of CH_4 and CO_2 was determined

The rate of the dry reforming reaction takes the following form:

$$Rate = k_f (CH_4)^{\alpha}(CO_2)^{\beta} - k_r (H_2)^{\nu}(CO)^{\omega}$$

To determine the reaction orders of CH_4 and CO_2, the reaction is operated far from equilibrium so that:

$$Rate = k_o \exp\left(\frac{-E_a}{RT}\right)(CH_4)^{\alpha}(CO_2)^{\beta}$$

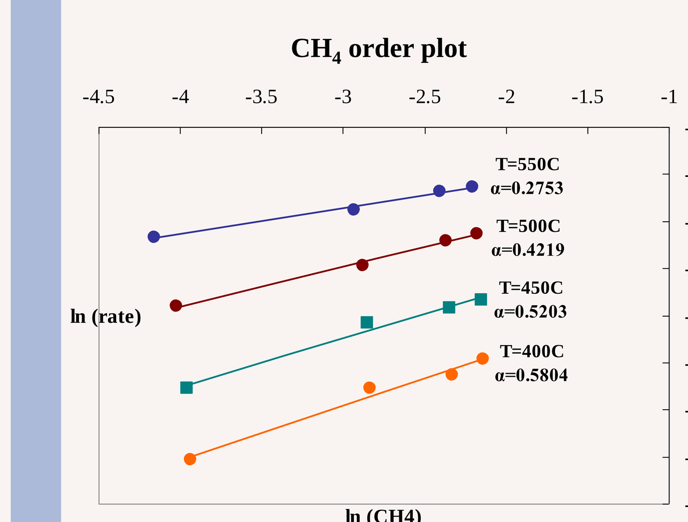


Figure 3. Plot of CH_4 order shows linear relationship between CH_4 concentration and rate

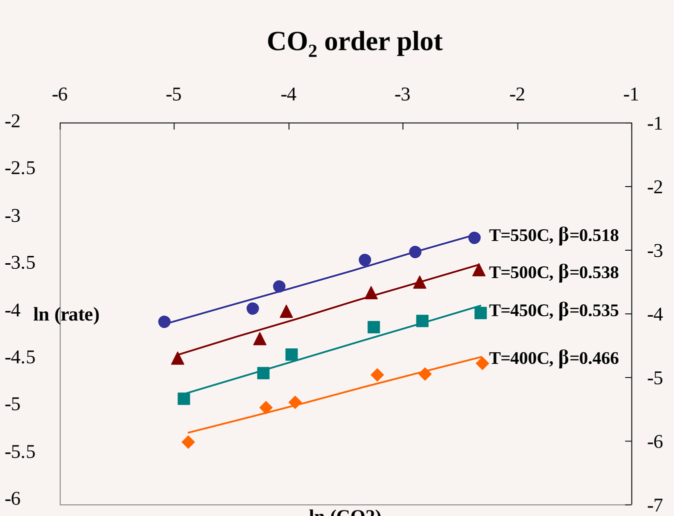


Figure 4. Plot of CH4 order shows linear relationship between CH4 concentration and rate

$$\ln(1-X) = \frac{-k_f'(CO_2)^{\beta}}{\alpha}\left(\frac{1}{GHSV}\right) \Rightarrow k_f = -\frac{\alpha \cdot m}{(CO_2)^{\beta}} \Rightarrow k_f = k_o \exp\left(\frac{-E_a}{RT}\right)$$

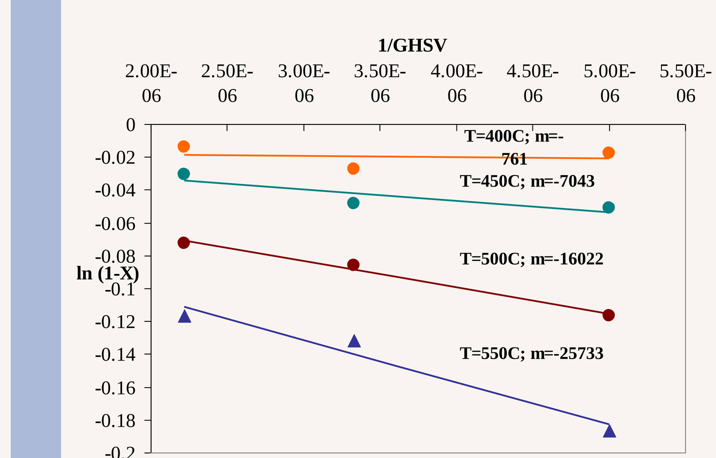


Figure 5. Plot to determine k_f'

