Local Hydrogen Production via Catalytic Reformation of Fossil and Renewable Feedstocks

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Start Date = June, 2002
Planned Completion = December, 2006

Research Goals and Objectives

- Develop an economically viable process for hydrogen production at the NASA-KSC site from natural gas and locally available renewable feedstocks (landfill gas, biomass) with minimal environmental impact.

- Develop novel efficient and durable catalysts for reformation of methane-containing feedstocks with production of high-purity hydrogen and value-added carbonaceous byproducts.

Relevance to Current State-of-the-Art

FSEC's technology offers several advantages over current state-of-the-art:

- **considerable reduction in greenhouse gas emissions**
- **production of value-added carbon byproducts: pyrolytic graphite, filaments, etc.**
- **smooth transition from fossil (NG) to non-fossil (renewable) feedstocks**
- **feedstock flexibility: practically any CH-containing feedstock could be utilized**

Relevance to NASA

- Research is needed to assess technical and economical feasibility of L-H_2 production at the NASA-KSC site
- Develop new hydrogen production technologies with minimal CO_2 emissions
- The technology could be used for distributed H_2 production (transportation)

Budget, Schedule and Deliverables

Budget (2004-2005): $250K

Schedule, Deliverables	Q-4 2004	Q-1 2005	Q-2 2005	Q-3 2005
Complete validation of autothermal pyrolysis of methane and down-select an efficient catalyst for the process				
Demonstrate production of high-value carbon products. Characterize carbon products, evaluate market for these products.				
Improve the process sustainability of methane pyrolysis (both autothermal and anaerobic regimes)				
Complete fabrication of 1 SCFM hydrogen production demo unit (catalytic reformer, gas conditioning system)				
Test 1 SCFM thermocatalytic hydrogen production unit at simulated operational conditions				

Anticipated Technology End Use

- On-site production of hydrogen from locally available feedstocks (natural gas, landfill gas, biomass waste)
- Hydrogen generators for distributed and portable power applications (in combination with fuel cells)
- Low Emission Alternative Power (LEAP), air-independent propulsion systems, UPS, soldier power
- Production of value-added carbonaceous products (AC, CB, pyrolytic graphite, carbon filaments)

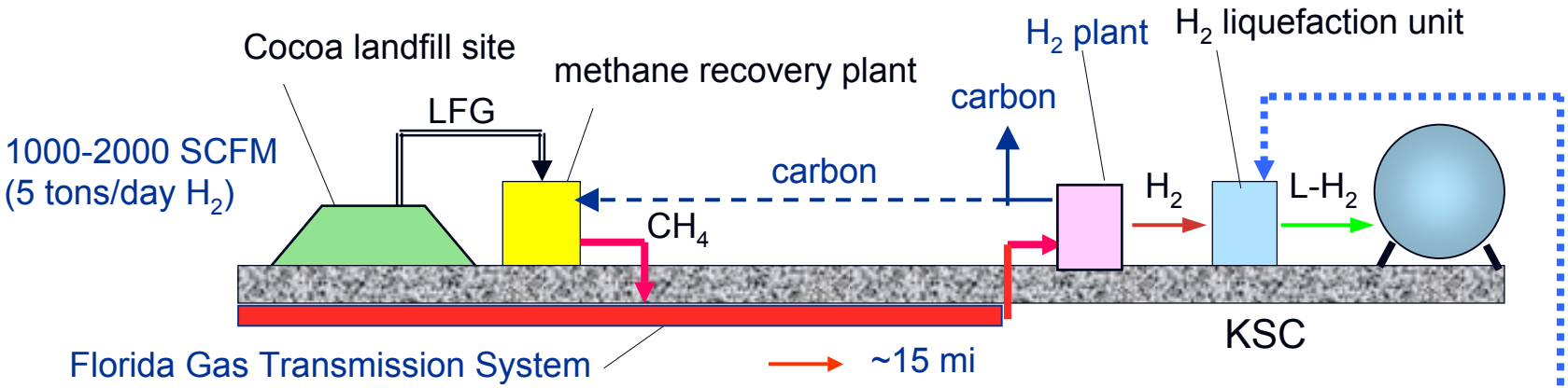
Accomplishments and Results

Summary:

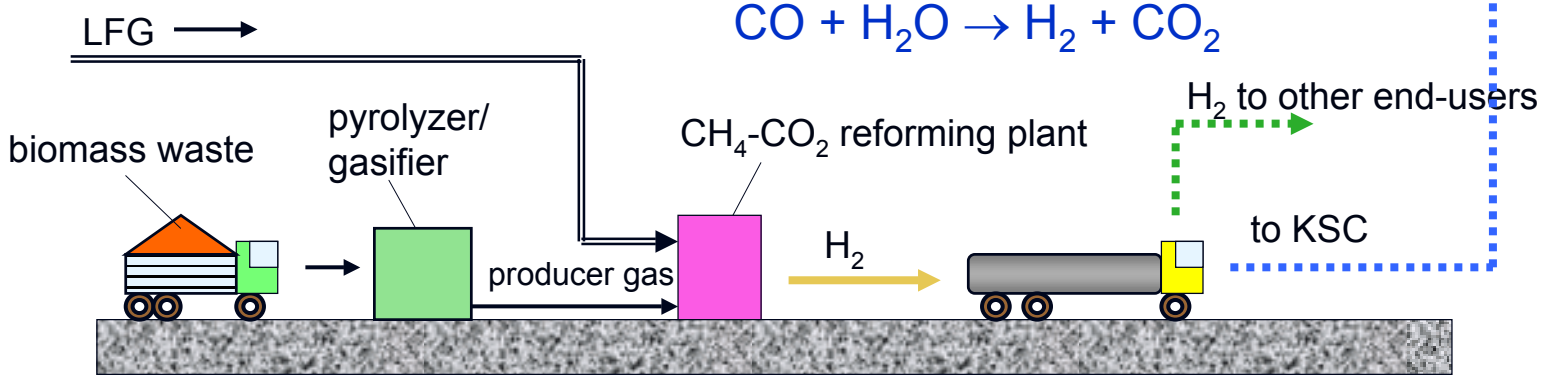
- Completed experimental validation of autothermal pyrolysis of methane. Down-selected an efficient carbon-based catalyst for the process.
- Demonstrated production of high-value carbon products (e.g., pyrolytic graphite, carbon filaments) via methane pyrolysis using novel carbon-based catalysts (un-doped and Fe-doped).
- Characterized carbon products and evaluated markets for these products.
- Improved the process sustainability of methane pyrolysis via in-situ generation of catalytically active nano-structured carbon aerosol particles (submitted patent disclosure)
- Completed fabrication of 1 SCFM hydrogen production demo unit (catalytic reformer, gas conditioning system)
- Tested 1 SCFM thermocatalytic hydrogen production unit in autothermal regime using gaseous mixtures mimicking the local landfill gas source.

