THERMOCATALYTIC CO_2-FREE PRODUCTION OF HYDROGEN FROM HYDROCARBON FUELS

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Relevance/Objective:

Objective: To develop an economically viable process for centralized and distributed production of hydrogen and carbon from hydrocarbon fuels with minimal CO_2 emissions.

Relevance to DOE/FreedomCAR/ Hydrogen technical targets and barriers

(From Table 4.1.1.) Distributed Production of H_2 from Natural Gas and Liquid Fuels

Characteristics	Units	2003 Status	2005 Target	2005, Expected
Cost	$/kg H_2	5.06	3.00	2.50 - 3.00*
Primary energy efficiency	%(LHV)	62	68	70**

* If carbon sold at >$0.30 /kg

** Total energy efficiency

4.1.3.2.1 (D) **CO_2 Emissions.** It is significantly more challenging to cost effectively sequester these [distributed] smaller volume carbon emissions than at central hydrogen production facilities that use fossil fuels. This production route should remain limited …. until some cost effective carbon sequestration option for distributed production is discovered.

Approach

The approach is based on thermocatalytic decomposition (TCD) of hydrocarbons over carbon-based catalysts in an air/water-free environment:

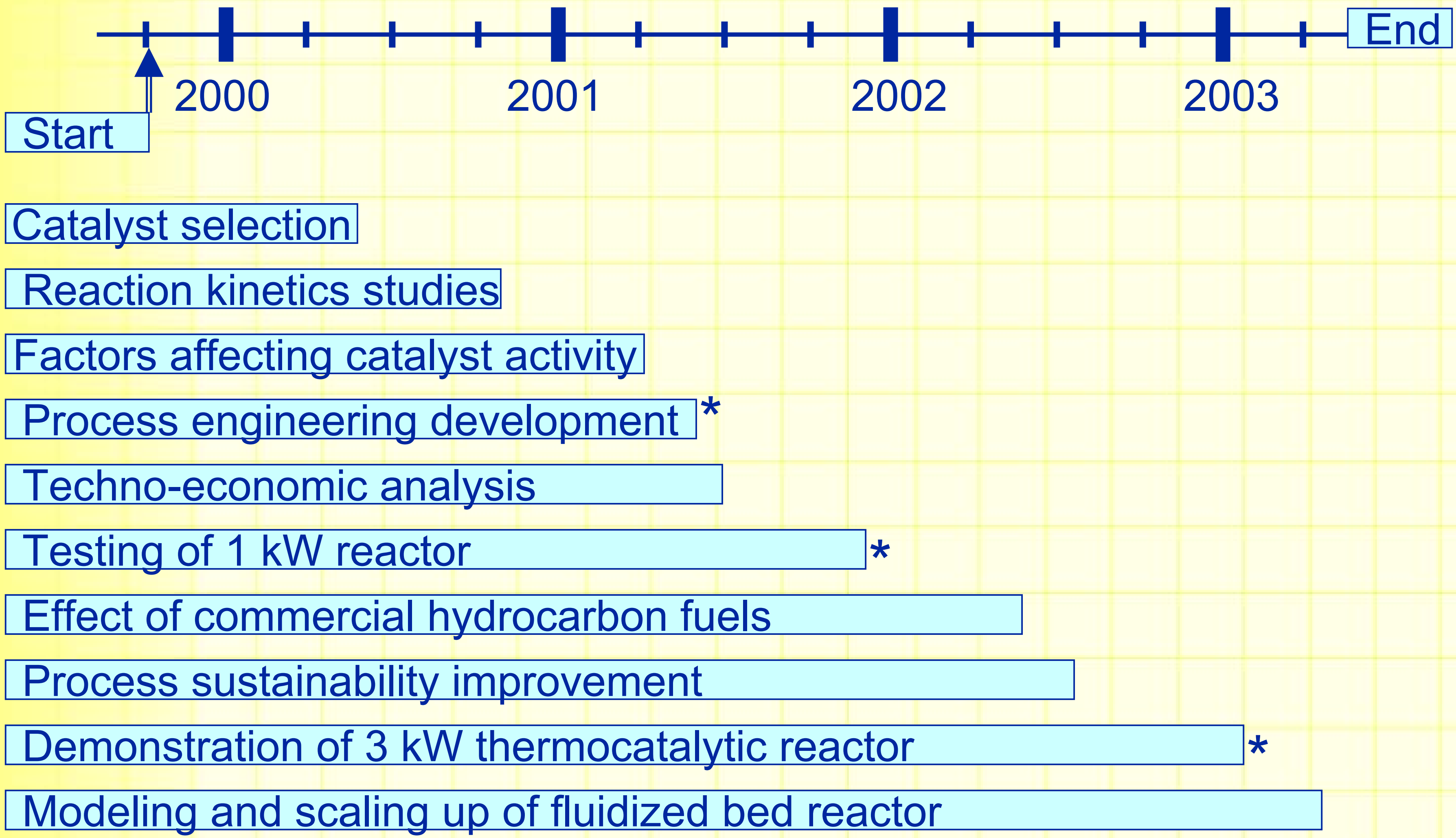
$$CH_4 \rightarrow C + 2H_2 \qquad (38\ \text{kJ/mol } H_2)$$

For comparison: $CH_4 + 2H_2O_{liq} \rightarrow CO_2 + 4H_2$ (63 kJ/mol H_2)

Advantages:

- The reaction is catalyzed by carbon particulates produced in the process (no external catalyst is required).
- No CO/CO_2 byproducts are generated during hydrocarbon decomposition stage. CO_2 emissions from the process could be drastically reduced (compared to conventional processes).
- The process produces several valuable forms of carbon that can be sold thus reducing the cost of hydrogen production.

