II.G.11 Solar Thermal Hydrogen Production*

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Project Start Date: February 4, 2010
Project End Date: December 31, 2011

*Congressionally directed project

Fiscal Year (FY) 2011 Objectives

- Quantify hydrogen yield from catalytic cracking of methane in the presence of molten salts.
- Determine the effects of different catalysts.
- Demonstrate hydrogen production at possibly reduced temperature.

Technical Barriers

- Salt mixture-catalyst stability.
- Reduce temperature for hydrogen generation.

The main objective of the proposed work is to examine the effects of exposure of a slat mixture to different temperature levels for an extend period of time (up to 8 hr). The 8 hr limit was established since the peak sun intensity is expected to last only that long in one continuous cycle. The parameters for this study and anticipated goals for hydrogen production are summarized in Table 1.

TABLE 1. Project Goals

Performance Measure	Units	Qtr 1 and 2	Qtr 3 and 4
Salt-Catlyst Thermal Stability	Hours	3	8
Temperature Range	Celsius	400-700	400-800
Volume of Hydrogen	Milli-liter	<10	100

FY 2011 Accomplishments

- The dissociation of methane in the presence of a metal catalyst follows a sequence of dehydrogenation steps:
  - $CH_{4,s} \rightarrow CH_{3,s} + H_s$
  - $CH_{X,s} \rightarrow CH_{X-1,s} + H_s$ (X = 3,2, 1; s = surface)
- The presence of Fe, Ni, and Co show hydrogen generation (Table 2).

TABLE 2. Hydrogen Conversion Percentages

Catalyst System	% Conversion at:		
	500°C	600°C	700°C
Licl+KCl Eutectic	0	0	0
Fe Catalyst in LiCl+KCl	5	8	17.5
Ni Catalyst in LiCl+KCl	11.5	28.0	30
Co Catalyst in LiCl+KCl	7.2	11	16

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Introduction

Conventional hydrogen generation process is often carried out at high temperature. This approach can be costly. The solar thermal approach seeks to use the high temperature obtained from solar energy with the help of concentrators. This process can, in principle, offset the need of fossil-based energy to produce high temperatures. A schematic of the approach to use solar energy in solar thermal process is given in Figure 1.

Approach

The approach is to use a simulated solar power condition using a box furnace. The furnace was customized to provide the necessary temperature ranges and the experimental conditions to perform catalytic cracking of methane. Summarily, the methane and carrier gas was delivered to a crucible containing the molten salt and the catalyst. The role of the catalyst and the temperature of the molten salt were monitored and its effects on methane cracking were monitored.

Figure 2 shows a schematic of the setup.

Results

The results (Figure 3) can be categorized into the following segments:

- Physical characterization of the eutectic.

