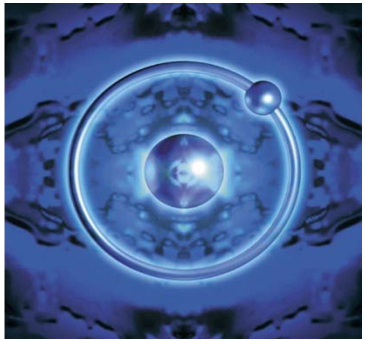




Solar Thermal Hydrogen Production

Using Molten Salt-Catalyst Mixture

P.I. Vaidyanathan (Ravi) Subramanian (University of Nevada, Reno)

Presenter | Vaidyanathan (Ravi) Subramanian

May 10, 2011 | Project ID # PD077

Overview

❑ Timeline
- 10/1/2009-9/30/2010
- 2/4/2010- 12/31/2011*1 (date funds became available)
- 100% complete

❑ Budget
- Total funding for NV institutions
  - 99,953 (DRI)
  - 258,235.00 (UNR)
- Funding received in FY 10
  - 99,953 (DRI)
  - 258,235.00 (UNR)*2
- Part of multi-university funding
  - Fed: 5,560,418 (2009-10)
  - Cost share: 1,396,413

❑ Barriers
- Role of metals in CH_4 decomposition
- Nature of carbon product formation

❑ Partners
- Desert Research Institute
- University of Nevada, Reno

*1 *Current funds are for photocatalyst development*

*2 *Includes funds for low cost, high capacity visible light solar cell*

Objective – Relevance

- The main objective of this work is to evaluate hydrogen generation from carbon sources using simulated solar thermal energy and molten salt – catalyst mixtures
  - Goal – To improve the kinetics of hydrogen production from hydrocarbons at reduced temperature

Performance measure	Units	Qtr 1 and 2	Qtr 3 and 4
Salt-catalyst thermal stability	hours	Three	Eight
Temperature Range	Celsius	400-700	400-600
Volume of hydrogen	Milli-liter	<10	100

Milestones

Activity	Progress	Plans	% activity completed
Experimental setup	Parts, chemicals, and custom devices obtained	Perform experiments over qtr 2,3,and 4	100 %
Modeling	Identify heat capacity, free energy of formation of potential byproducts	To be started	10 %
Product analysis	GC setup	Product gas, Carbon forms to be determined	100 %

Background

❑ Conventional hydrogen production

- Conventional hydrogen generation from natural gas by steam reformation produces CO_2 as a byproduct.

$CH_4 + H_2O \rightarrow CO + H_2$ (at 800 -1000 ° C)

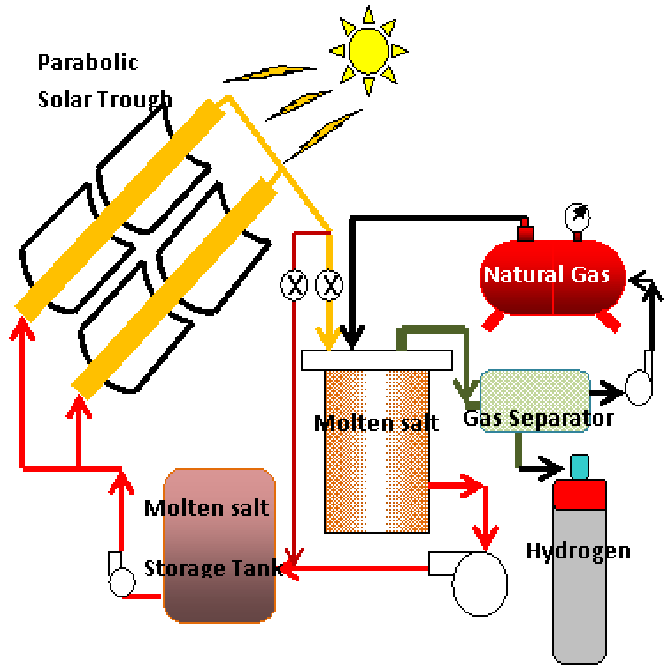
$CO + H_2O \rightarrow CO_2 + H_2$ (at 250 -450 ° C)

