

# **HYDROGEN FROM BIOMASS FOR URBAN TRANSPORTATION**

## **Collaborating Project Team**

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**Hydrogen, Fuel Cells and Infrastructure Technologies Program Review Meeting**

**Berkeley, CA**

**May 18-22, 2003**

# ABSTRACT

Hydrocarbon fuels produce emissions during combustion that cause pollution. From the standpoint of heating value per unit mass and emissions, hydrogen is the best fuel producing only water when combusted. However, hydrogen does not occur naturally in appreciable quantities and the current cost of producing it makes it less economical than other fuels for most applications. This poster summarizes the progress on the DOE funded pilot-scale project aimed at producing 25 kg/day hydrogen from biomass, such as peanut shells, for urban transportation. The process involves pyrolysis of the biomass followed by catalytic steam reforming of the gas and bio-oil products to produce H<sub>2</sub> at \$2.90/kg H<sub>2</sub> by 2010 and \$2.30 by 2015.

Successful operation for 100 hours demonstrated technical feasibility of the process, discovered agricultural uses of the carbon product, and identified economical co-product options for the bio-oils. Use of the reformer gas in an engine resulted in significant reduction of NO<sub>x</sub>. Further R & D over 1,000 hours process operation and higher hydrogen production rate could lead to a viable hydrogen and integrated bioconversion process to fulfill the President's FreedomCAR and Hydrogen Fuel Initiative goals.

# BACKGROUND

- **There is a need for clean fuels to address global climate change.**
- **Hydrogen is the most environmentally friendly and highest energy per mass fuel.**
- **FreedomCAR and Hydrogen Fuel Initiative are now national energy priorities.**
- **There is a need to produce and deliver economically competitive hydrogen (e.g., \$1.50 by 2010 vs. \$6 per gasoline gallon equivalent in 2003 from natural gas and liquid fuels)**
- **Potential sources of hydrogen include biomass, natural gas and other fossil fuels.**

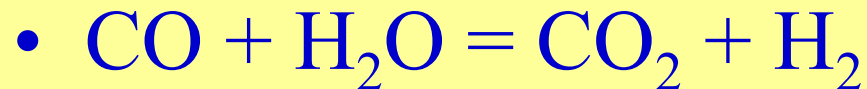
# BACKGROUND (Contd)

- **Biomass offers several advantages:**
  - Renewable, zero-net CO<sub>2</sub> impact.
  - Target costs of \$3.80/kg H<sub>2</sub> (2003), \$2.90 (2010) and \$2.30 (2015)
- **Agriculture is Georgia's largest industry and will provide biomass feedstock.**
  - Peanut shells are a start, other forms of biomass will be investigated.
- **Hydrogen can be used for transportation and stationary fuel cell power generation.**
- **Integrated biomass conversion process can revitalize rural economy.**