Schematics of the Concept

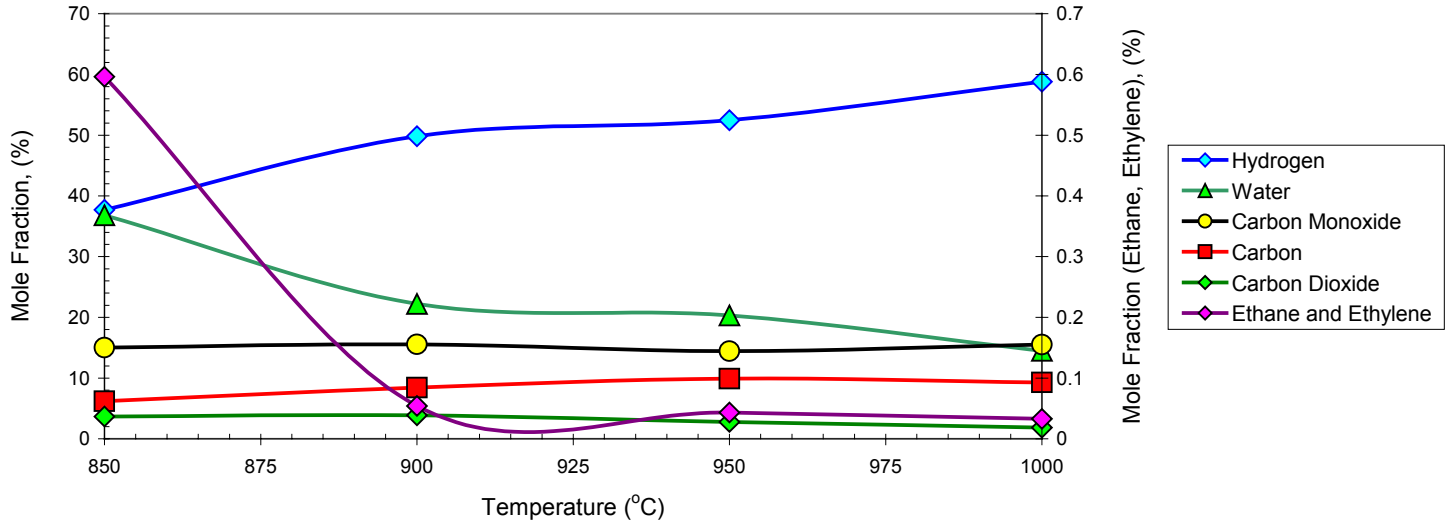
Option 1. CH_4 Pyrolysis $CH_4 \rightarrow C + 2H_2$

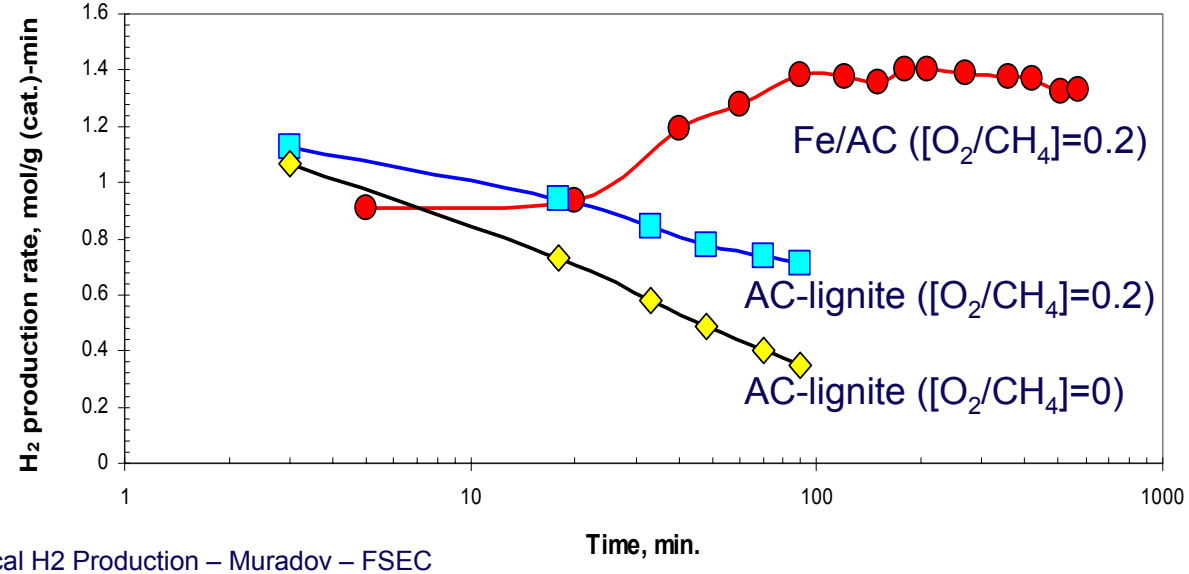


Option 2: Direct Reforming $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ $CO + H_2O \rightarrow H_2 + CO_2$



