PARAMETRIC STUDY OF AUTOTHERMAL REFORMING OF LPG

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Introduction

Generating electricity by fuel cell technologies is under extensive research recently with a potential for commercialization in the near future. Sources of hydrogen for fuel cell are diverse and fuel processing is a key part to ensure reliable performance and competitive economy of fuel cell applications. Conventional hydrocarbon fuels are cheap and widely available. In Hawaii, the majority of electricity is generated from fossil fuels. There are ample supplies of Liquid Petroleum Gas (LPG) and its price is competitive to that of gasoline. Being safe and non-toxic, LPG is a promising source of hydrogen for off-grid applications in Hawaii.

Hydrocarbon fuels can be converted into high quality hydrogen for PEM fuel cells through reforming, water-gas shift reaction, and CO cleanup. Steam reforming, catalytic partial oxidation and autothermal reforming are the main processes employed to convert hydrocarbons to hydrogen rich gas. Compared with natural gas, LPG, mainly propane, contains C-C bonds that will be broken at higher temperature.

Coking is a main cause of catalyst failure in hydrocarbon reforming. Carbonaceous deposits on catalyst surfaces block active sites, leading to catalyst deactivation. Coke formation from thermal cracking can accompany catalytic reforming above approximate 650°C [1]. Therefore for LPG reforming at high temperature, coking must be carefully controlled.

Ethyl mercaptan is commonly added to LPG as an odorant. Ethyl mercaptan will mainly be converted to hydrogen sulfide in autothermal reforming. For steam reforming catalysts, sulfur will readily bind with nickel causing severe deactivation. The effects of sulfur on catalyst activity are weaker at high temperature and correlate with sulfur concentration in the feedstock [2].

This paper reports preliminary results from a parametric study of autothermal reforming of LPG. Reforming temperature, steam to carbon ratio (S/C), and oxygen to carbon ratio (O/C) were studied. Performance indicators, the extent of LPG conversion and catalyst coking, and sulfur poisoning, are reported.

Experimental

Experiments were performed in a 1.93 cm I.D. tubular reactor. The reactor was heated by electrical furnace with a heating length of 30.5 cm. Two G90 steam reforming catalysts, G-91 EW and C11-NK, from Süd-Chemie were tested. The LPG supply contained 90-100% propane/propylene, 0-2% ethane, 0-10% butane and 40 ppm ethyl mercaptan.

A stream of 2 slpm air was fed into a water vaporizer to produce a steady flow with steam. When temperatures in the reactor reached desired set point values, LPG was introduced and the gas mixture was switched from a bypass mode to the catalyst reactor. Air and LPG flow rates were maintained using mass flow controllers. About 20 to 40 g catalyst were located in the constant temperature zone in the reactor. Temperatures in the reactor were measured at three locations, 7.5 cm in front of the catalyst bed (T1), directly in front of the catalyst bed (T2) and immediately after the catalyst bed (T3). The dry effluent gas was analyzed using a Shimadzu GC 14A equipped with a Carbonex packed column and a thermal conductivity detector. The gas components H_2, N_2, CO, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8, were quantified.

Catalyst temperature, S/C, O/C and catalyst mass (i.e. space velocity) were studied at 2-3 levels. Both steam reforming and autothermal reforming were investigated. Steam-to-carbon ratio was 0.6 or 1.5. Oxygen-to-carbon ratio was 0.76 or 1.0. The amount of catalysts was 20 or 40 g. Temperature of the reformer was set at 680, 770, 850°C. Real temperatures in the reactor were shown by T1, T2 and T3. Temperature at the end of the catalyst bed, T3 was used to represent the catalytic reactor temperature.

Results and Discussion

Catalyst. Two catalysts tested are designed for different feed stocks, G91 EW for natural gas/LPG and C11-NK for naphtha. Both catalysts showed similar activity in LPG conversion, however, G91 EW was more active in converting methane and ethylene (Table 1) under the conditions tested. Since the amount of catalyst was in excess, the influence of catalyst type on hydrocarbon conversion was weak in the test range.