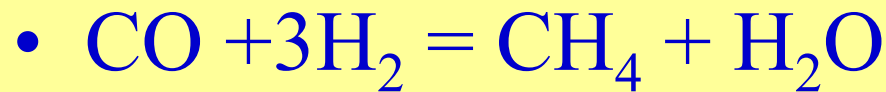
# Reforming Reactions



$$(-\Delta H^\circ_{298} < 0)$$

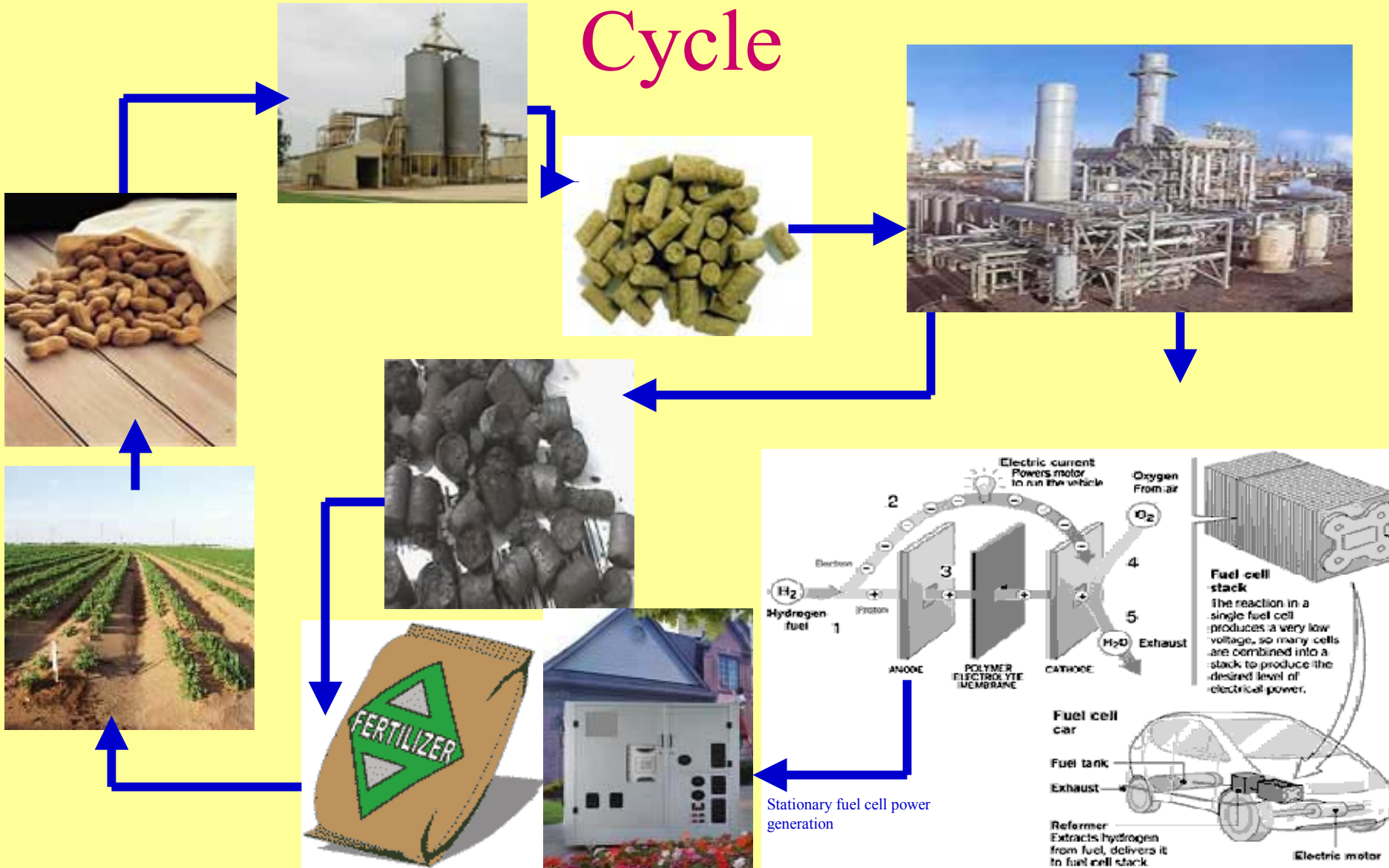


$$(-\Delta H^\circ_{298} = 9.48 \text{ kcal / mol})$$

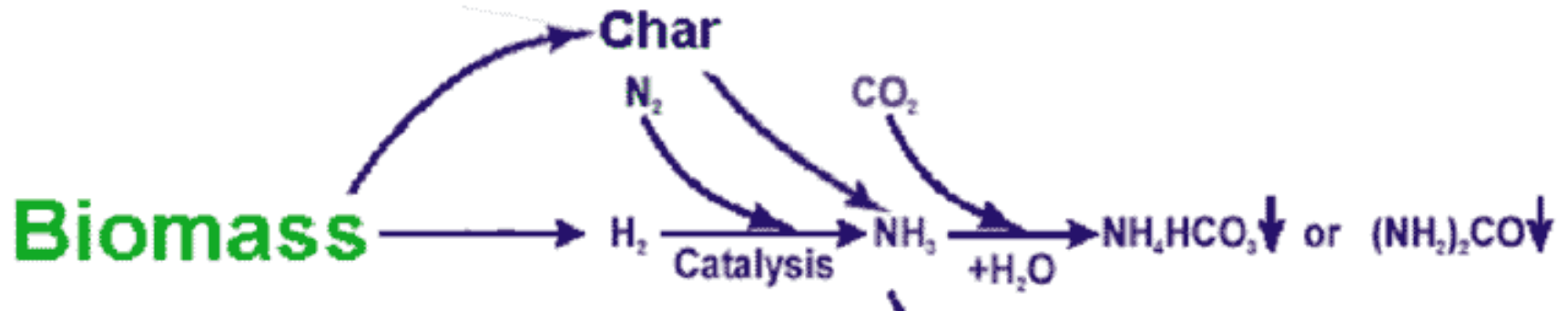


$$(-\Delta H^\circ_{298} = 49.27 \text{ kcal / mol})$$

# The Peanut Shell to Hydrogen Cycle



# Biocarbon-Based Fertilizers



Courtesy  
D. Day,  
Eprida/  
Scientific Carbons  
Inc.



# Relevance to DOE, FreedomCAR, and Hydrogen Initiative

- Project is developing technology (pyrolysis-reformer process) that will:
  - Produce hydrogen from biomass (e.g., peanut shells)
  - Utilize the biomass hydrogen for transportation and/or stationary power generation
  - Reduce cost, and develop improved technologies
- Project addresses national and global issues related to:
  - Improvement in America's energy security by reducing the need for imported oil
  - Improving air quality and reducing greenhouse gas emissions
  - Revitalization of rural economy (e.g., Georgia)
  - The four E's: Energy, Environment, Economy, and Education



# OBJECTIVES

- Undertake the engineering research and pilot scale process development studies relating to:
  - Production of hydrogen from biomass (e.g., agricultural residues) for \$2.90/kg H<sub>2</sub> by 2010; \$2.30 by 2015
  - Separation, safe storage and utilization of the hydrogen
  - Production and identification of uses of the co-products
- Increase diversity of the Nation's workforce and the broader impact of the project through the education and training of underrepresented minorities.