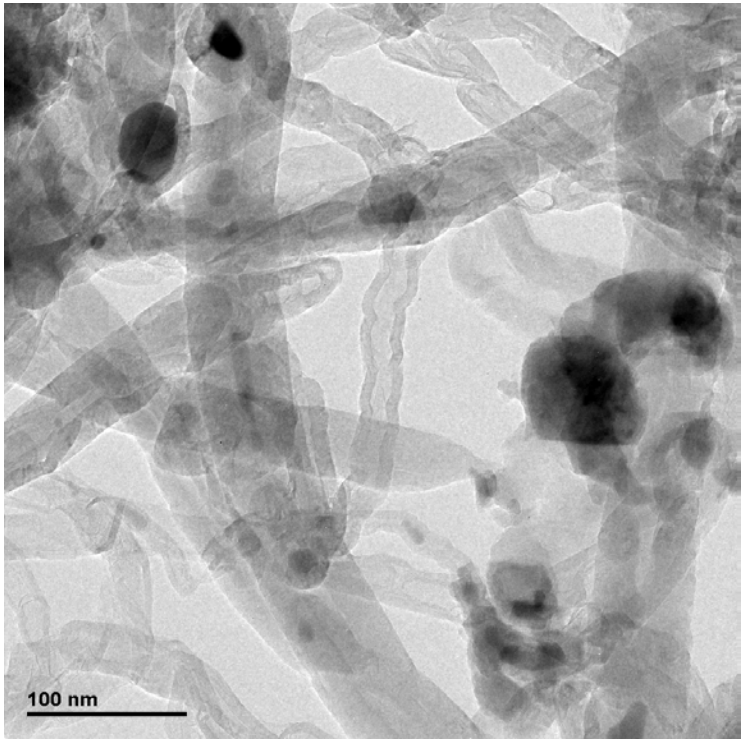
Autothermal Pyrolysis of Methane



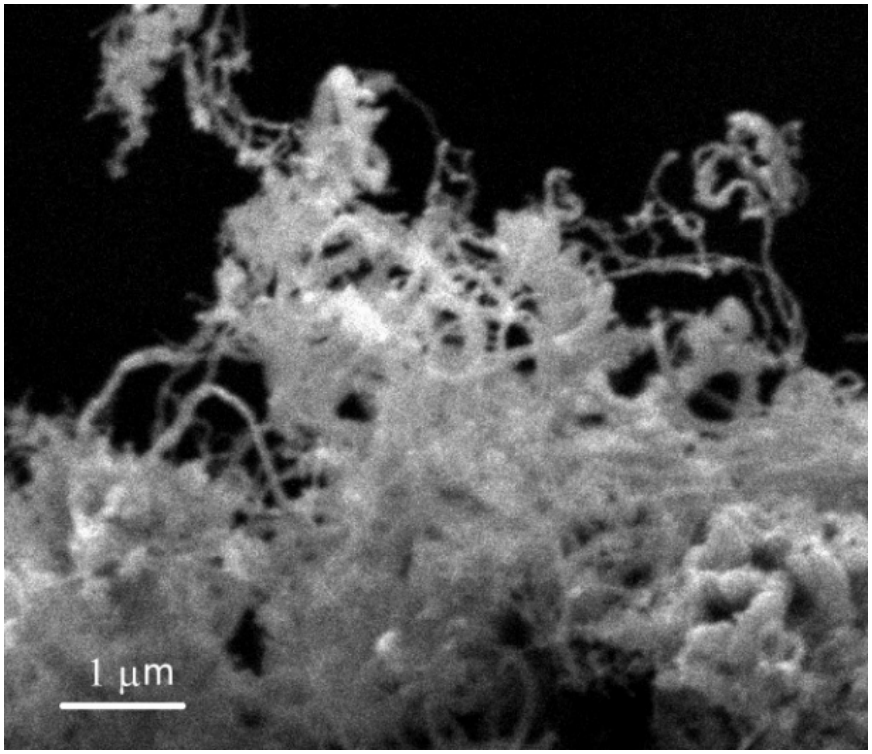


Carbon Products of CH_4 Pyrolysis

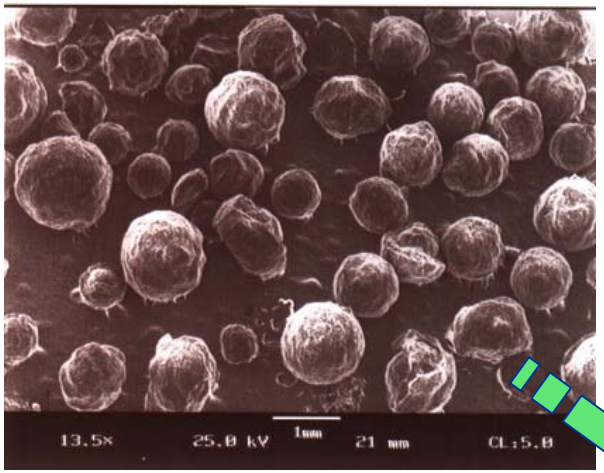
TEM image



SEM/FIB image



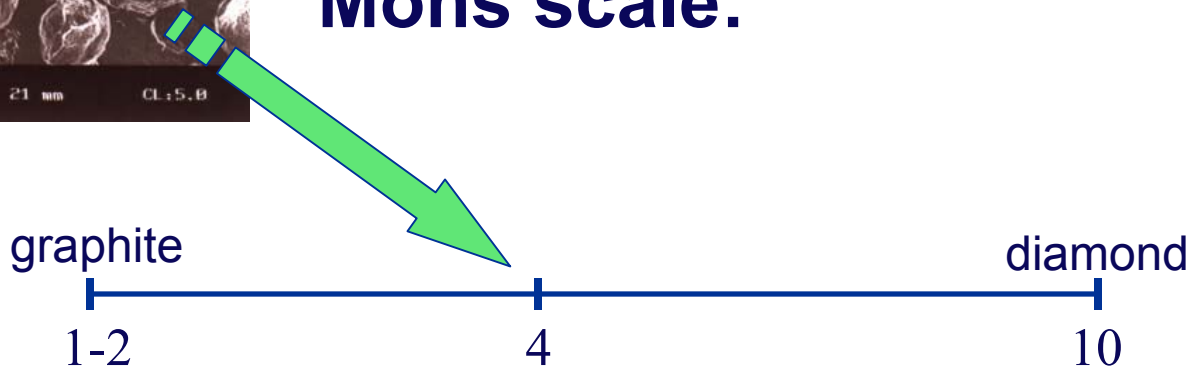
Testing of Carbon Products



Microhardness Test (Vickers method)*

HV = 184 (graphite: 12)