❑ Solar thermal hydrogen

- Concentrated solar radiation leads to high temperature that can be used in hydrogen production

❑ Advantages

- Non-fossil-based renewable source
- Possibility for 24-hour operation



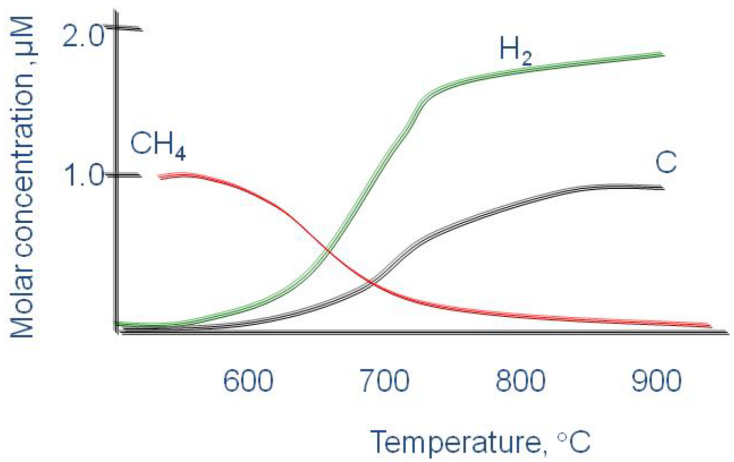
Schematic Arrangement for Conversion of Natural Gas into Hydrogen Using Solar Heating of Molten Salt

Using molten salt as a heat carrier and nano-structured metal particles or liquid metal-solid solutions as catalysts, natural gas can be converted to hydrogen and value added carbon product. There is a potential for the reaction temperature to be reduced.

Approach

- Thermal decomposition of methane or natural gas to hydrogen and carbonaceous materials occurs at high temperatures (>700 °C). We will study this process.

$$CH_4 \xrightarrow[\text{molten salt eutectic})]{\substack{\text{Solar thermal} \\ (\text{nano-catalyst in}}} 2H_2 + \underbrace{C}_{\text{value added}}$$



- The goals are to:
  - Utilize solar thermal energy as heat source for thermal decomposition,
  - Develop catalyst to reduce the conversion temperature, and
  - Increase the kinetics of hydrogen generation.

Approach…contd.

Tasks	Specifics
Identifying eutectics	Examining thermodynamic parameters that provide insight into eutectic point of custom molten salt mixtures.
Characterizing product(s)	Identifying carbon product(s) following methane decomposition.
Screening eutectics	Testing hydrogen generation kinetics and hydrogen yield from methane using eutectics identified in step 1.
Determining catalyst activity	Examining the contribution of catalysts to product composition and hydrogen yield.