# APPROACH

- **Develop process based on biomass pyrolysis and steam reforming of pyrolysis vapors (bio-oils and gases).**
- **Perform catalytic steam reforming in a fluidized-bed (25-250 kg/day H<sub>2</sub> production)**
- **Conduct pyrolysis at: T: 500°C; P: 10 psig; Feed Rate: 50-500 kg/hr pelletized peanut shells.**
- **Study reforming at: T: 850°C; P: 6 psig; H<sub>2</sub>O/C = 5, Catalyst: nickel-based (300-500 microns)**

# APPROACH/ PROJECT TASKS

- **Task 1: Feedstock supply, process economics and deployment strategies (modeling, extraction, and property estimation)**
- **Task 2: Process modifications, integration, and shakedown**
- **Task 3: Long term (1,000 hours) catalyst and process testing**
- **Task 4: Hydrogen separation, storage, and utilization**
- **Task 5: Environmental and technical evaluation**
- **Task 6: Partnership building and outreach**

# PROJECT TIMELINE

## TASK/ACTIVITY

## YEAR

9/2000    2001    2002    2003    3/2004

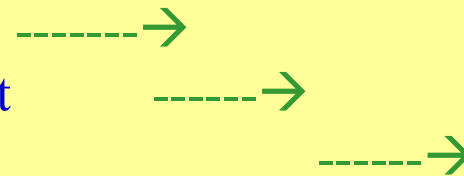
### Task 1: Modeling and Extraction Studies

- Develop model of network steps
- Solubility & Parameters Estimations



### Task 2: Design, Construction and Shakedown

- Reformer Design, Construction, and Testing
- Integration of Pyrolyzer- Reformer Unit
- Modifications for 1,000 hours run



### Task 3: Long-term Catalyst Testing

- 100 hour Testing of Unit
- 1000-hour testing of catalyst and unit



# PROJECT TIMELINE(contd.)

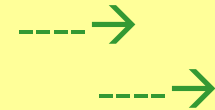
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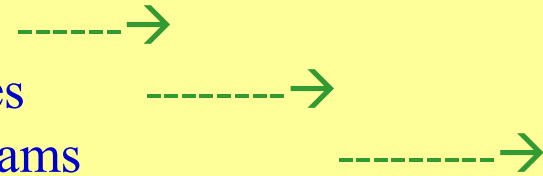
### Task 4: Hydrogen Separation

- Design and acquisition of PSA
- Installation and testing of PSA



### Task 5: Environmental and Technical Evaluation

- Acquisition of analytical instruments
- Development of methods and procedures
- Analysis and monitoring of process streams



### Task 6: Partnership and Outreach

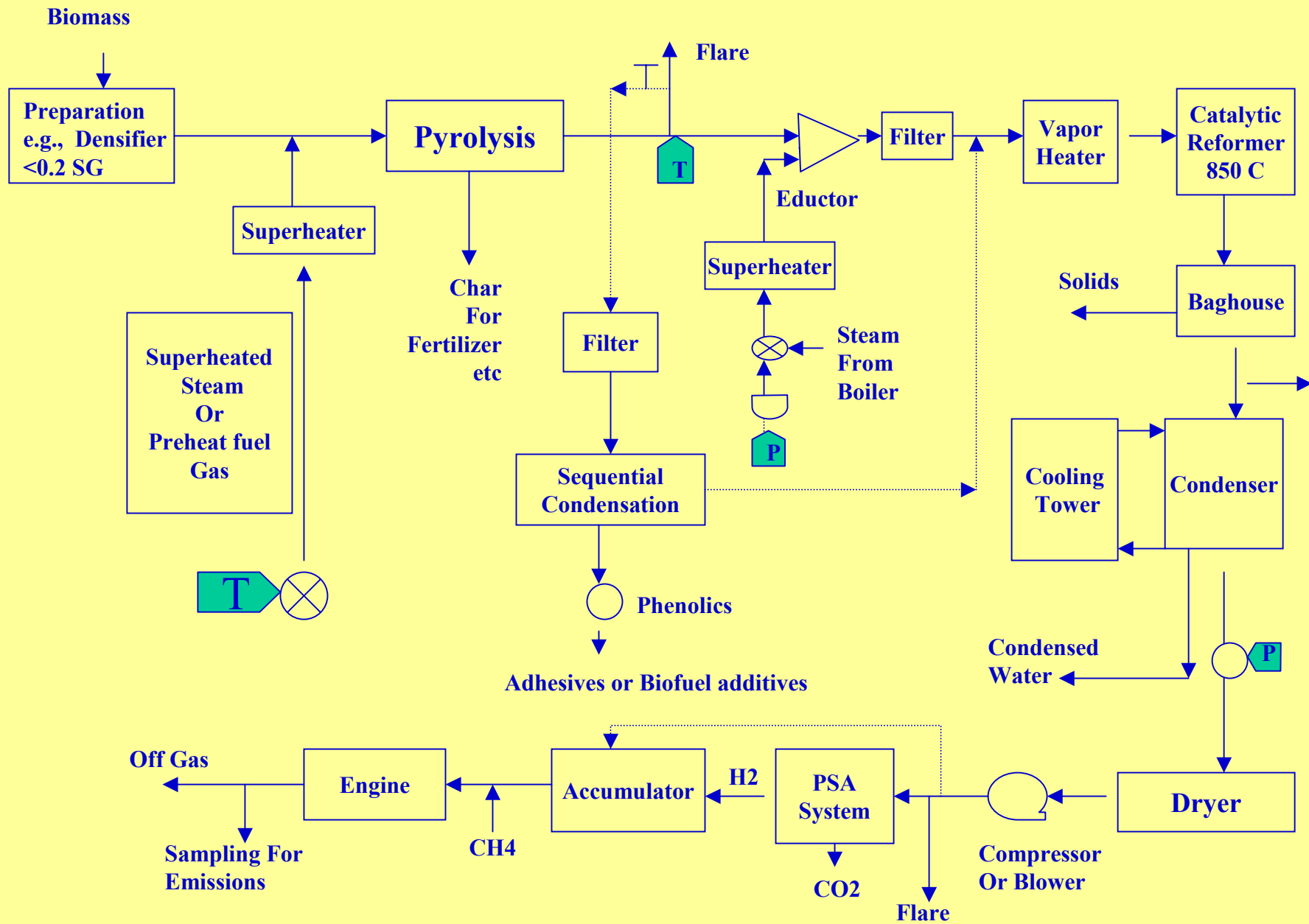
- Partnerships and collaborations
- Education and training of students