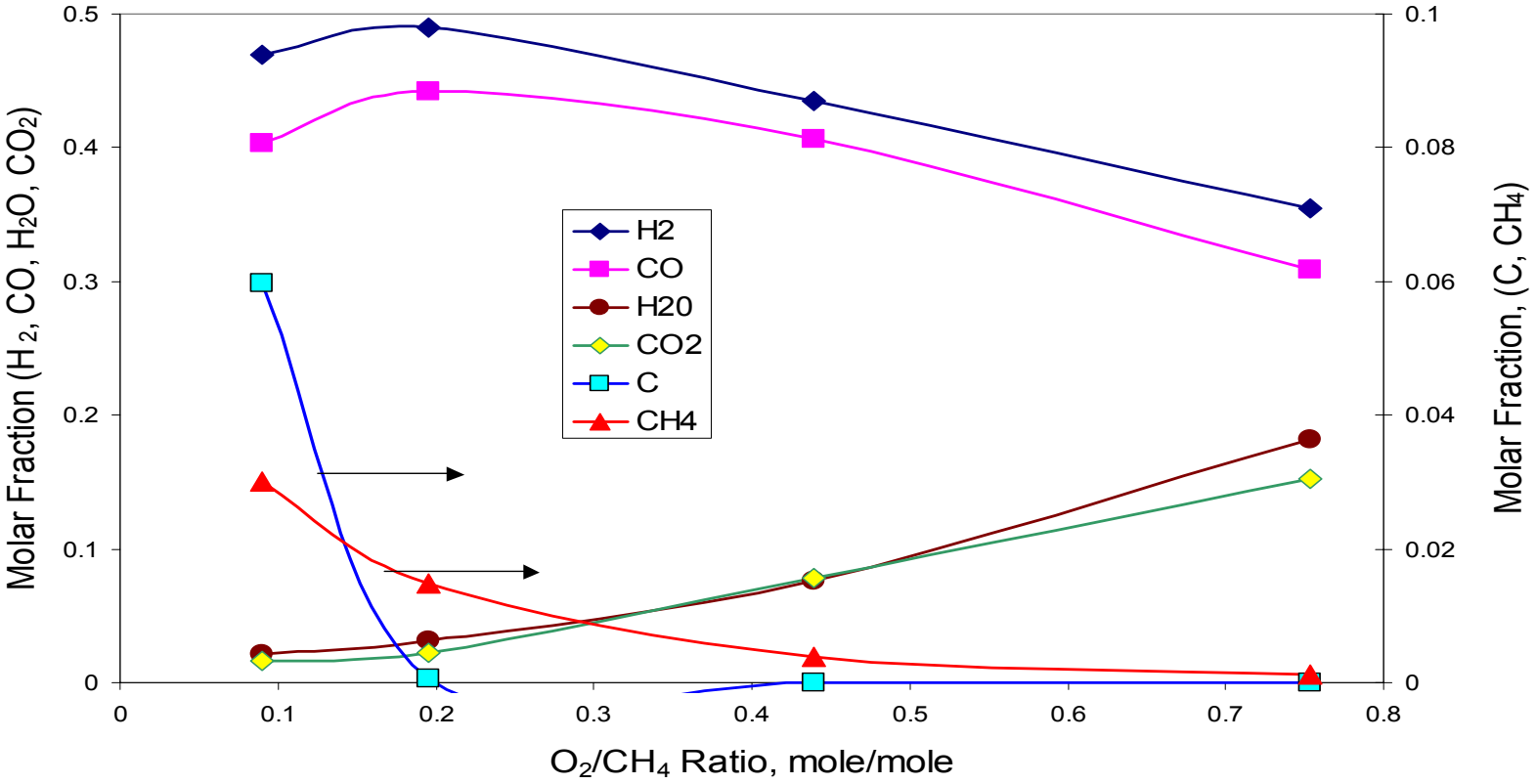
Mohs scale:



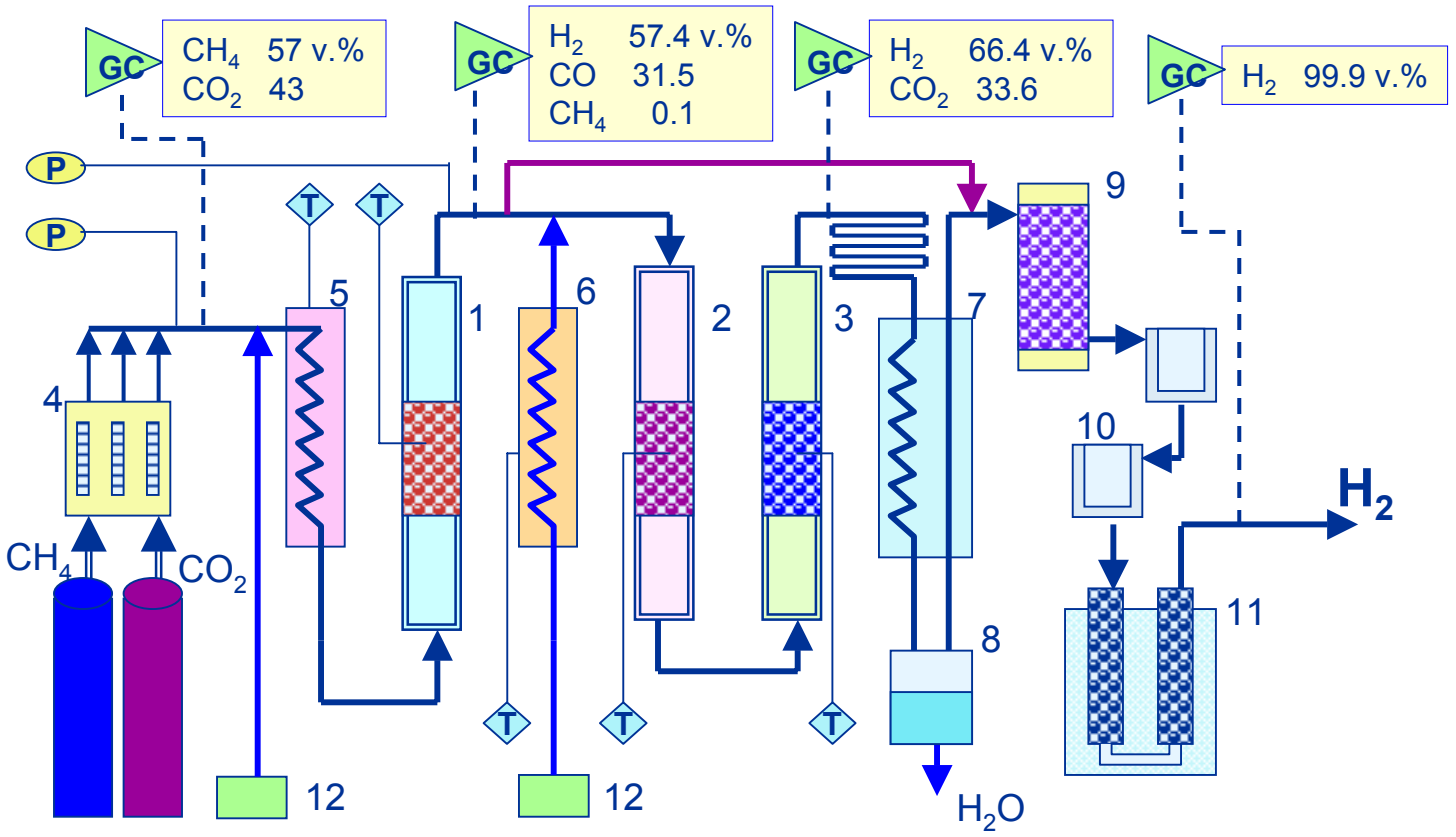
*Credits: Dr. F. Ebrahimi, Y. Wang (UF)