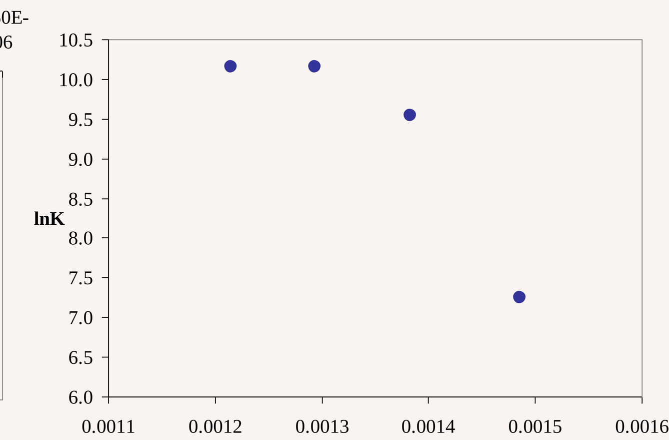


Figure 6. Plot shows non linear relationship between lnK and 1/T

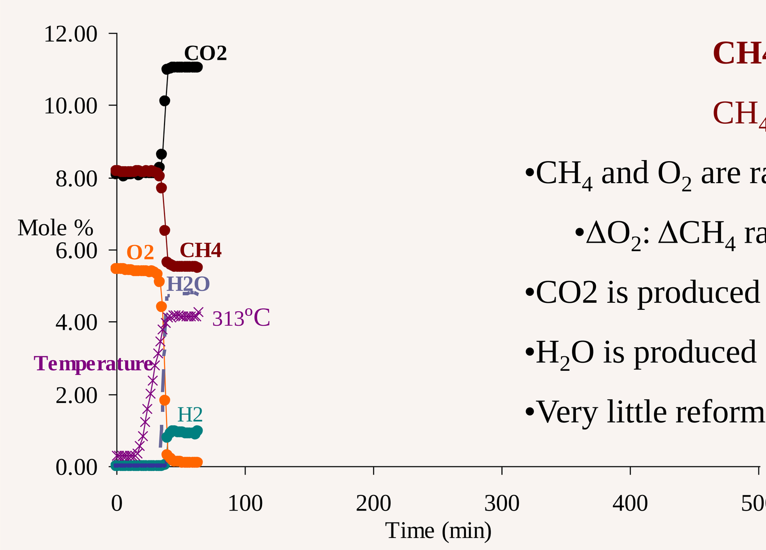
Results

3. ATR gives heat benefit and allows for H_2/CO ratio tuning

The following reactions are dominant in an ATR reaction:

Methane combustion	$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$	ΔH=-802 kJ/mole
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	ΔH= 206 kJ/mole
Dry reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	ΔH= 247 kJ/mole
Reverse water gas shift	$CO_2 + H_2 \rightarrow CO + H_2O$	ΔH= 41 kJ/mole

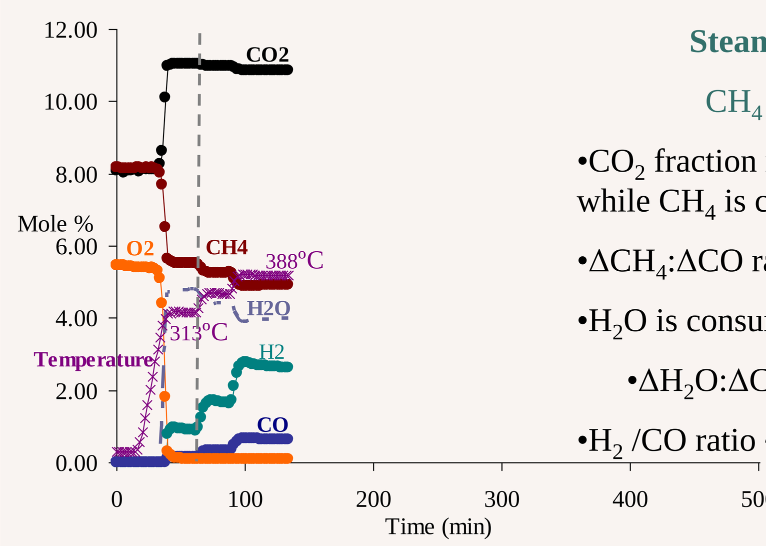
GHSV=5000hr^{-1}, 8.2% CH_4, 8.2% CO_2, 5.3% O_2