# ACCOMPLISHMENTS/PROGRESS

- **Completed design, construction and testing of reformer (Phase 1)**
- **Completed integration of reformer with pyrolyzer (Phase 2)**
- **Completed 100 hours of successful operation of pilot unit (Phase 2)**
- **Identified modifications for 1,000 hours operation run**
- **Identified potential co-products options**
- **Developed partnership and collaboration with potential companies/ organizations**
- **Educated and trained several underrepresented minorities on project**
- **Planning on 1000-hour run in 2003**

# Schematic Flow Diagram of the Biomass Refinery for Hydrogen, Char and Chemicals





# PICTURES OF PILOT PLANT



# PICTURES OF PILOT PLANT





# Blakely, Georgia Site



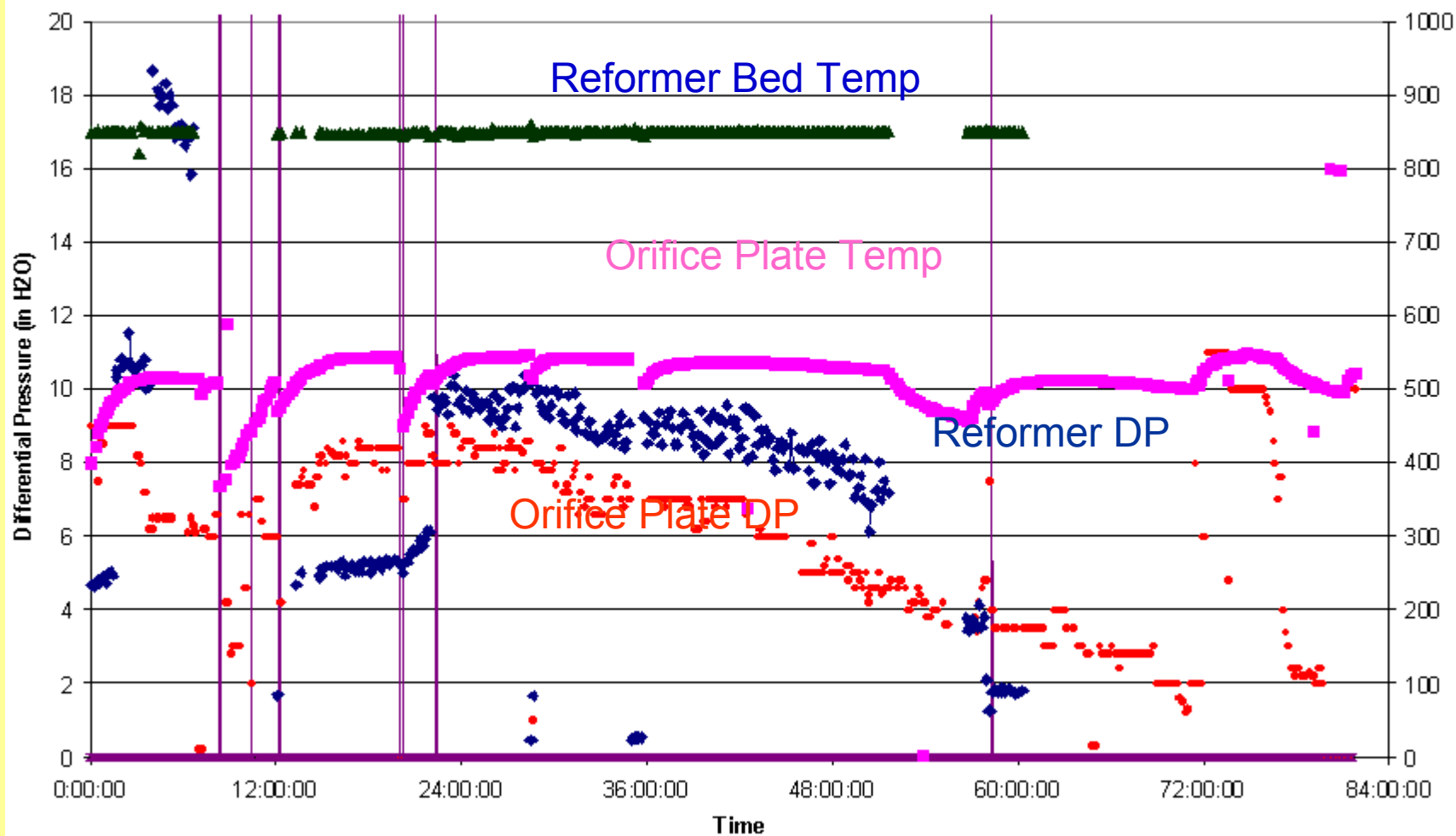
# Typical Analysis of Peanut Shell Feedstock