Project Timeline



*critical milestones

Accomplishments

- Catalyst activity / stability and process sustainability
  - Effect of moisture
  - Effect of sulfur
  - Carbon catalyst activation
- Demonstration of 3 kW thermocatalytic reactor
  - Effect of commercial hydrocarbon fuels
  - Testing of 3 kW reactor
- Modeling and scaling-up of fluidized bed reactor
- Assessment of market and application areas for carbon products

Effect of Moisture

- The presence of moisture ($\leq$ 2.0 v.%) in methane feedstock improves catalyst activity and stability.

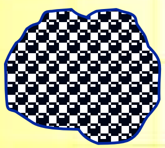
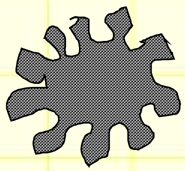
- The improvement results from the increase in surface area of carbon catalyst (via surface carbon gasification)

- The presence of moisture causes contamination of H_2 with carbon monoxide at the level of 0.1-0.5 v.%

- The concentration of CO could be decreased to 10 ppm level by subsequent methanation reaction:

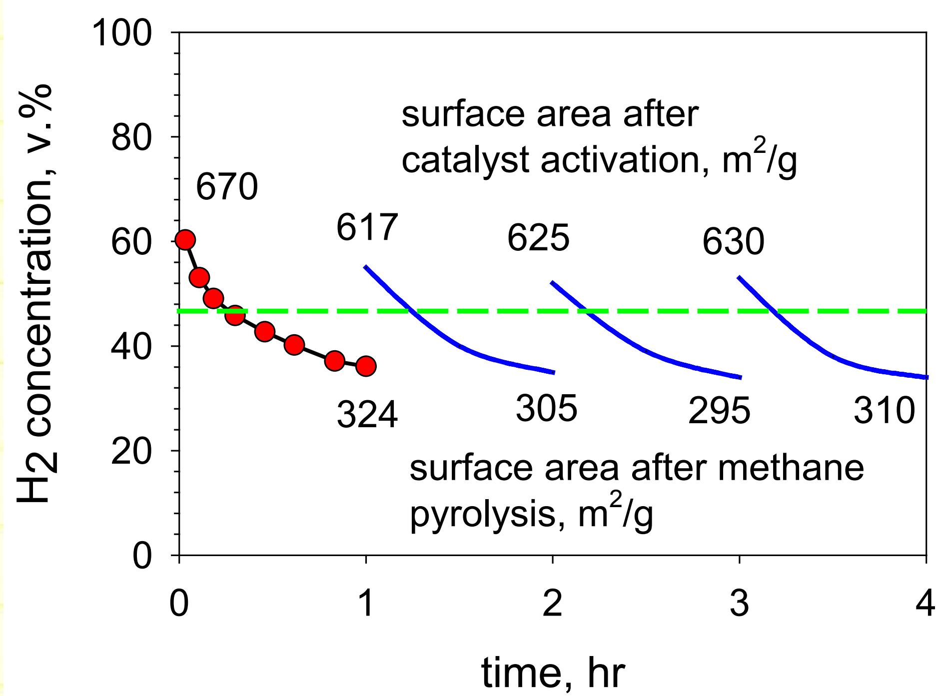
$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (Ru\text{-}0.5\%/Al_2O_3,\ 350^{o}C)$$

Activation of Carbon Catalyst

 $+ \; H_2O, \; CO_2, \; O_2 \rightarrow$  $+ \; H_2, CO, CO_2$

carbon
particle

Cyclic Activation of Carbon Catalyst with Steam, 900°C



Activation reactions:

$C + H_2O \rightarrow H_2 + CO$

$C + CO_2 \rightarrow 2CO$

$C + O_2 \rightarrow CO_2$

Activating ability:

$H_2O > CO_2 > O_2$

Effect of Sulfur

- H_2S does not adversely affect the activity and stability of carbon catalysts at 800-900°C (at $[H_2S] \leq 2.5$ v.% in CH_4)

- Carbon catalyst remains free of sulfur compounds

- Reactions of H_2S in the system:

$$\left.\begin{array}{l} H_2S \rightarrow H_2 + 1/2S_2 \text{ (catalyzed)} \\ 2H_2S + C \rightarrow 2H_2 + CS_2 \end{array}\right\} H_2S \text{ conversion } 50\%$$