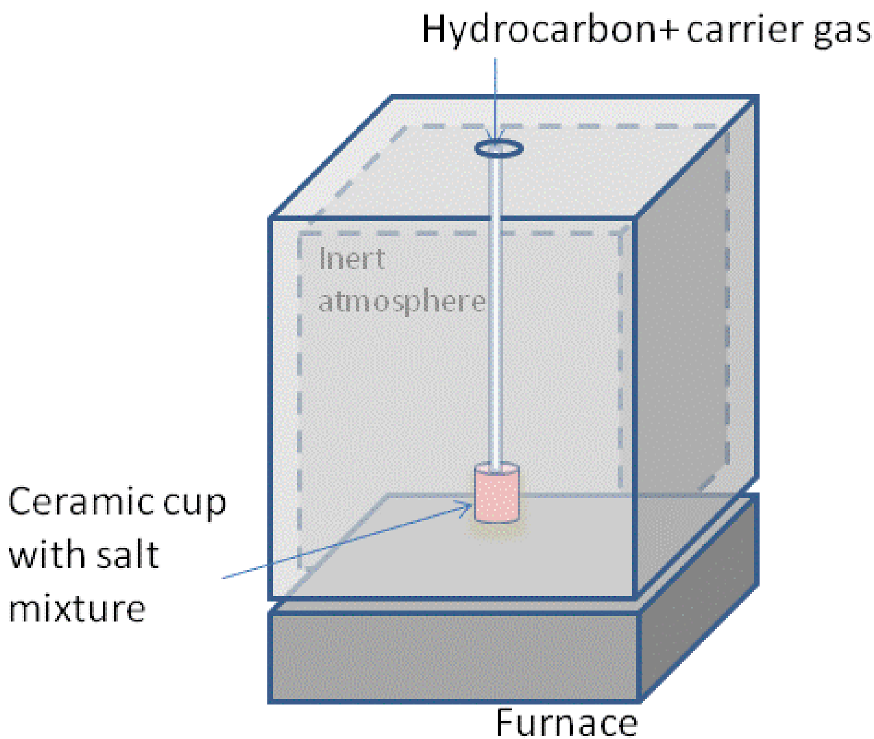
Approach…contd.

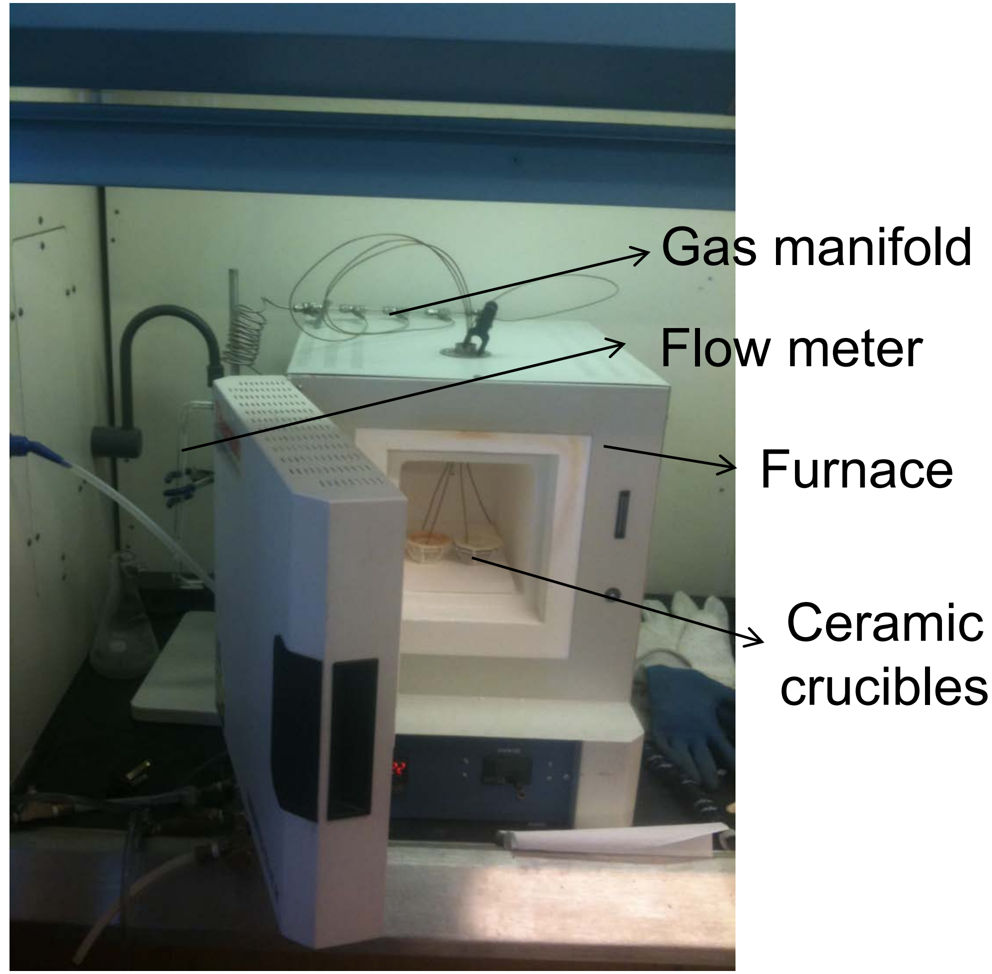
Design parameters and methodology for experimentation