<b>• Component</b>	<b>%</b>
– Lignin -----	<b>34.8</b>
– Glucan -----	<b>21.1</b>
– Extractives -----	<b>14.2</b>
– Protein -----	<b>11.1</b>
– Xylan -----	<b>7.9</b>
– Ash -----	<b>3.4</b>
– Arabinan -----	<b>0.7</b>
– Galactan -----	<b>0.2</b>
– Mannan -----	<b>0.1</b>
– Others (e.g., free carbohydrates) -----	<b>6.5</b>

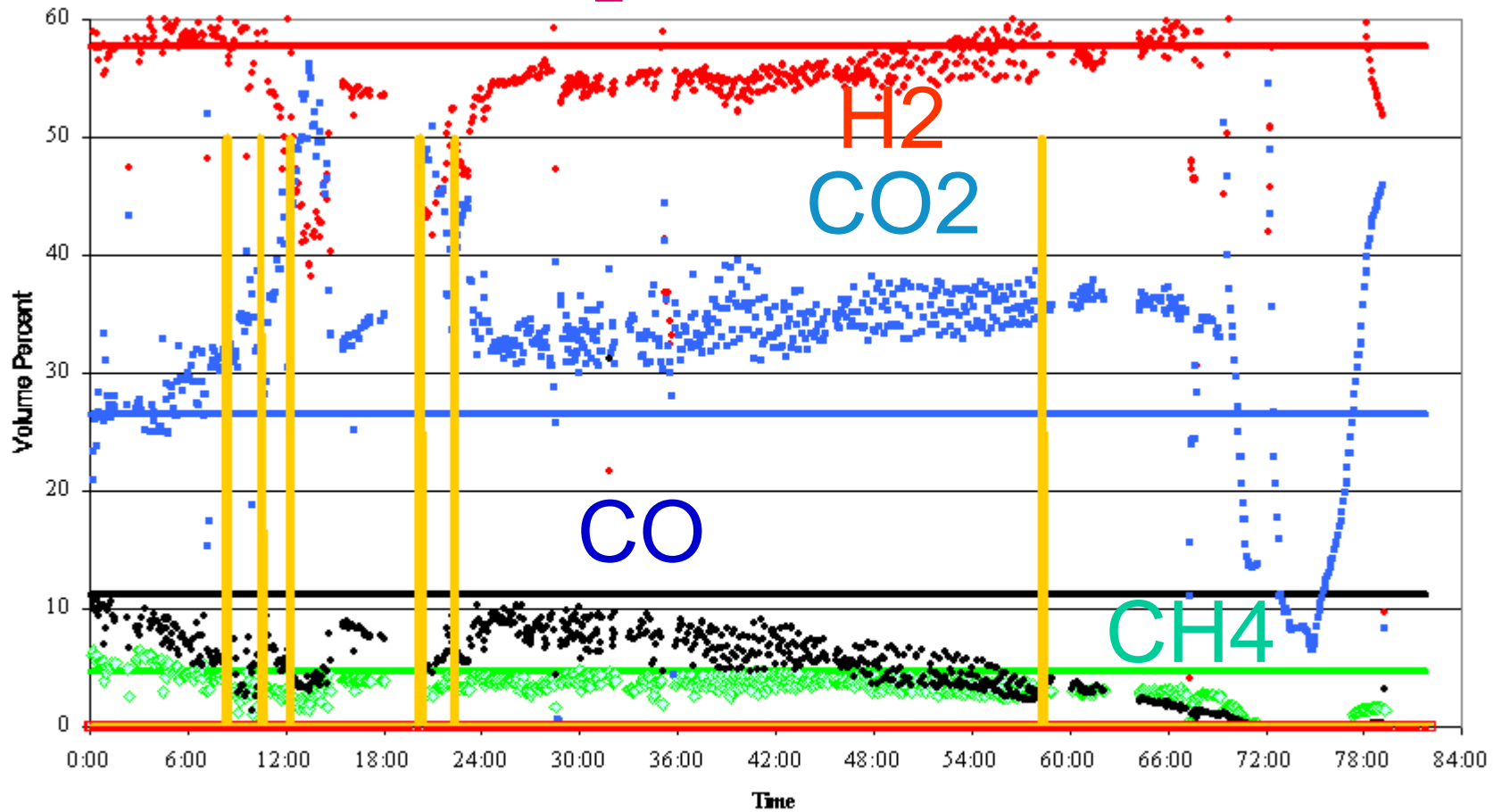
## RESULTS: TYPICAL PRODUCT COMPOSITION/ YIELD