- Conversion of H_2S in presence of CO_2:

$$H_2S + CO_2 \rightarrow H_2, CO, S_2, H_2O \text{ (COS)} \quad (95\%)$$

Testing of 3 kW Unit Using Pipeline NG

Experimental Set-up with 3 kW Reactor

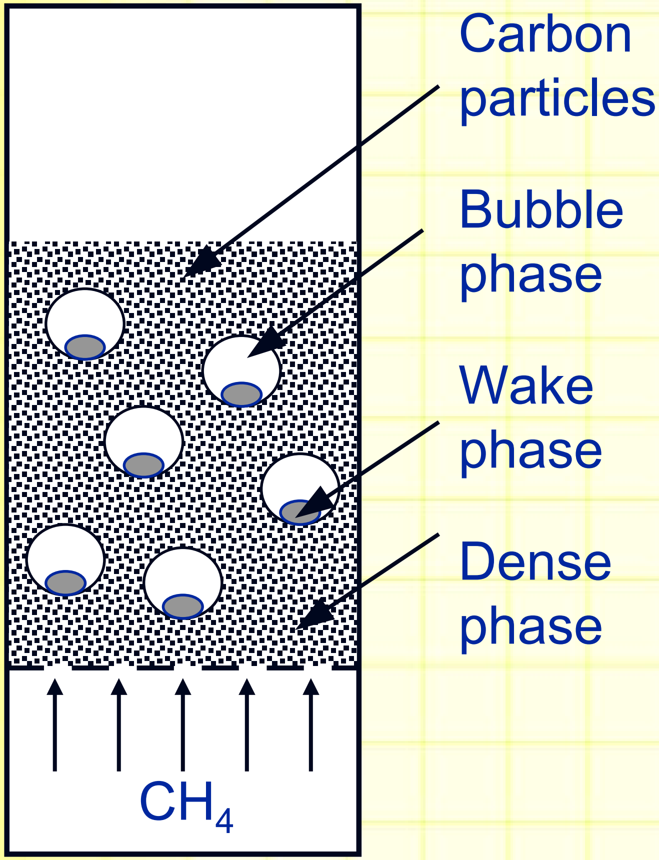
NG, v.%:	
N_2-	0.9
CH_4-	93.1
C_2H_6-	4.1
C_3H_8-	0.7
C_4+-	0.3
CO_2-	0.9
CH_3SH-	4 ppm

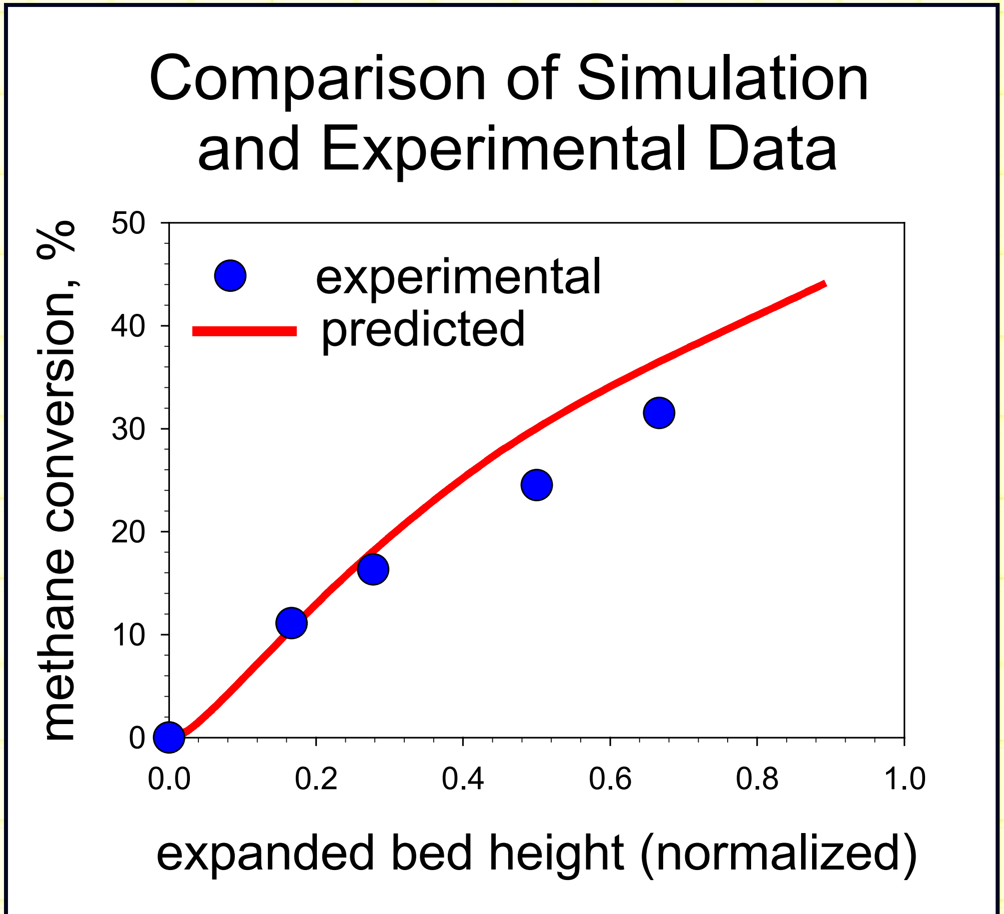
Feedstock	T, °C	Composition of gaseous products, v.%					
		H_2	CH_4	C_2H_6	C_2H_4	CO	CO_2
Pipeline Natural Gas	870	45.5	53.6	0.0	0.0	0.7	0.1
Commercial Propane	850	61.8	30.4	2.1	5.1	0.1	0.0

