Hydrogen from Biomass Pyrolysis: Integrated Co-Products and Services

Biorefining Videoconference
(June 17, 2004)

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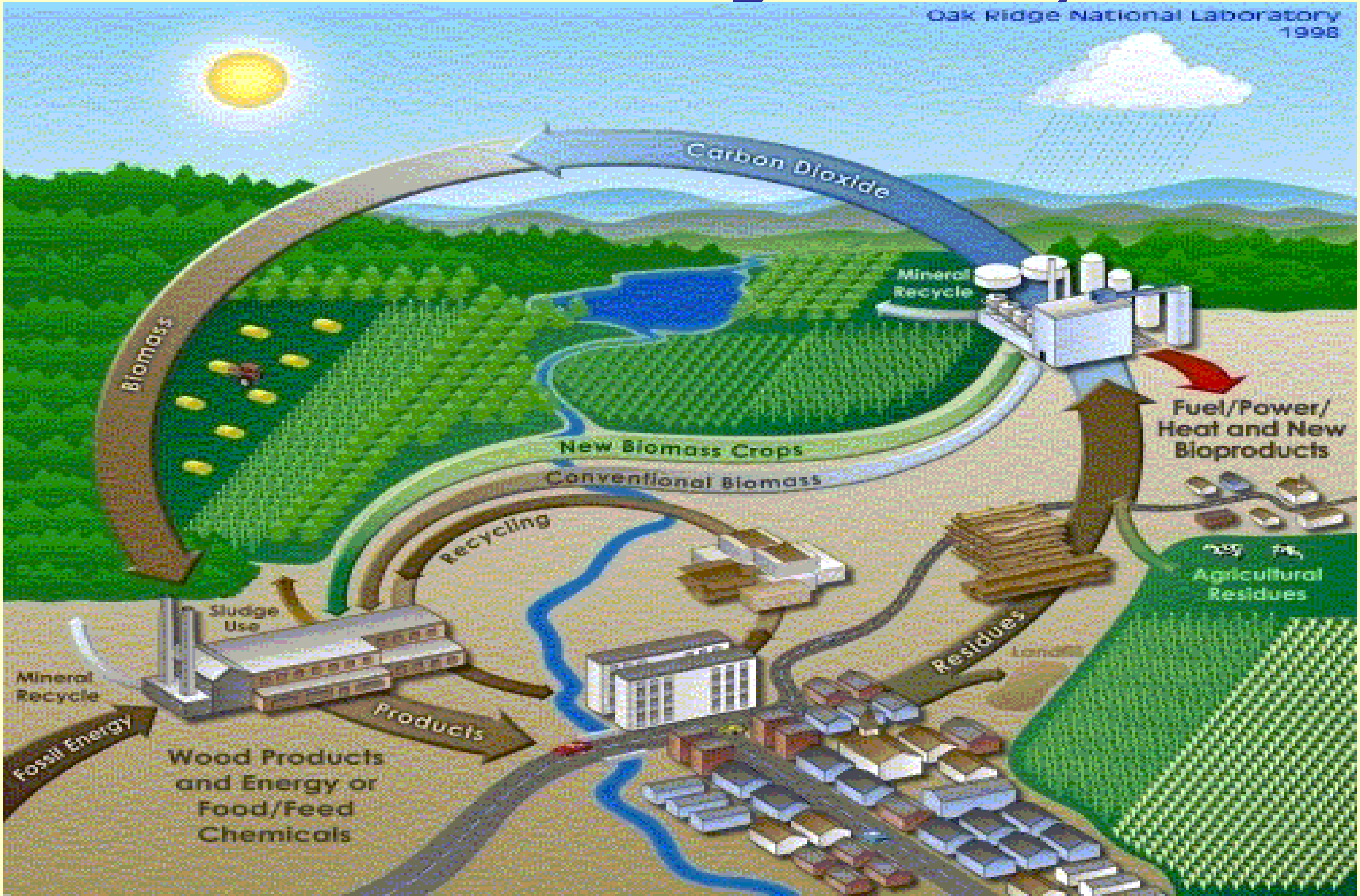
Our Future: Integrated Systems



Pyrolytic conversion offers cost effective options

The 2001 report by Spath* offered that pyrolytic conversion of biomass offered the best economics for hydrogen production, partly because of the opportunity for co-product production and reduced capital costs.