CH4 combustion region

$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$

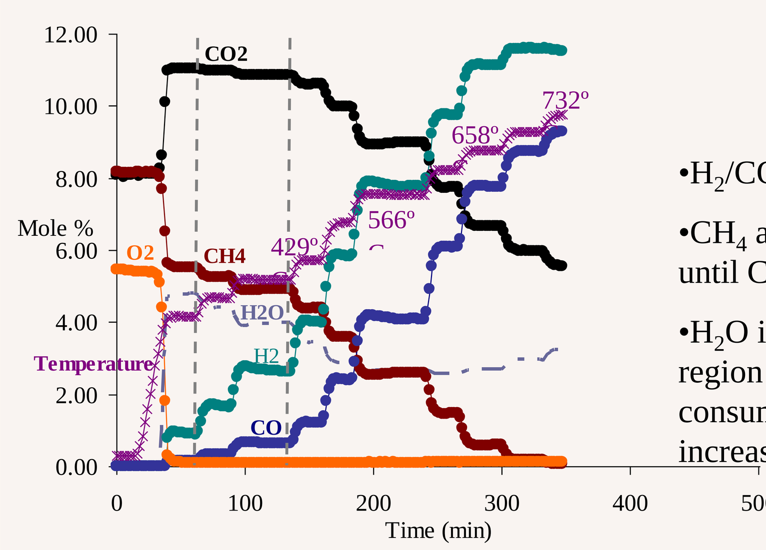
- •CH_4 and O_2 are rapidly consumed
  - •ΔO_2: ΔCH_4 ratio = 1.85:1
- •CO2 is produced -ΔCH_4: ΔCO_2 ratio = 1.06:1
- •H_2O is produced
- •Very little reforming occurs



Steam Reforming Region

$CH_4 + H_2O \rightarrow CO + 3H_2$

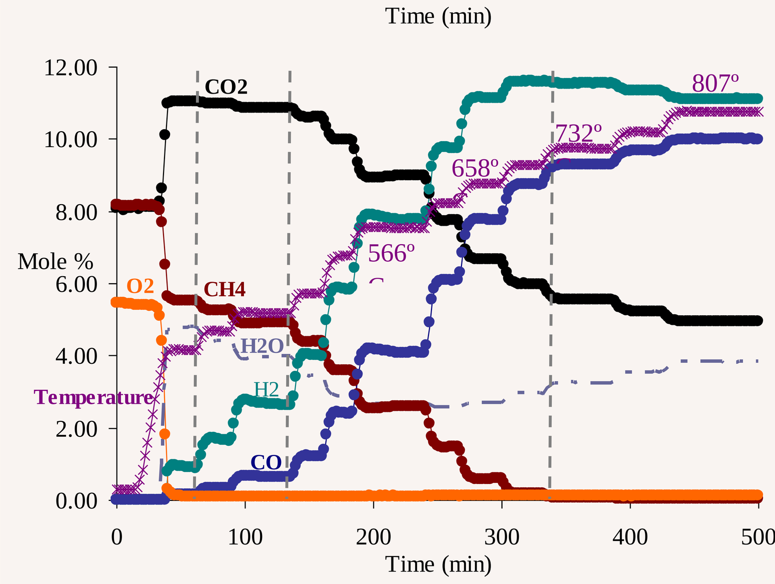
- •CO_2 fraction remains mostly constant while CH_4 is consumed
- •ΔCH_4:ΔCO ratio = 1.02:1
- •H_2O is consumed
  - •ΔH_2O:ΔCH_4 ratio = 1.31:1
- •H_2 /CO ratio ~ 4



Dry Reforming Region

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$

- •H_2/CO ratio decreases from 4.17 to 1.24
- •CH_4 and CO_2 consumed at 1.02:1 ratio until CH_4 is depleted
- •H_2O is consumed at the onset of this region due to steam reforming, but consumption levels off as temperature increases