Modeling of Fluidized Bed Reactor (FBR) for Catalytic Decomposition of Methane

(in cooperation with REI)

Three-phase model for FBR (bubbling regime):

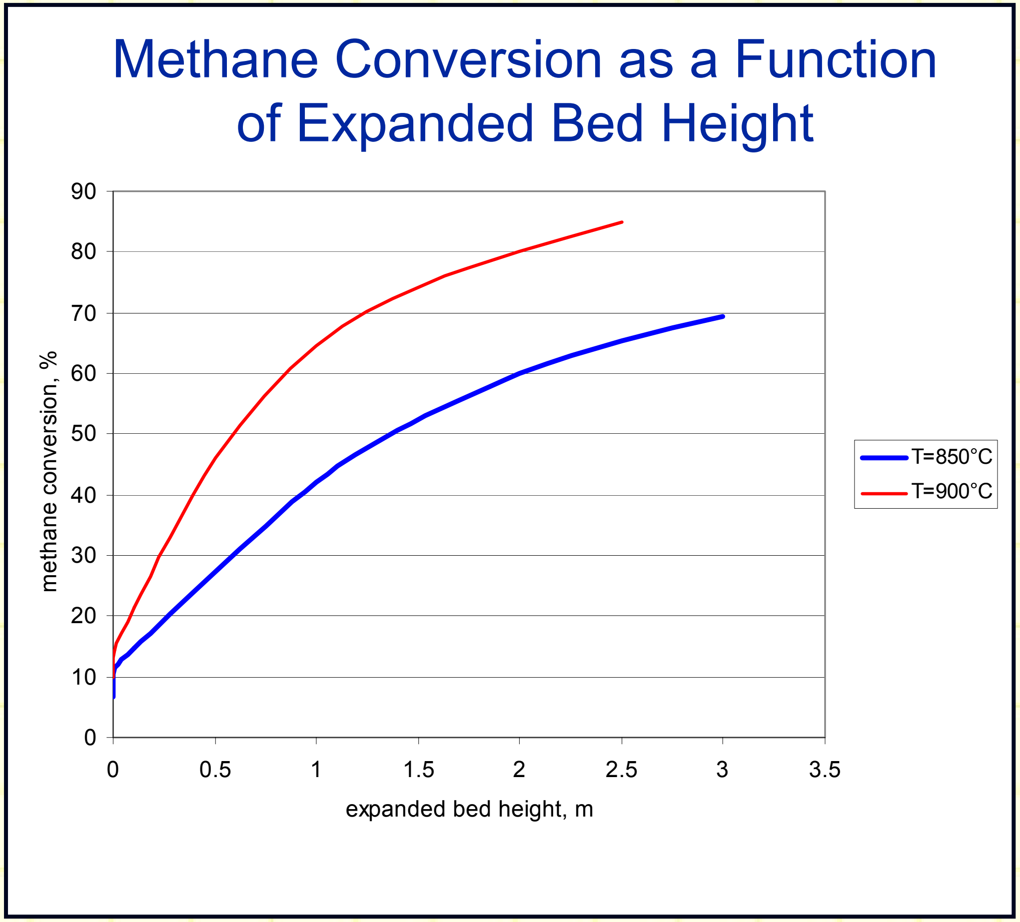




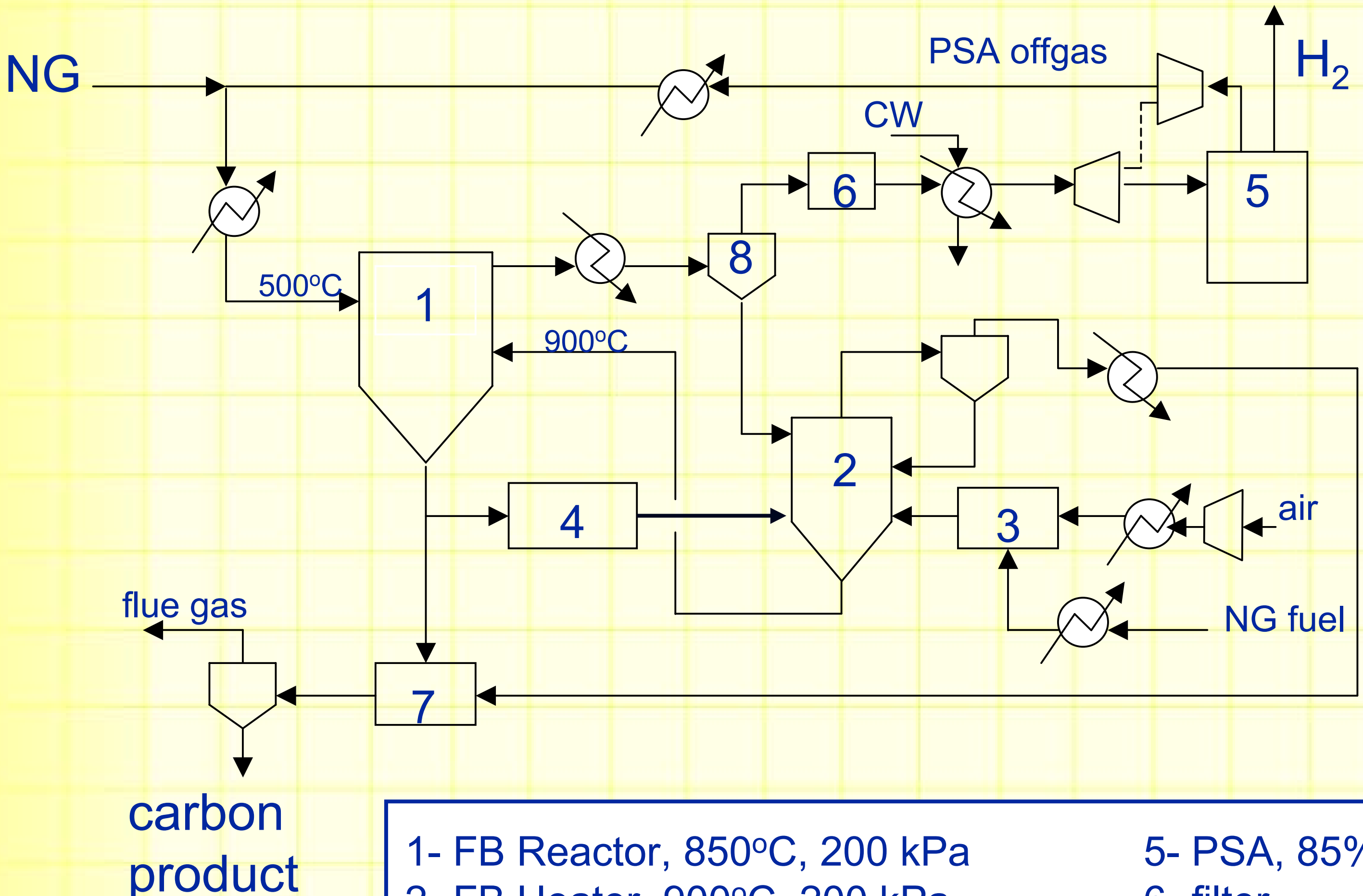
Modeling and Scaling-up of FBR for Catalytic Decomposition of Methane
(in cooperation with REI)

Large scale H_2 plant:
50 t/day H_2
109 t/day Carbon
FB reactor diameter:
Bubbling regime- 4.2 m
Turbulent regime- 2.1 m

Small scale unit:
500 kg/day H_2
1090 kg/day Carbon
FBR diameter: 0.5 m
FBR height: 4.2 m