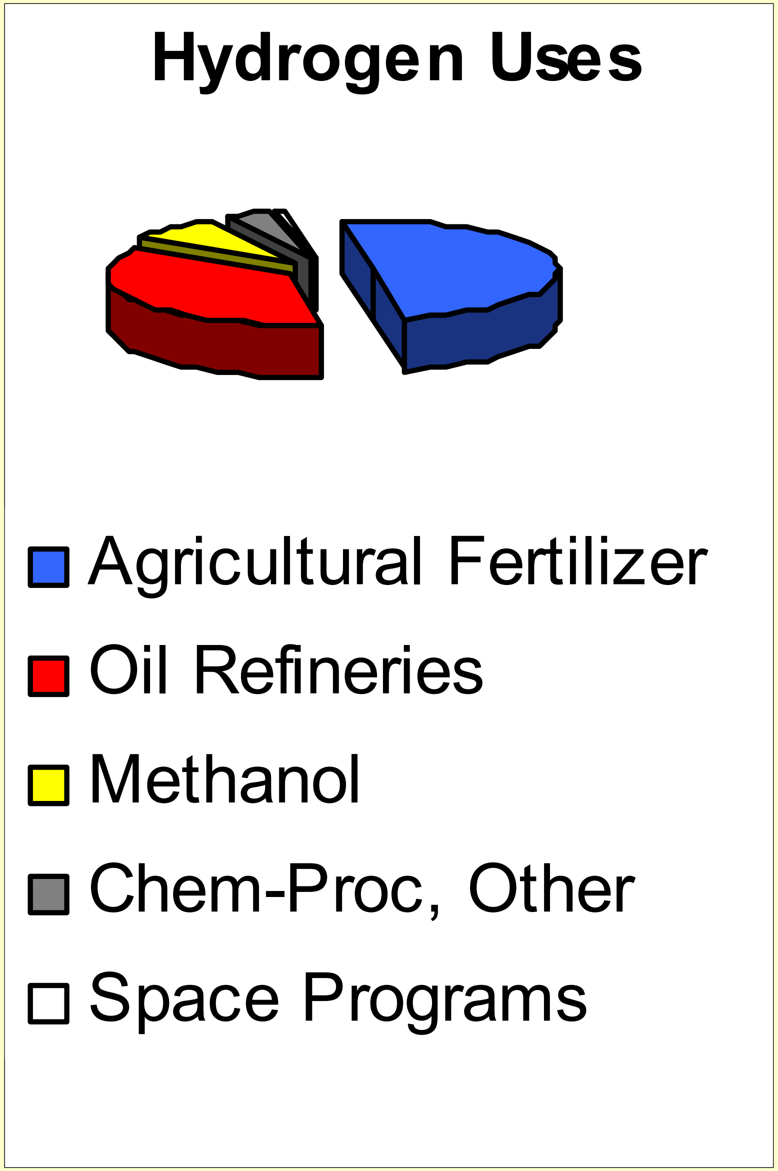
*Spath, *et al*, Update of Hydrogen from Biomass -Determination of the Delivered Cost of Hydrogen, National Renewable Energy Laboratory, Milestone Report for the U.S. Department of Energy's Hydrogen Program 2001