Table 1. Gas Compositions after Reforming by Two Catalysts. S/C=1.5, O/C=1.0, T3=800°C, GHSV=9000 1/h.

%	H_2	N_2	CO	CH_4	CO_2	C_2H_4	C_3H_8
C11 NK	33	46	11	1.4	9.3	0.38	0
G91 EW	35	45	11	0.24	8.7	0.06	0

Temperature. Temperature of the catalyst bed was the most important factor for LPG conversion. Complete conversions of C_3H_8 and C_3H_6 was achieved at catalyst bed temperature of 840°C (average of T2 and T3), at S/C=1.5 and O/C=1.0 (Table 2).

Table 2. Effect of Temperature on Propane Conversion. S/C=1.5, C11-NK 42 g, O/C=1.0.

T bed, °C	704	725	840
C_3H_8 conversion, %	98.5	98.7	100

O/C ratio. In autothermal reforming, the role of oxygen is to provide heat required to drive steam reforming reactions and to break fuel into smaller compounds. At high O/C ratio, the chemical energy of fuel may be converted to sensible heat rather than the desired H_2 product. At low O/C ratio, coke may form due to thermal cracking of hydrocarbons. In the present work, O/C ratio of 1.0 was chosen since experience indicated that coke formation was generally lower at this condition. This ratio was equal to about 30% of oxygen needed for complete combustion of propane. In gasification research, this O/C ratio was usually found to be optimal. Further experiments are planned to quantify the effects of O/C ratio on system performance.

S/C ratio. In autothermal hydrocarbon reforming, partial oxidation reactions occur faster than steam reforming reactions. Since partial oxidation is very exothermic while steam reforming is extremely endothermic, the occurrence of these two sets of reactions can be deduced from the temperature profile in the reactor (Figure 1). The "No LPG" curve indicates that flow through the reactor does not reach the furnace control set point temperature of 770ºC until close the location of x/L=0.5. Compared with this, low S/C ratios of 0.6 and 1.0 resulted in high temperature before the catalyst bed indicating that heat released from oxidation (O/C=1.0) dominated the heat demand of the steam reforming reactions. At S/C ratio of 1.5,

enhanced steam reforming reactions result in lower temperatures at the entrance of the reactor (x/L=0.25). All three S/C ratios have roughly equal temperatures (~850ºC) in excess of the furnace temperature set point at x/L=0.5 indicating the heat release by the oxidation is dominant at this location. Differences in total flow rate through the reactor are not accounted for in this discussion.

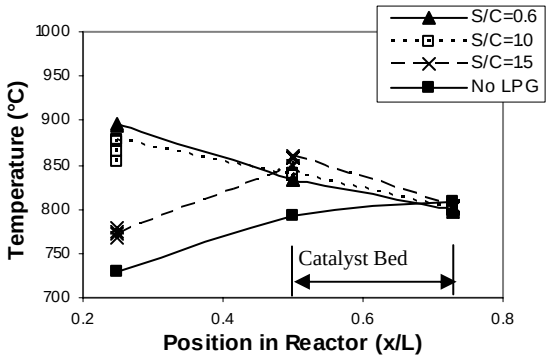

Figure 1. Influence of S/C on temperatures in the reactor. L: total heated reactor length, x: distance from inlet in the reactor. T3=800°C, O/C=1.0, G91 EW: 22 g.

Steam reforming was slow and was kinetically controlled (Figure 2). Though propane and propylene were completely converted, methane levels in the effluent were higher than values predicted by equilibrium calculations. Concentration of ethylene, a precursor of coking, was low. Both methane and ethylene decreased with increasing S/C ratio.

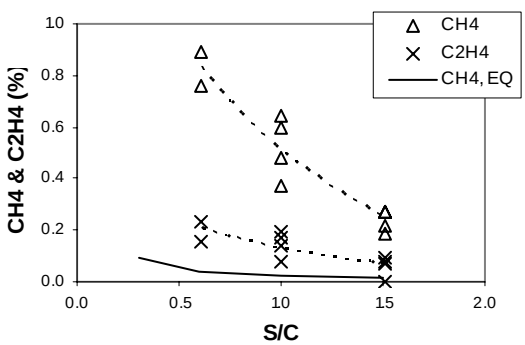

Figure 2. Effect of S/C ratio on methane and ethylene. Equilibrium value for methane is given for comparison. T3=800°C, O/C=1.0, G91 EW:22 g, GHSV=9000 1/h.