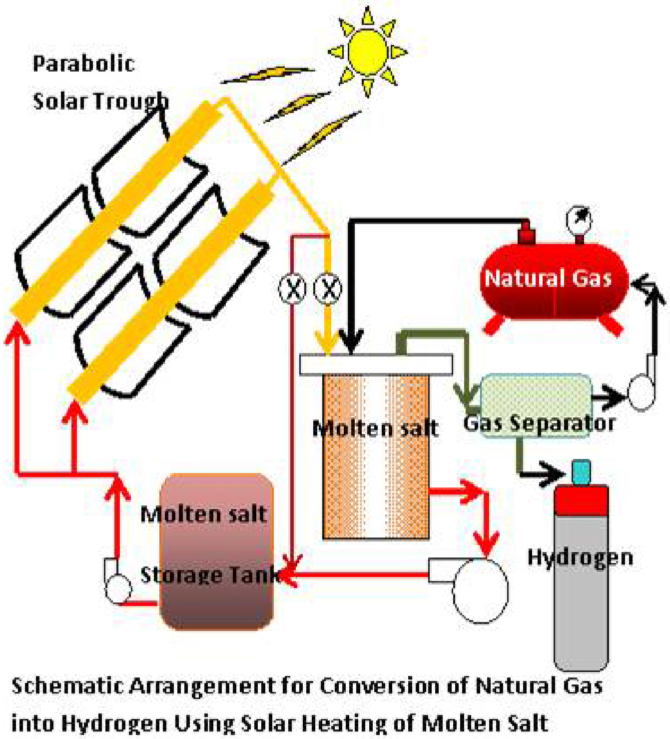

FIGURE 1. General Schematic of the Approach to Utilize Solar Thermal Energy

- Reaction products were noted to have varying color at different depths.
  - Therefore, while the reaction products were in liquid state, they were poured out and shock cooled (salt pour).
- Visual inspection shows the formation of black precipitates at the bottom.

FIGURE 3. A representative photograph of the texture of the salt-catalyst mixture obtained after the catalytic cracking of methane.

  - The possible products could be carbon-based materials and may have value.
- Surface characterization of the salt mixture (Figure 4):
  - X-ray diffraction (XRD) analysis was performed to identify the residue after the reaction.
  - Solid–salt mixture was washed several times with water and dried before analysis.

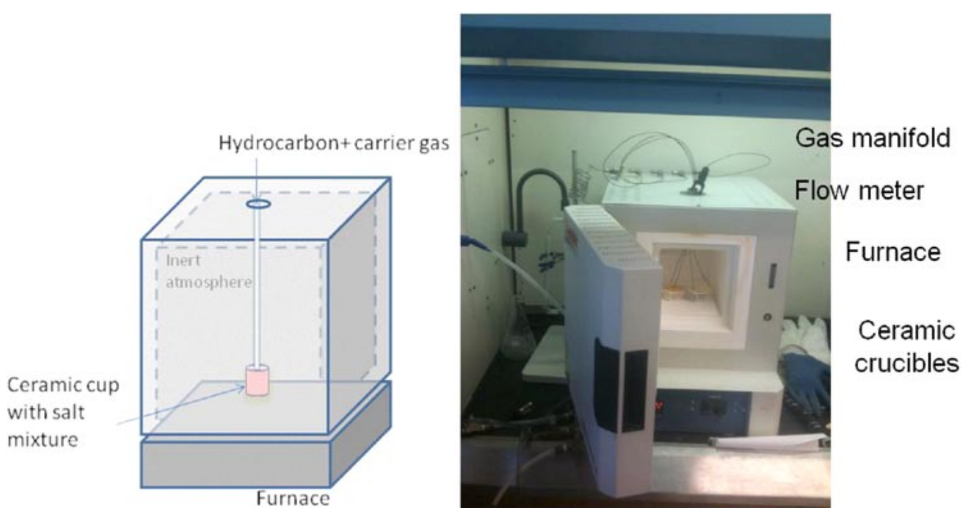

FIGURE 2. The setup that was developed to simulate a solar thermal process to produce hydrogen from methane using a catalyst.

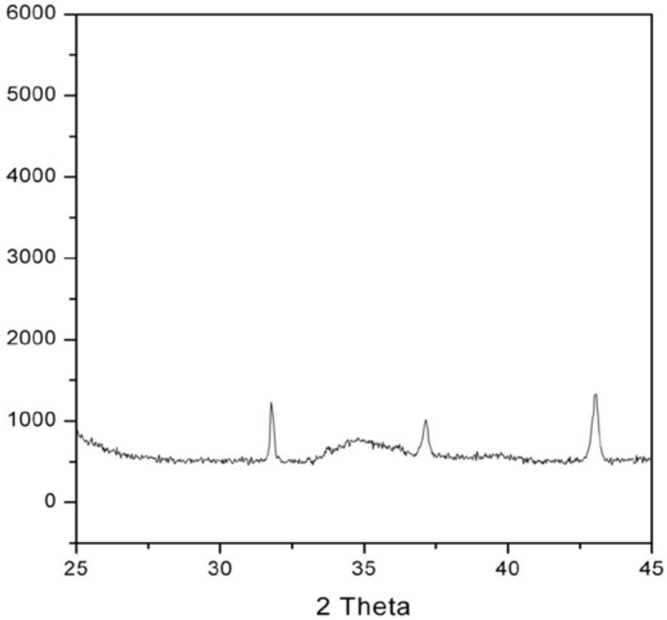

FIGURE 4. XRD of the products after the catalytic cracking indicates the formation of carbon-based residue.