Pyrolyzer (Yields)		Reformer (Gas product composition, on dry N <sub>2</sub> -free basis)	
Char	32%	Hydrogen	57%
Water	32%	Carbon Dioxide	26%
Bio-Oils	31%	Carbon Monoxide	12%
Gases	5%	Methane	5%

# Reformer Performance



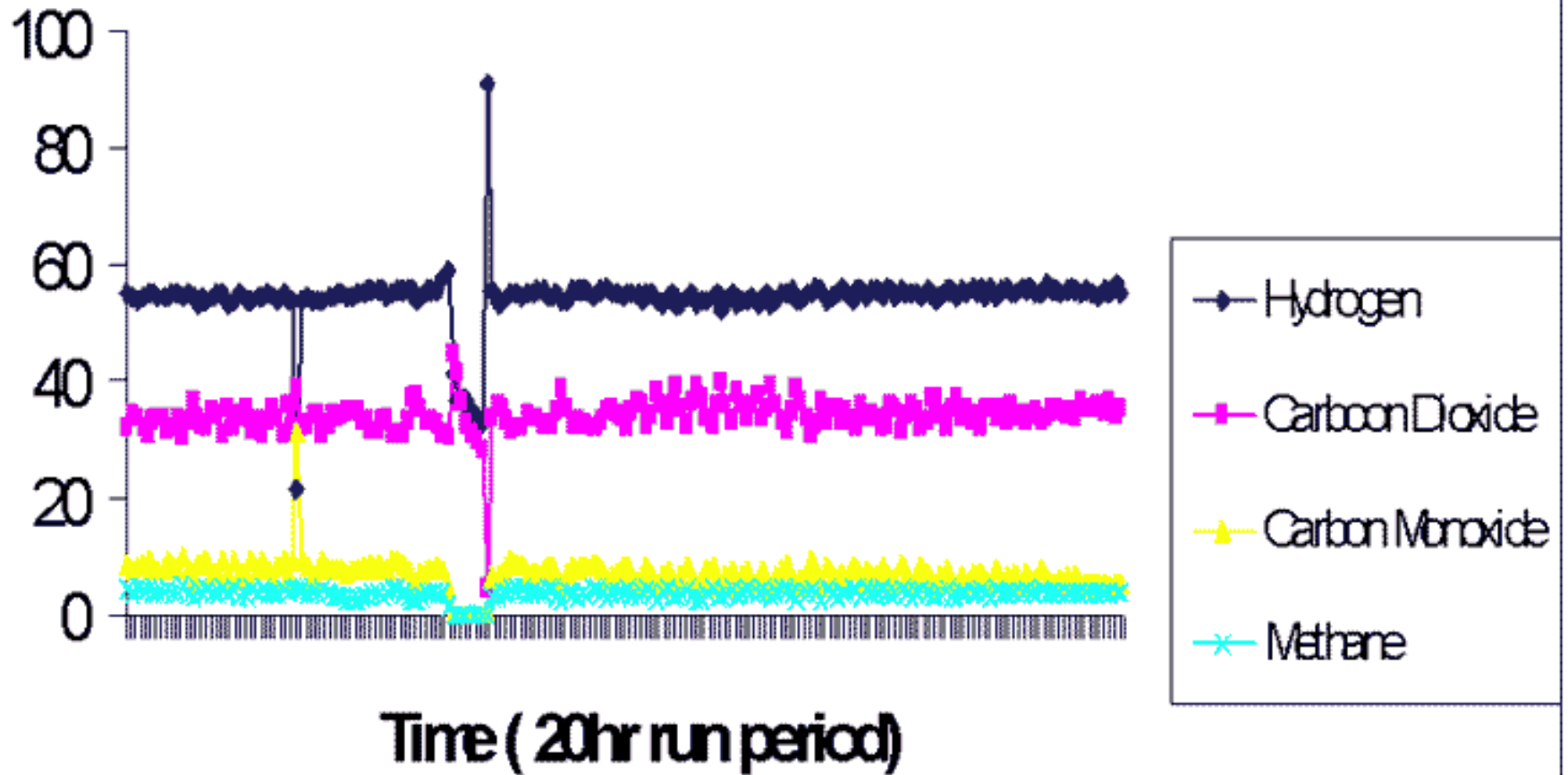
# Gas Composition



• Hydrogen    ♦ Methane    ■ Carbon Dioxide    • Carbon Monoxide    — H2    — CH4    — CO2    — CO    — 2 per. Mov. Avg. (Shutdown)



# Plot of Gas Composition Vs. Time (hrs)



# Pyrolysis Bio-Oil Product

- **Empirical Formula:**  $\text{CH}_{1.9}\text{O}_{0.7}$
- **Water:** 15 – 25%
- **Organics:** 75 – 85%
  - Aldehydes, alcohols and acids from carbohydrate fraction
  - Phenolics from lignin fraction
- **Representative Compounds**