Autothermal Dry Reforming

$$CH_4 + CO_2 + \chi[O_2] \rightarrow 2H_2 + 2CO$$

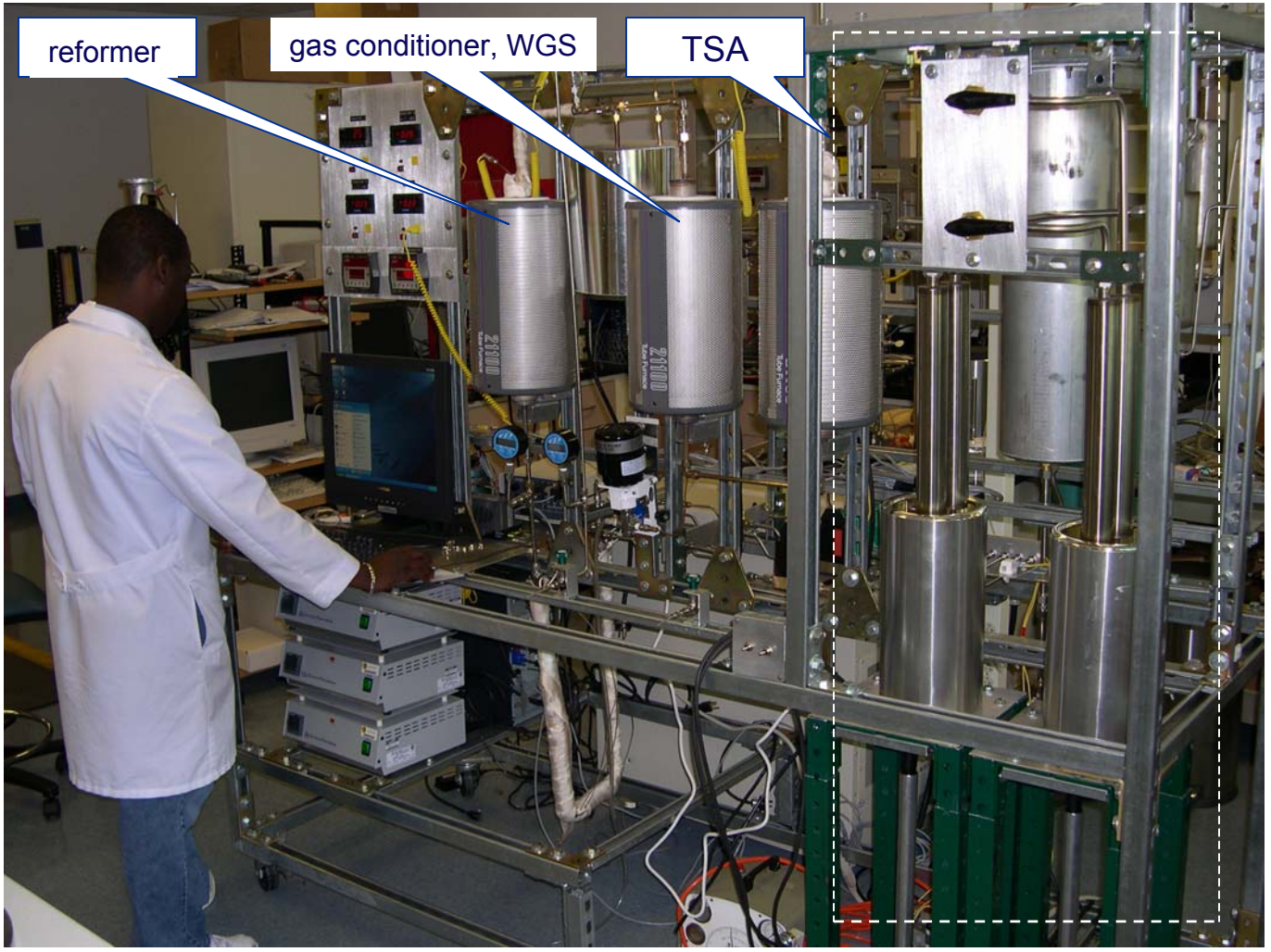


Schematics of 1 SCFM Hydrogen Production Unit



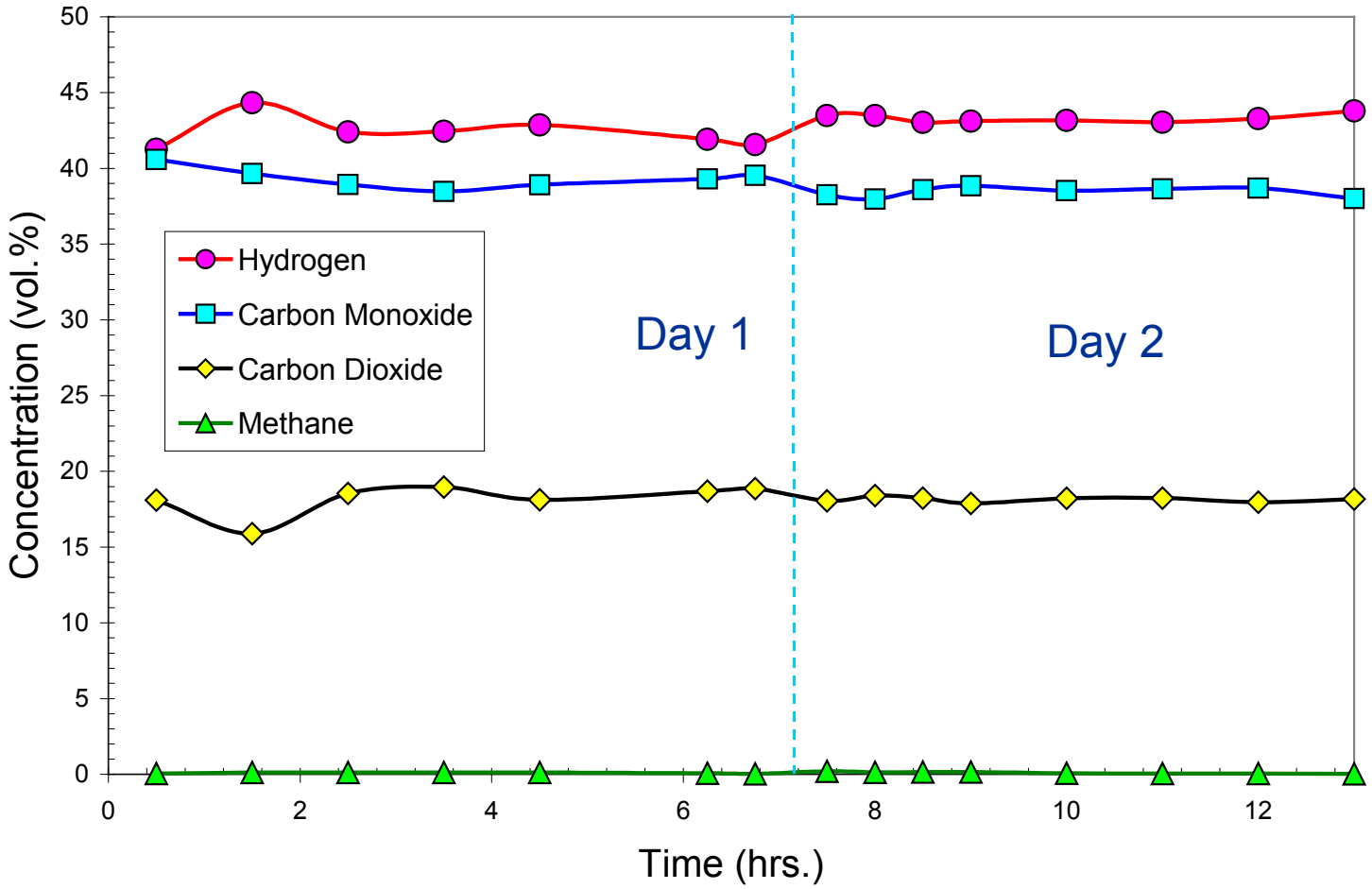
1- reactor (reformer), 2- HT shift reactor, 3- LT shift reactor, 4- gas metering system, 5- pre-heater, 6- steam generator, 7- condenser, 8- water collector, 9- adsorbent, 10- cryo-trap, 11- cryogenic adsorption system, 12- water pump.