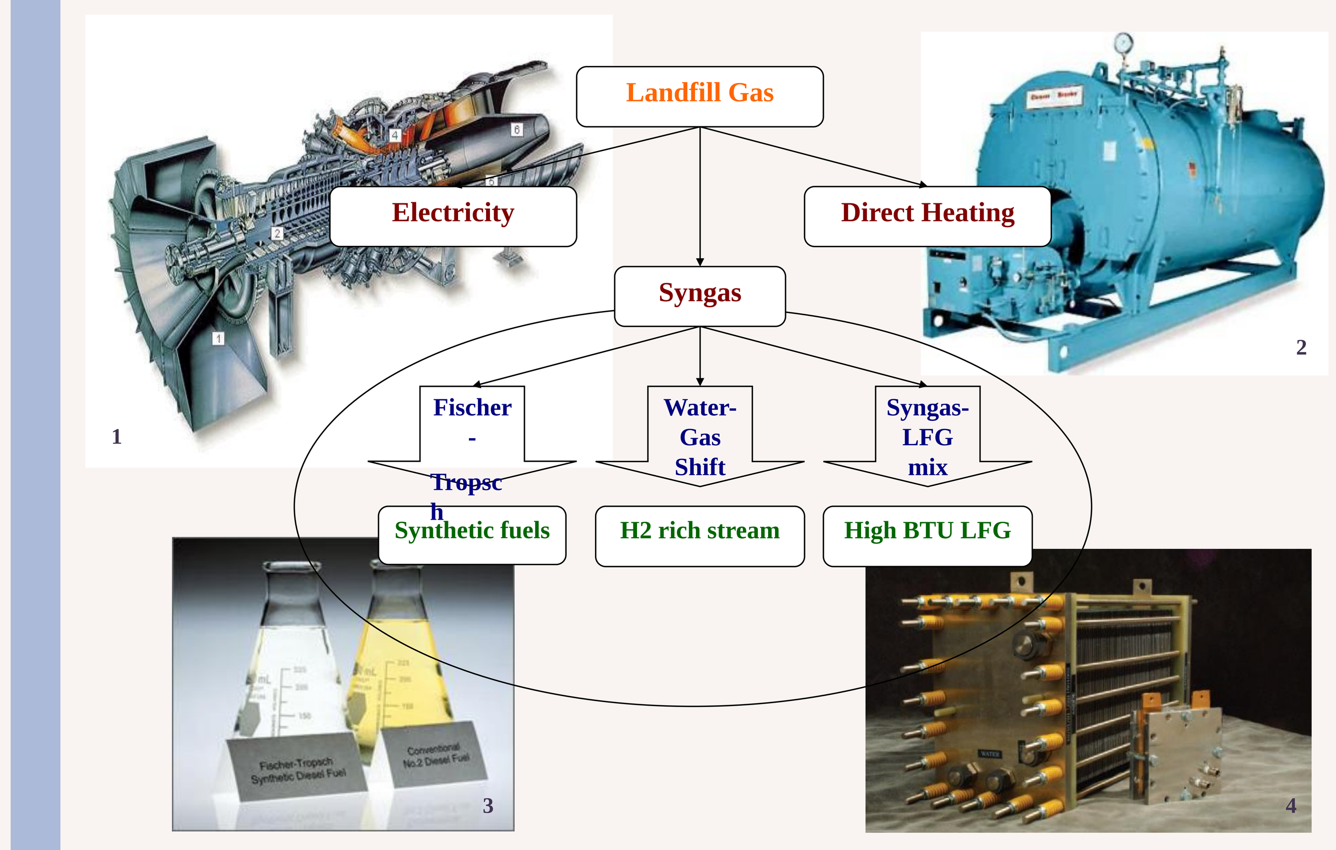
Reverse Water-Gas shift

$CO_2 + H_2 \rightarrow CO + H_2O$

- •No CH_4 is left to react
- •H_2/CO ratio decreases from 1.24 to 1.11
- •CO_2 and H_2 are consumed
  - •ΔCO_2:ΔCO ratio = 0.94
- •H_2O and CO are produced

Figure 7-10. Auto-thermal reforming plots

Application



1. www.energysolutionscenter.org 2. www.plumbersinstalbans.co.uk 3. www.nrel.gov 4. www.anl.gov

Conclusions

- •Rh/γAl$_2$O$_3$ catalyst reaches equilibrium conversions
- •Reactions occurring during ATR are mostly sequential and well understood
- •ATR can be used to control H_2/CO ratio of products

Table 1. CH_4 and CO_2 orders determined in this work compared to literature

CH_4 order	CO_2 order	Ea (kJ/mole)	Source
0.28-0.58	0.47-0.54	?	This Work
0.52-0.82	0.10-0.51	31.1	Cui, Zhang, Xu, Li, 2007[1]
0.61	0.37	53.3	Munera et al 2007[2]
1	0	111	Wei and Iglesia 2004[3]

1. Cui, Y., Zhang, H., Xu, H., and Li, W. "Kinetic study of the catalytic reforming of CH4 with CO2 to syngas over Ni/α-Al2O3 catalyst : The effect of temperature on the reforming mechanism." Applied catalysis A 318(2007): 79-88.

2. Munera, J.F., Cornaglia, L.M., Cesar, D.V., Schmal, M., and Lombardo, E.A. "Kinetic Studies of the Dry Reforming of Methane over the Rh/La2O3-SiO2 Catalyst." Ind. Eng. Chem. Res. 46(2007): 7543 – 7549.

3. Wei,J. and Iglesia, E. "Isotopic and kinetic assessment of the mechanism of reactions of CH4 with CO2 or H2O to form synthesis gas and carbon on nickel catalysts." Journal of Catalysis 224(2004): 370-383.

Future Work

- •ATR kinetics
- •Determine the effect of poisonous gases commonly found in landfills on catalyst
  - -chlorinated compounds -sulfur compounds
  - -higher order hydrocarbons -ethanol
- •Determine the effect of aging and regeneration possibility of Rh/γAl$_2$O$_3$

Acknowledgements

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