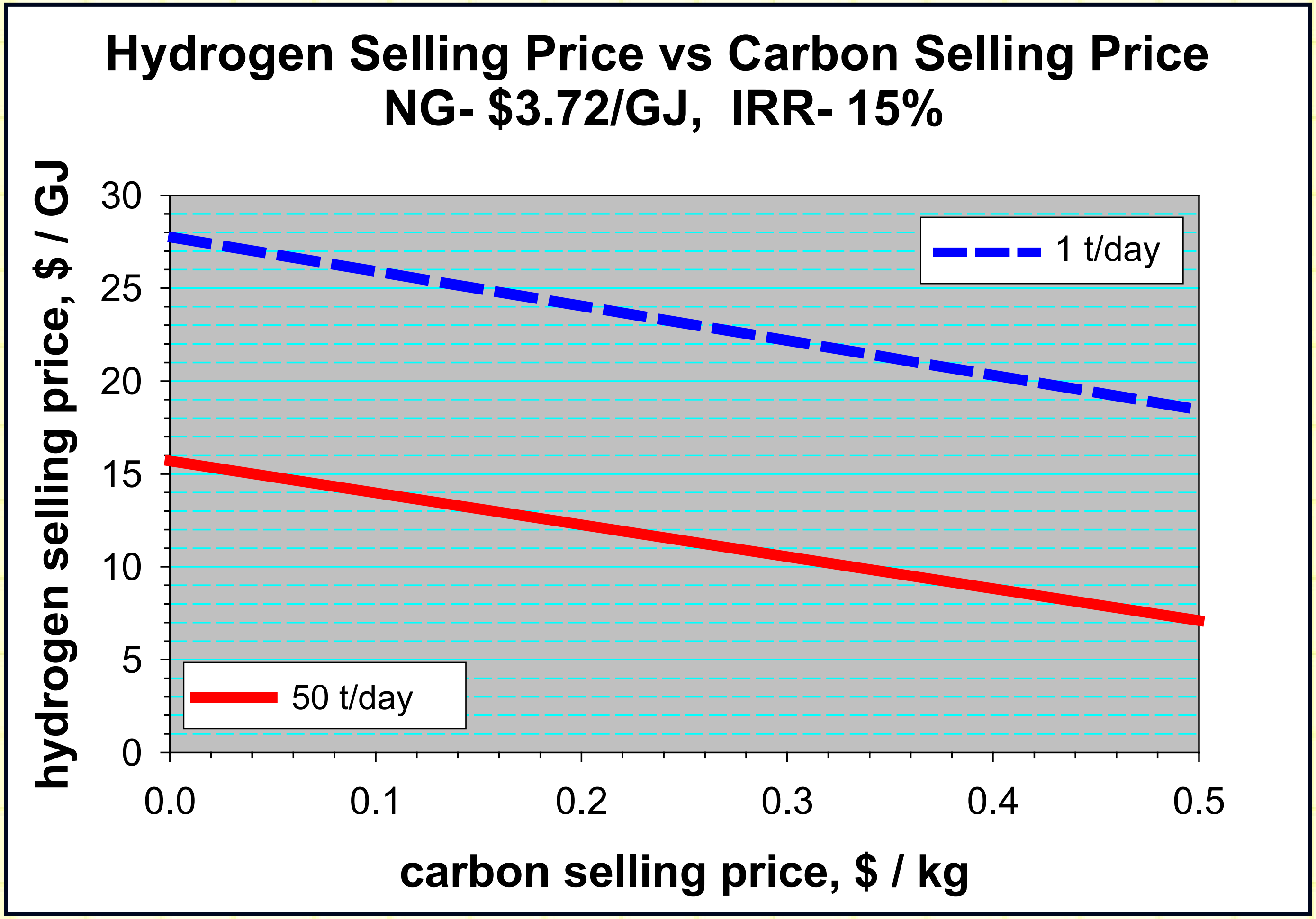
Process Flowsheet for Thermocatalytic Decomposition of Natural Gas
(in cooperation with NREL)



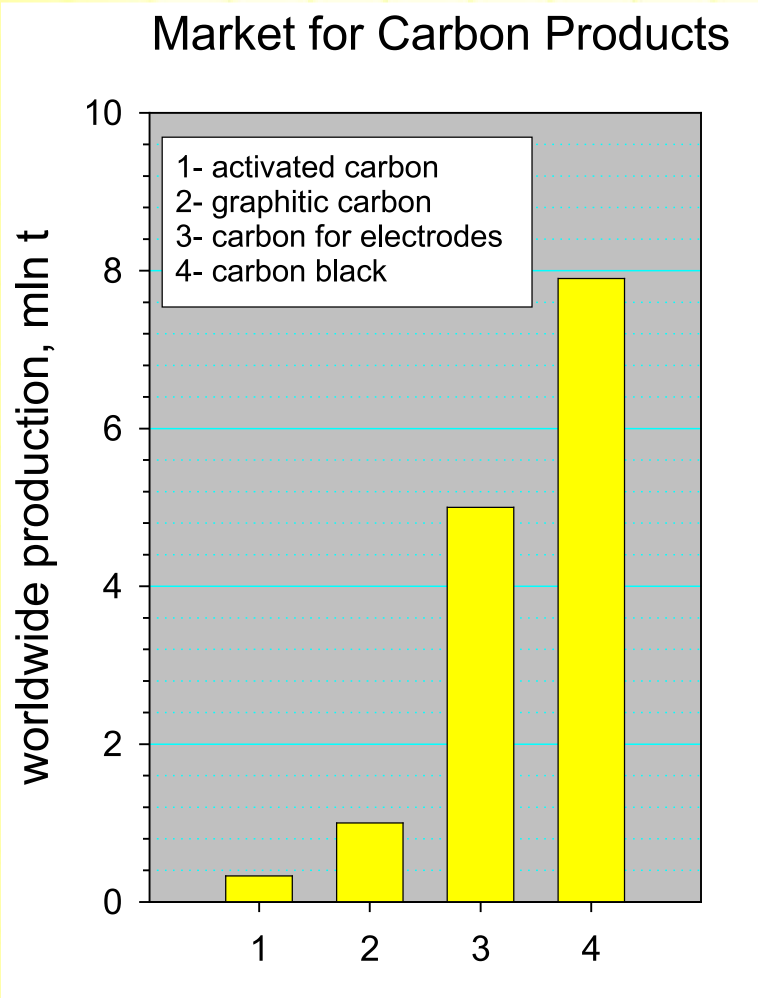
- 1- FB Reactor, 850°C, 200 kPa
- 2- FB Heater, 900°C, 200 kPa
- 3- combustor, 1250°C, 200 kPa
- 4- grinder
- 5- PSA, 85% H_2 recovery
- 6- filter
- 7- quencher
- 8- cyclones