S/C ratio affected conversions of C_3H_8 and C_3H_6 to some extent. Trace amount of C_3H_8 was detected at 800°C (T3) when S/C and O/C were lowered to 1.1 and 0.76, respectively.

The choice of a proper S/C ratio should also take into account energy balance of the reformer system. Equilibrium calculations indicate that with preheating of inlet gas by exhaust gas, autothermal reforming could be operated without external heat supply at S/C=1.5 and O/C=1.0.

Deactivation of the catalyst. Autothermal reforming of LPG was tested for more than 40 hours under conditions of S/C=1.5, O/C=1.0, GHSV=9000 1/h, and a reactor set point temperature of 770°C. The gas compositions are plotted in Figure 3. Under these conditions, gas composition was generally stable. No propane or propylene was detected. Hydrogen declined slightly with increasing time on stream. Methane increased considerably, which was a sign of catalyst deactivation. Ethylene increased as well, and ethane started to appear after 35 hours on stream.

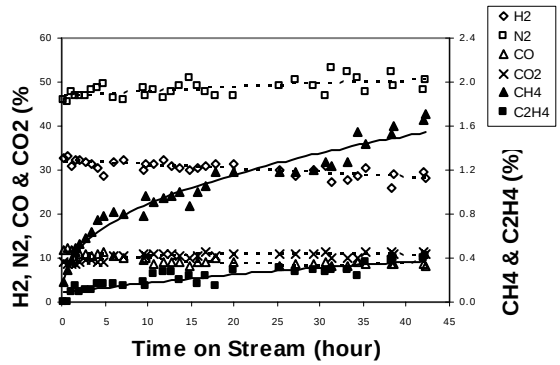

Figure 3. Autothermal reforming of LPG. T3=800°C, S/C=1.5, O/C=1.0, G91 EW: 23 g, GHSV=9000 1/h, ethyl mercaptan in LPG: 40 ppm.

Upon visual inspection at the conclusion of the test, the first piece of the catalyst in the catalytic bed was discolored, indicating partial oxidation was dominant at that point. No clear carbon deposition on the used catalyst was evident. With 40 ppm sulfur in LPG, sulfur poisoning was the likely cause of deactivation due to the formation of nickel sulfide on the active sites of the catalyst surface. More detailed analysis of sulfur on the catalyst surface is expected to be obtained soon.

Conclusions

Effects of different parameters on autothermal reforming of LPG were studied for hydrogen production. Two nickel-based G90 steam reforming catalysts were used. Experiments were carried out in a fixed-bed reactor to study the effects of catalyst type, reforming temperature, S/C ratio, and O/C ratio. Temperature was found to be most important. Complete conversion of LPG was achieved above 800°C (T3). Higher S/C ratio (S/C=1.5) resulted in the reduced levels of methane and ethylene. Controlling O/C and S/C, heat for steam reforming could be provided by partial oxidation in situ and C3 hydrocarbons could be partially oxidized to smaller molecules with less thermal cracking. Finally, autothermal reforming of LPG was tested by more than 40 hours on stream at S/C=1.5, O/C=1.0, 800°C and GHSV=9000 1/h. The propane conversion remained complete, but a slight drop of methane conversion was observed. No clear carbon deposit was found. The deactivation was probably due to poisoning by 40 ppm sulfur from LPG feed.

References

(1) Rostrup-Nielsen, J.R., *Catalysis Today*, **1997**. *37*, 225-232.
(2) Rostrup-Nielsen, J.R., *Catalytic Steam Reforming*, in *Catalysis: Science and Technology*, J.R. Anderson and M. Boudart, Editors. 1984, Springer-Verlag: Berlin. pp. 1-117.