1 SCFM Hydrogen Production Unit



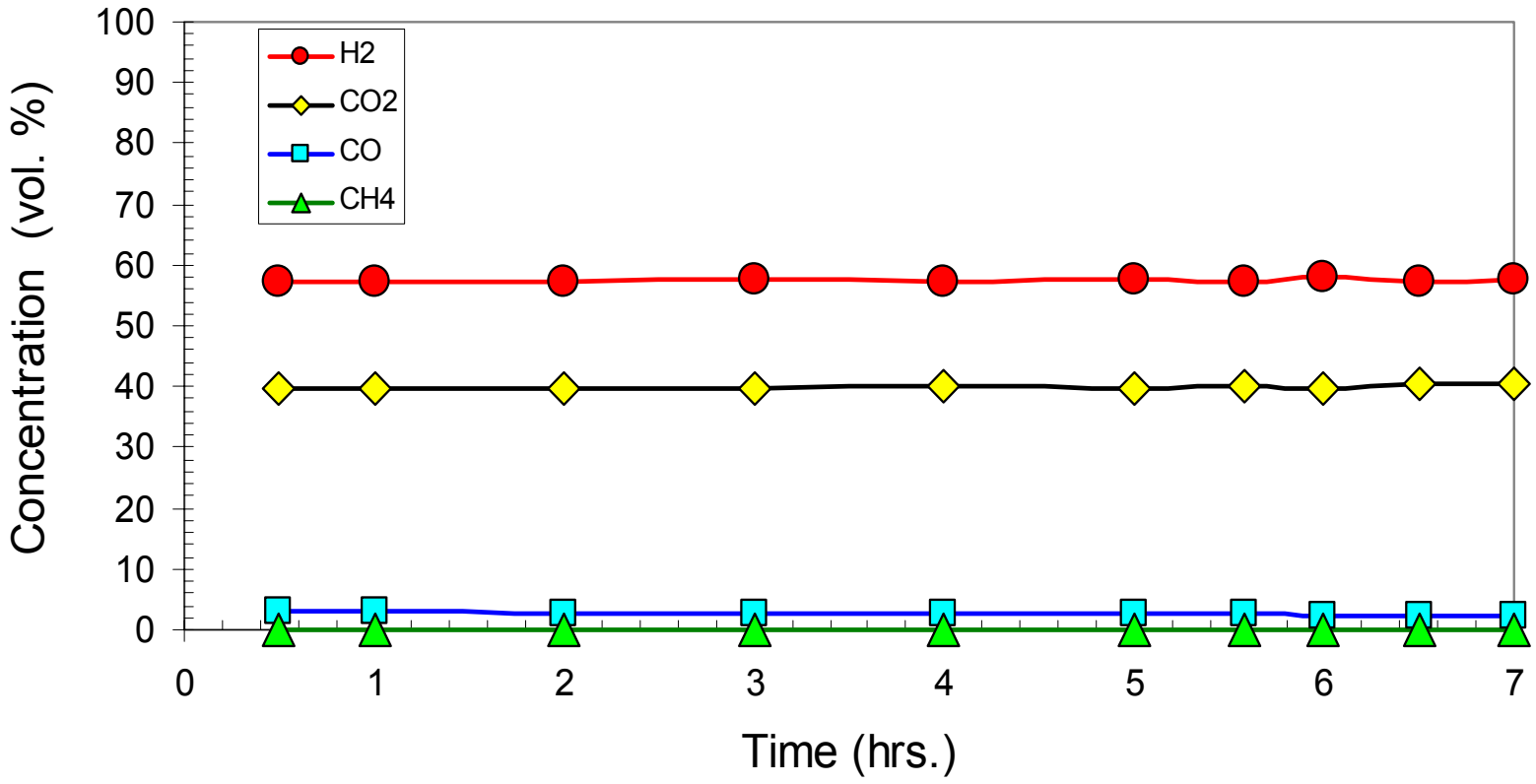
Testing 1 SCFM Unit (Reforming Stage)

CH_4:CO_2=1.3 mol., O_2:CH_4=0.7 mol., T=850°C

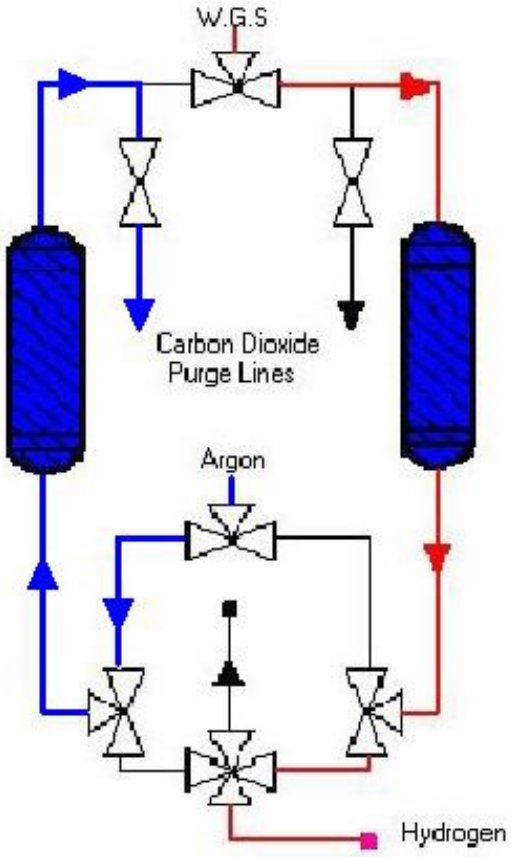


Testing 1 SCFM Unit (Water-Gas Shift Stage)

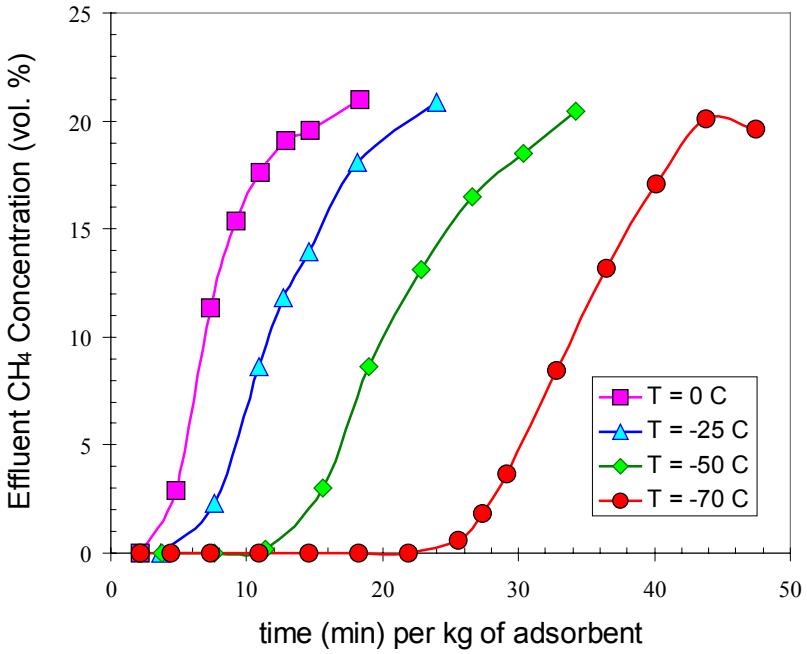
CH_4:CO_2=1.3 mol., O_2:CH_4=0.7 mol., T=850°C