- Reactor configuration
- Combinatorial approach to screen molten salt +catalyst system. The main steps are:
  - Prepare various molten salt + catalyst mixtures
  - Introduce methane
  - Identify mixtures that produce hydrogen using gas chromatograph
  - Identify the carbonaceous residue
- Other experiments
  - Examine effect of temperature on hydrogen and carbon product(s) formation
  - Examine effects of gas flow rate on composition

Approach…contd.

- Schematic and picture of the experimental setup





Progress – Product Analysis

- Reaction product 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
- The possible products could be carbon-based materials and may have value

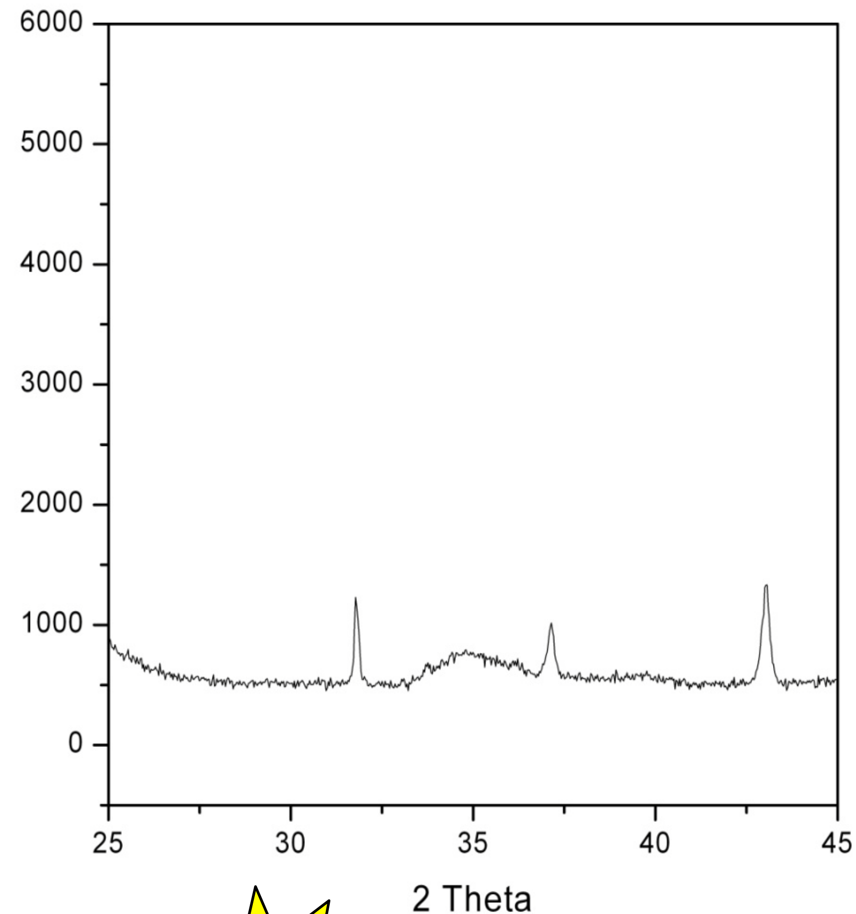
Product at Surface

Product at bottom

New work

Product analysis-XRD