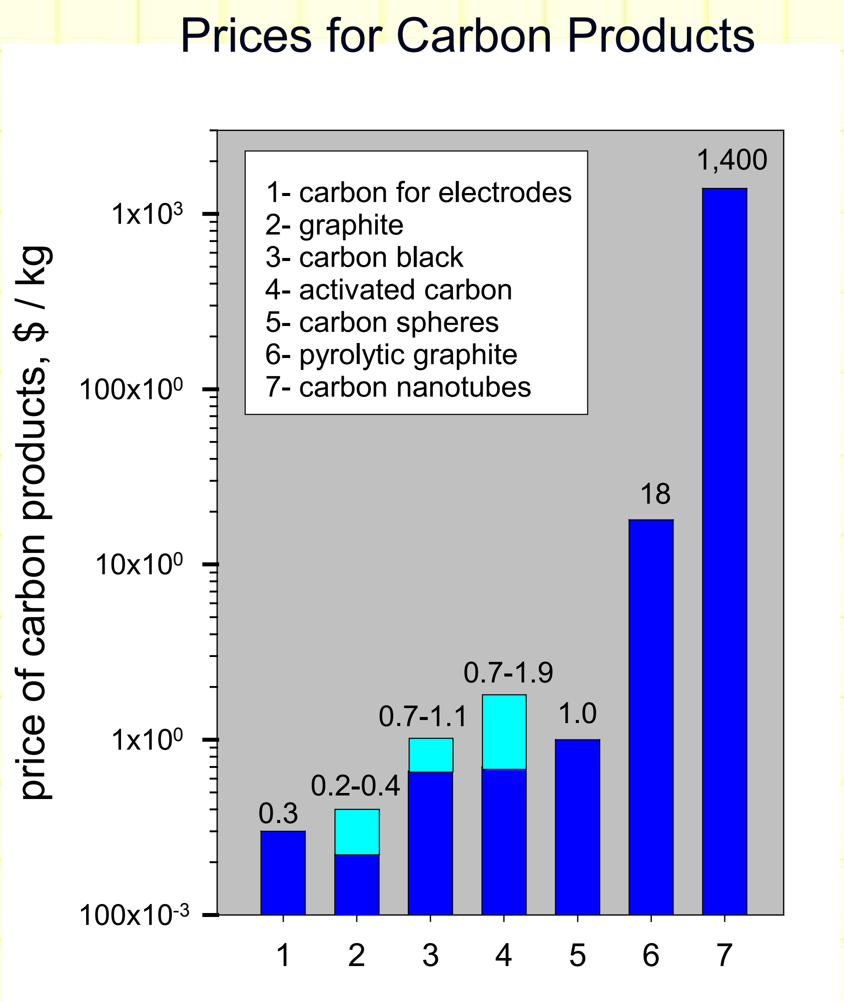
Techno-economic Analysis

(in cooperation with NREL)