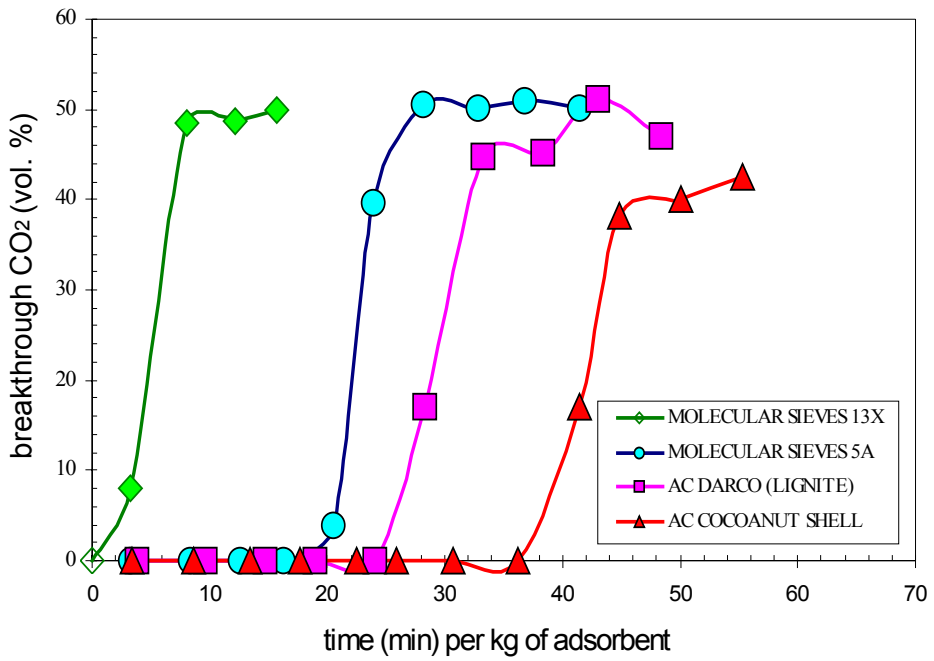


H_2 Purification Stage.
Temperature Swing Adsorption System



Separation of H_2-CH_4 and H_2-CO_2 Mixtures





H_2 purity achieved: 99.9 vol.%

Publications and Patents

- N. Muradov, F. Smith, A. T-Raissi, "Catalytic Activity of Carbons for Methane Decomposition Reaction", *Catalysis Today*, 102/103, 225-233 (2005)
- N. Muradov, Z.Chen, F.Smith, "Fossil Hydrogen with Reduced CO_2 Emission: Modeling Thermocatalytic Decomposition of Methane in a Fluidized Bed of Carbon Particles", *Intern. J. Hydrogen Energy*, 30, 1149-1158 (2005)
- N. Muradov, F. Smith, C. Huang, A. T-Raissi, "Autothermal Pyrolysis of Methane as a Novel Route to Production of Hydrogen with Reduced CO_2 Emissions", *2nd European Hydrogen Conference*, Saragossa, Spain, 2005
- N. Muradov, N. Veziroglu, "From Hydrocarbon to Hydrogen-Carbon to Hydrogen Economy", *Intern. J. Hydrogen Energy*, 30, 225 (2005)
- N. Muradov, F. Smith, C. Huang, A. T-Raissi, "Autothermal Pyrolysis of Methane over Carbon Catalysts", *Catalysis Today*, invited paper
- N. Muradov, F. Smith, C. Huang, A. T-Raissi, Decentralized Production of Hydrogen from Hydrocarbons without CO_2 Emission, 16th *World Hydrogen Energy Conf.*, Lyon, France, 2006
- N. Muradov, F. Smith, M. Elbaccouch, A. T-Raissi, Hydrogen Production via Catalytic Processing of Renewable Feedstocks, 16th *World Hydrogen Energy Conf.*, Lyon, France, 2006
- N. Muradov, F. Smith, A. T-Raissi, Process and Apparatus for Hydrogen and Carbon Production via Carbon Aerosol-Catalyzed Dissociation of Hydrocarbons, Patent disclosure submitted to UCF Patent Committee.

TOP25 articles within the journal:

International Journal of Hydrogen Energy

1. Co-production of hydrogen, electricity and CO"2 from coal with commercially ready technology. Part B: Economic analysis
International Journal of Hydrogen Energy, Vol. 30, Issue 7, Pages 769-784

2. From hydrocarbon to hydrogen-carbon to hydrogen economy
Muradov, N., Veziroglu, N.
International Journal of Hydrogen Energy, Vol. 30, Issue 3, Pages 225-237

Future Plans

- Improve sustainability of catalytic methane pyrolysis by using in-situ generated carbon aerosol particles. Increase the yield of high-value carbon products.
- Continue characterization of carbon byproducts, evaluate potential application areas
- Field-test 1 SCFM hydrogen production demo unit at simulated operational conditions
- Increase throughput and optimize hydrogen purification unit (TSA system)
- Conduct system optimization, integration and scale-up studies for on-site hydrogen production.

Thank you.