   – XRD suggests the formation of carbonaceous species possibly ordered structures as noted from the XRD peaks.

- Product analysis (Figure 5):
   – Hydrogen and oxygen peaks are detected together. Oxygen peaks are attributable to the leaks in the oven.
   – In general:
      - Hydrogen is detected upwards of 600°C in the absence of catalyst in the salt mixture.
      - Hydrogen has been detected at lower temperatures with catalysts.

Conclusions and Future Directions

The preliminary work has shown that:

1. Including Fe as a catalyst with Li/K salt mixture will reduce the temperature at which hydrogen is produced from methane. Ni and Co may be promising as well.
2. The formation of carbonaceous residue indicates that the system does lead to cracking of methane.
3. The temperature from cracking appears to be reduced by at least a 100°C (possibly up to 200°C).

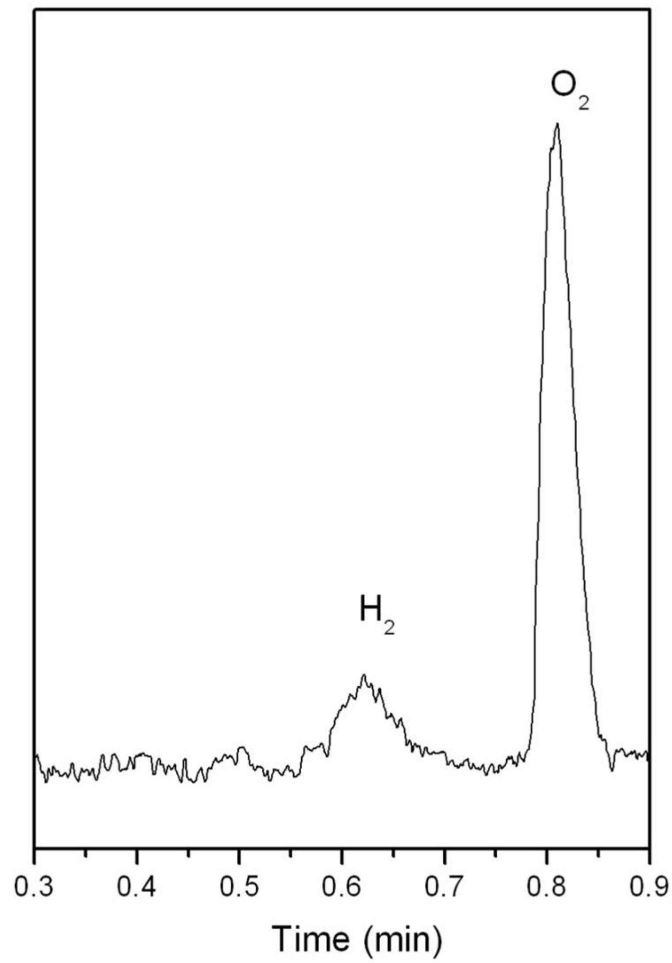

FIGURE 5. Representative gas chromatograph data indicating the products identified after the catalytic cracking of methane.

Future directions:

- To systematically interpret some of the compositional as well as the qualitative nature of the post cracking product(s).
- To finish an ongoing manuscript in this area based on this work.
- There are a few grant opportunities from state and federal agencies that will be explored for future funding.

FY 2011 Publications/Presentations

1. A poster titled "Solar thermal hydrogen production" was presented by Ravi Subramanian at the NVREC Project Meeting on August 20, 2010.

2. Ravi Subramanian also presented an update on this work at the annual DOE merit review meeting in Washington, D.C., May, 2011.