Water

Ethanol

Methanol

Cyclohexanol

Formic Acid

Acetic Acid

Glucose

Phenol

O-cresol

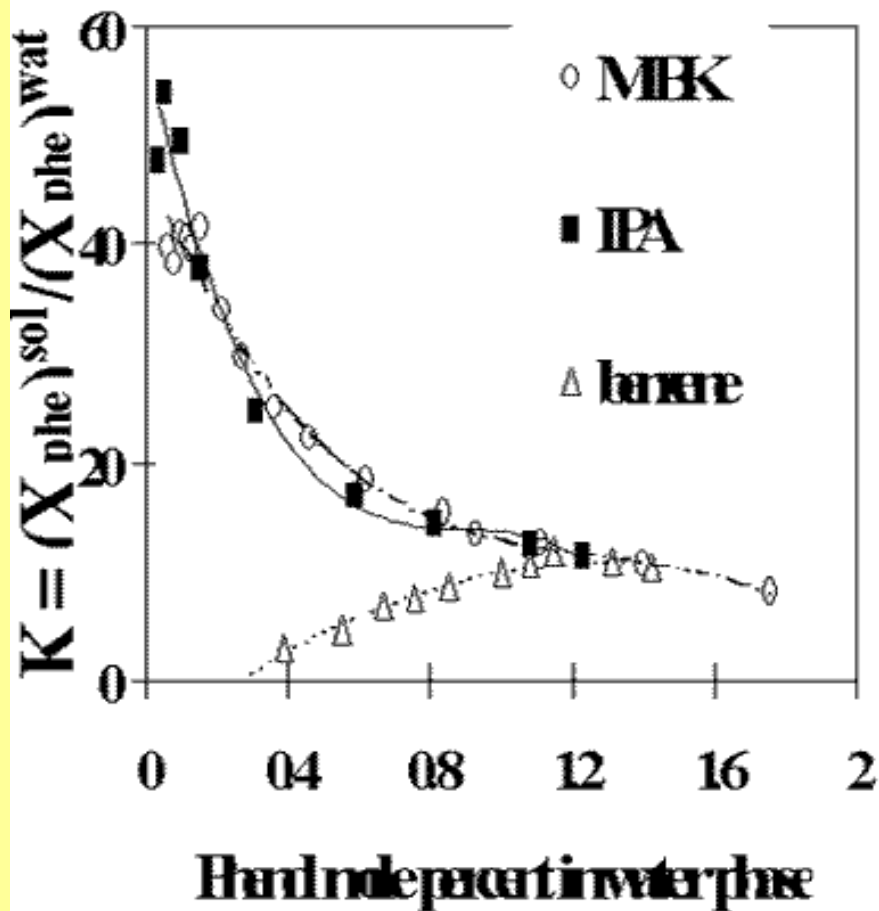
2-Butanone

Dodecanoic acid

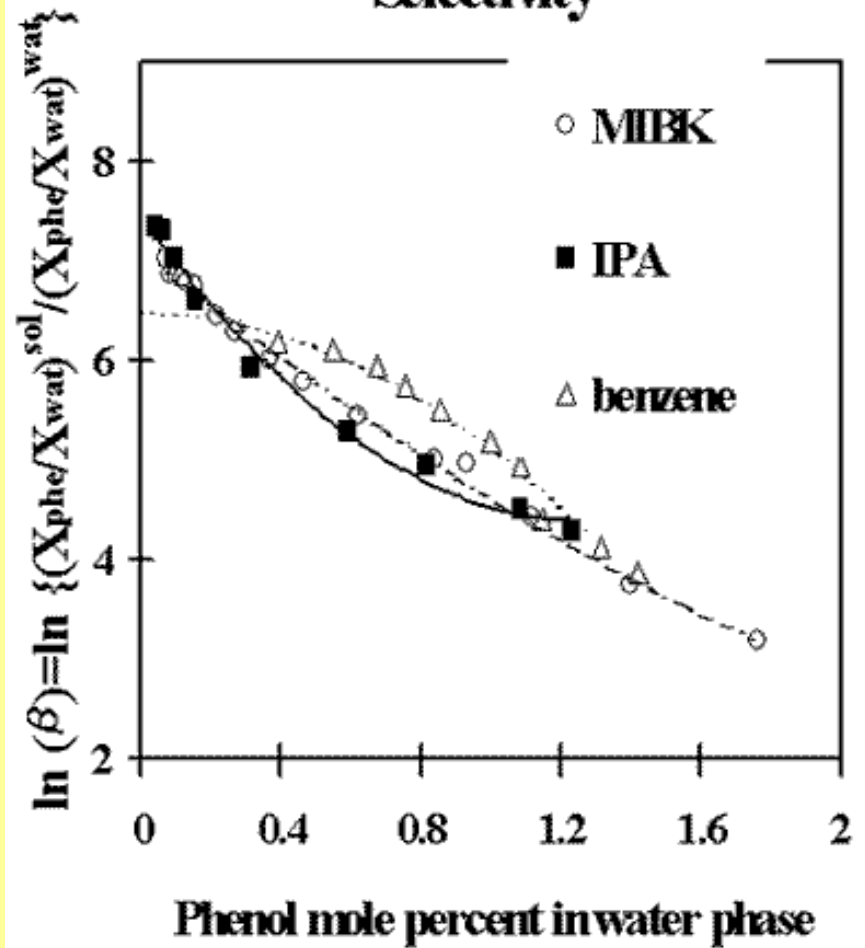
Tannin

# Selectivity / Distribution Plot

## Distribution coefficients



## Selectivity



# SIGNIFICANT INTERACTIONS AND COLLABORATIONS

- **The project has resulted in significant interactions and collaborations between the following organizations:**
  - Clark Atlanta University, Atlanta, GA
  - Eprida Scientific Carbons Inc., Blakely, GA
  - Enviro-Tech Enterprises Inc., Matthews, NC
  - Georgia Institute of Technology, Atlanta, GA
  - National Renewable Energy Lab, Golden, CO
  - Oak Ridge National Lab, Oak Ridge, TN
  - Southern Company, Atlanta, GA
  - University of Georgia, Athens, GA

# FUTURE PLANS

- **Demonstrate process control and operability for 1,000 hours of operation (Phase 3).**
- **Undertake further research and development studies in a larger scale pilot plant (250 kg H<sub>2</sub>/day).**
- **Develop process models for scale up and process optimization.**
- **Perform detailed techno-economic analysis based on pilot results.**
- **Identify and evaluate integrated bioconversion process for different feed stocks and product options.**

# PLANS AND FUTURE MILESTONES (Phase 3)

## ACTIVITY

## COMPLETE BY

- |  |                |
|--|----------------|
| • Modeling and solubility studies            | September 2003 |
| • Evaluation of co-products options          | December 2003  |
| • Modifications and installation of controls | August 2003    |
| • Integration of analytical systems          | September 2003 |
| • Shakedown runs before 1,000 hr run         | September 2003 |
| • 1,000 hours of operation of pilot unit     | November 2003  |