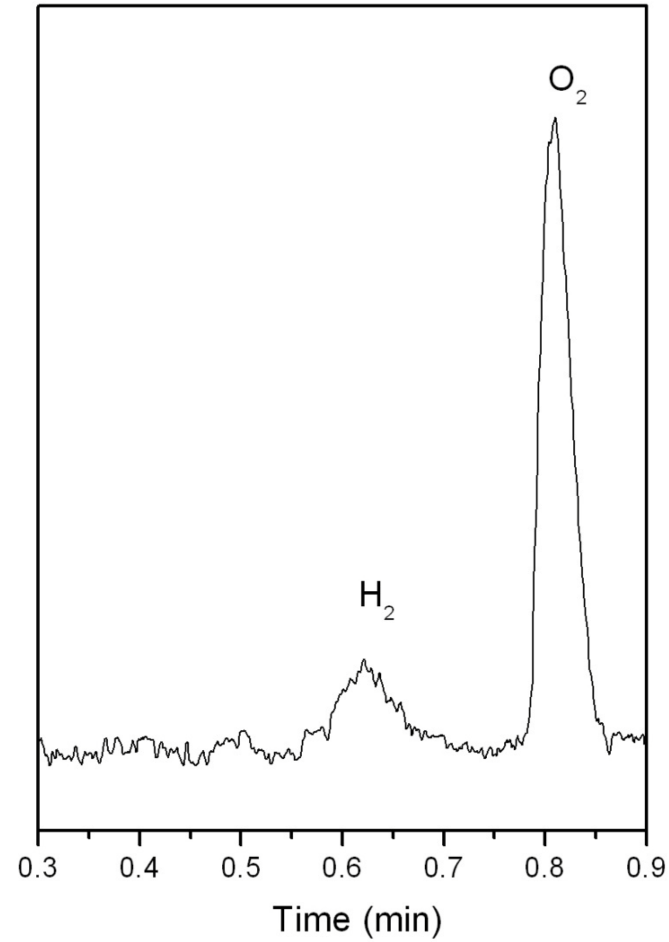
- XRD analysis was performed to identify the residue after the reaction
- Solid –salt mixture was washed several times with water and dried before analysis
- XRD suggests the formation of carbonaceous species possibly ordered structures as noted from the XRD peaks



New work

Product analysis - GC

- Hydrogen and oxygen peaks are detected together. Oxygen peaks are attributable to the leaks in the oven.
- In general
  - Hydrogen is detects upwards of 600 ^{0}C in the absence of catalyst in the salt mixture.
  - Hydrogen has been detected at lower temperatures with catalysts.



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 and s=surface)
  - The activation energy of dissociative adsorption of methane on transition metal surfaces:

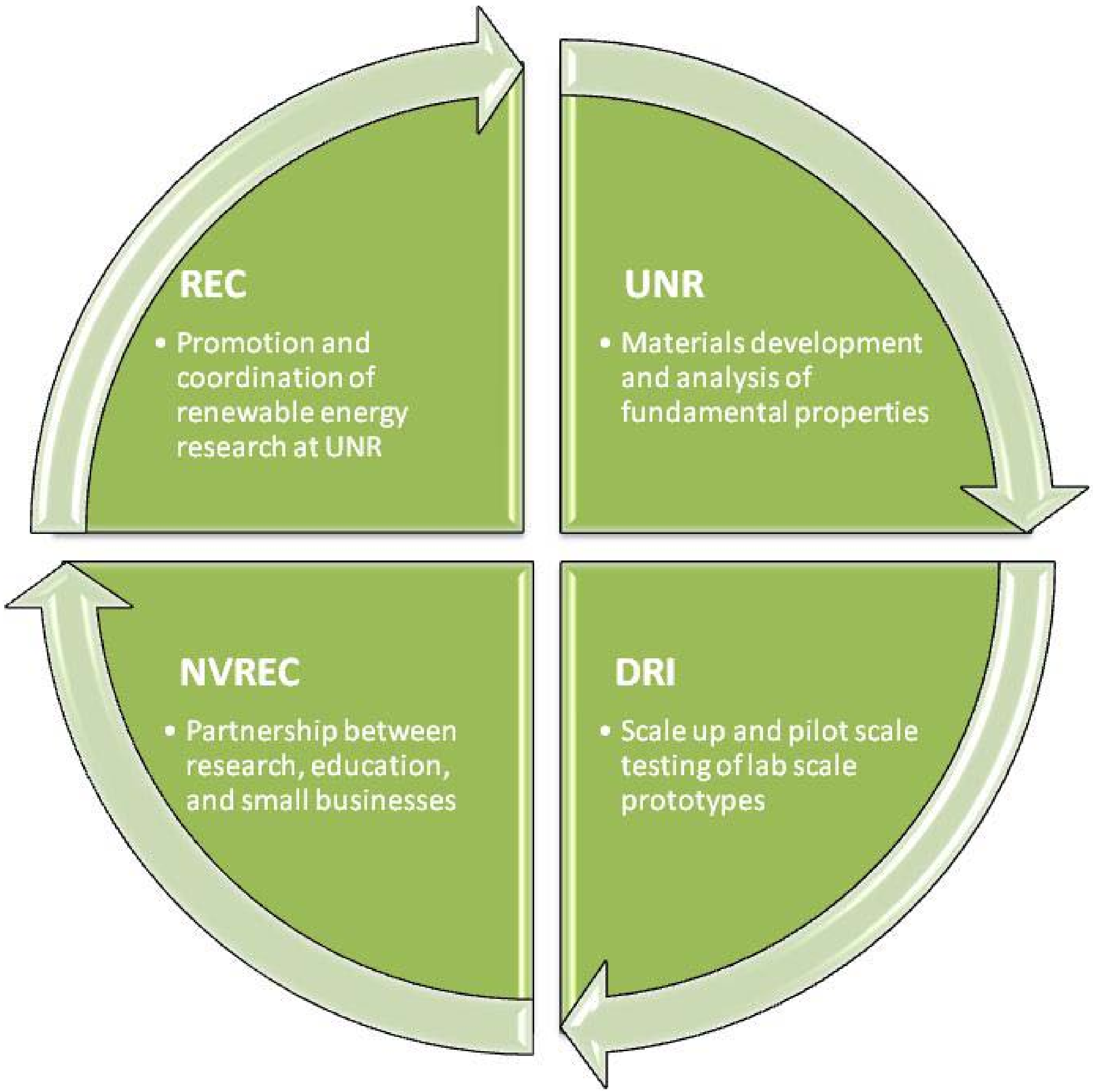
Metal	Activation Energy kJ/mol
Ni	52.6
Pt	71.6
Fe	158

- Results
  - The presence of Fe, Ni, and Co show hydrogen generation

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

- J. Molecular Catalysis.A: Chem 136 (1998) 185-194
- Appl. Catal. A. (2004) 135-144

Collaborations



This project is one of twelve 12 year one research projects under the DOE funded Nevada Renewable Energy Consortium

Summary

- Relevance – Examine feasibility of hydrogen production using solar heat simulated in a laboratory furnace
- This method can be a cost-effective heat storage media
- Approach – Proof of concept has been demonstrated using abundantly available molten salt and inexpensive metal catalyst as a media to store solar heat and produce Hydrogen on-demand
- The formation of carbon based products confirm catalytic cracking of methane
- Technical accomplishments – Results suggest that inexpensive metals such as Ni, Co, and Fe are very promising catalyst
- Reduction in hydrogen generation temperature up to 200° C can be achieved
- Collaboration
    - DRI – Alan Gertler, Kent Hoekman
    - UNR – Ravi Subramanian (experimental), Manoranjan Misra (NV-REC), Victor Vasquez (modeling)

This project is one of the 12 year one research projects under the DOE funded Nevada Renewable Energy Consortium

Proposed Future Work

Hydrogen generation using solar energy

- Solar thermal hydrogen generation
- Salt mixture modeling
- Salt mixture studies and hydrogen generation

Photocatalytic water splitting using visible light materials

- DFT modeling on multi-metal oxide phases
- Development of wet chemical methods for oxide synthesis