Market for Carbon Products





Publications, Patents

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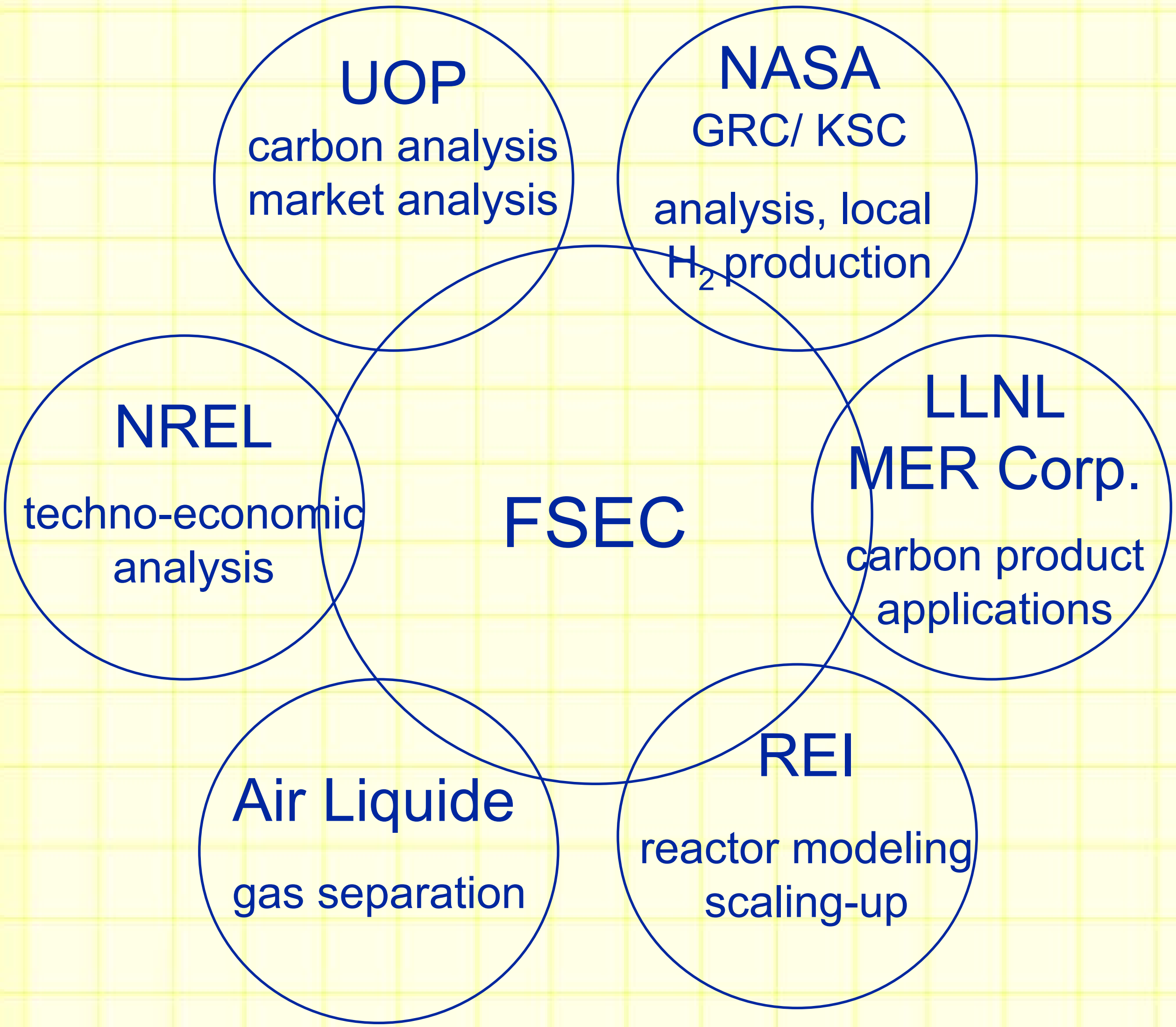
2. Muradov, N. *Symposium: Hydrogen Energy for 21st Century, Amer. Chem. Soc. Meeting,* New Orleans, 2003
3. Muradov, N. *Symposium: Fuel Clean-up Considerations for Fuel Cells, Amer. Chem. Soc. Meeting*, *Petroleum Division*, New Orleans, 2003
4. Muradov, N., T-Raissi, A. *HYPOTHESIS-V Symposium*, Porte Conte, Italy, 2003
5. Muradov, N., Schwitter, A. *Nano Letters*, v.2, No.6, 673, 2002
6. Muradov, N. *Fuel Cells Science and Technology,* Amsterdam, Netherlands, 2002
7. Muradov, N. *14th World Hydrogen Energy Conference*, Montreal, Canada, 2002
8. Muradov, N., Noland, G., Manikowski, A. *14th World Hydrogen Energy Conference*, Montreal, Canada, 2002
9. Muradov, N. *U.S. Patent Appl. No. 60/194,828 (2002)*
10. Muradov, N. *U.S. Patent Appl. No. 60/203,370 (2002)*
11. Muradov, N. *U.S. Patent Appl. No. 60/346,548 (2003)*

Interactions / Collaborations



Plans, Future Milestones

Task	Milestones	
1	Optimize the performance of pyrolytic reformer coupled with a gas clean-up system for distributed production of hydrogen with concentration of CO and H_2S below 25 ppm	2004, Q1
2	Increase the yield of high-value carbon products (>$1/kg) (preferably, for construction materials applications)	2004, Q3
3	Determine the feasibility of using alternative feedstocks for the pyrolysis reformer (including biomass-based feedstocks)	2004, Q4
4	Optimize the reformer for the increased energy efficiency (total energy efficiency of 70%) and reduce cost of H_2 production to $2.50-3.00/kg H_2	2005, Q2

Responses to Reviewers' Comments

- ❖ Carbon Catalytic Activity Measurements

Catalytic activity of carbon samples toward methane decomposition was determined on the basis of both mass and surface area.

- ❖ Carbon Utilization Issues

Since carbon represents half of methane fuel value, carbon should be used for:

- ➢ additional hydrogen production via steam gasification, or
- ➢ power generation (as an ultra-clean coal substitute)

Determine whether the efficiency and CO_2 reduction are improved compared to conventional SMR

Responses to Reviewers' Comments (cont.)

Comparative Assessment of Three Scenarios:

(A) Steam Methane Reforming (SMR)
(B) TCD coupled with steam gasification of carbon
(C) TCD coupled with carbon combustion (power generation)

- Scenario (B) does not offer any advantages over SMR:

$CH_4 \rightarrow C + 2H_2$
$C + 2H_2O \rightarrow CO_2 + 2H_2$
Total: $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

- Scenario (C) can be justified if TCD is coupled with direct carbon fuel cell:

$CH_4 \rightarrow C + 2H_2$
$C + O_2 \rightarrow CO_2$ (MCFC, efficiency 80%)
Total: $CH_4 + O_2 \rightarrow CO_2 + 2H_2 + \text{electricity}$