| • Engine tests with reformer gas             | November 2003  |
| • Installation and testing of PSA unit       | September 2003 |
| • Education and training of students         | March 2004     |

# RESPONSE TO SIGNIFICANT QUESTIONS/ CRITICISMS

- **Reviewers recommended appropriate safety reviews and operational readiness inspection prior to start-up of the pilot plant demonstration unit.**
  - Safety has always been of top priority in this project
  - It has been incorporated in all designs, operations and phases of this study based on input from safety experts from NREL.
  - Safety reviews and operational readiness inspections will be undertaken by safety experts from NREL, University of Georgia, and the project team prior to start-up of the pilot demonstration unit.



# CONCLUSIONS

- **Demonstrated successfully pyrolysis-reformer concept for 100 hours operation**
- **Discovered agricultural uses and carbon sequestration strategy: Novel carbon slow release sequestered fertilizer.**
- **Identified economical co-product options for bio-oils: Adhesives.**
- **Run successfully the product gas in an engine with significant reduction of NO<sub>x</sub>**
- **Further R & D over 1,000 hours operation and higher hydrogen production rate could lead to economically competitive hydrogen and a viable integrated bioconversion process.**

# ACKNOWLEDGEMENTS

- **Support of Department of Energy under Grant # DE-FC36-00GO10528.**
  - Doug Hooker, James Alkire, Beth Dwyer
  - Chris Bordeaux, Sigmund Gronich, Neil Rossmeissl
- **Support of the Partner Institutions**
  - Clark Atlanta University
  - Eprida Scientific Carbons Inc.
  - Enviro-Tech Enterprises Inc.
  - Georgia Institute of Technology
  - National Renewable Energy Laboratory