Drivers for sustainable biohydrogen production

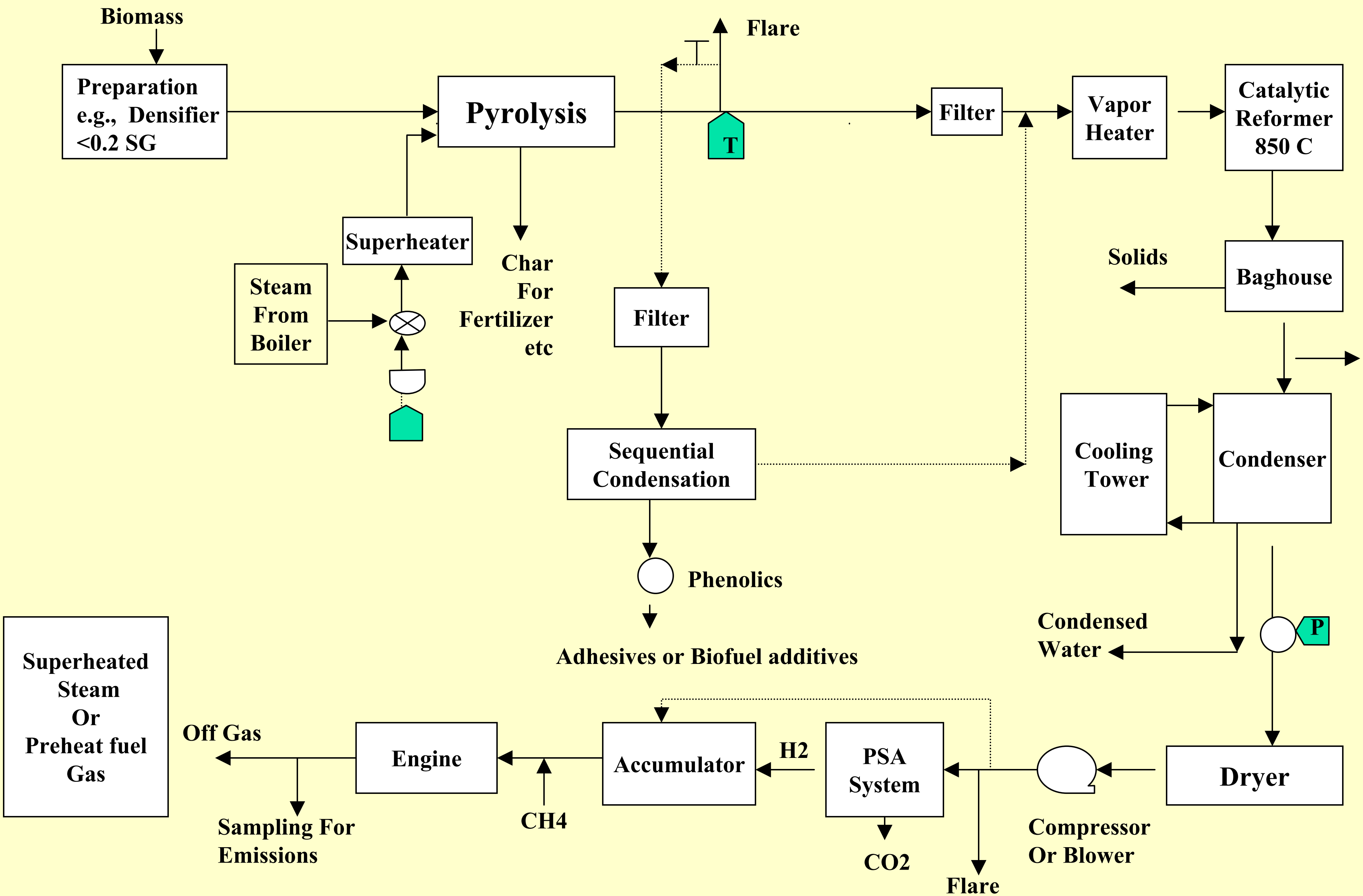
- Energy Independence
- Dwindling Oil Reserves
- Global Warming
- Distributed Socio-Economic Impacts
- Ability to co-locate and integrate unrelated business, symbiotic processing

Current uses of non renewable hydrogen

- Synergistic opportunities for renewable hydrogen can be found in hydrogen's largest use
- Under intensive modern agriculture Hydrogen = Food



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



Demonstration of Hydrogen Production

A 3 year DOE/NREL project resulted in a pilot demonstration of hydrogen from biomass. The aim was to safely operate a continuous process catalytic steam reformer to process the oxy-hydrocarbon gas from biomass pyrolysis and capture 24 hours of stable data. Peanut hulls pellets were heated with natural gas in an oxygen free system, producing an off-gas rich in hydrogen. The steam reformer was externally heated to 850C.

Pyrolysis Reactor

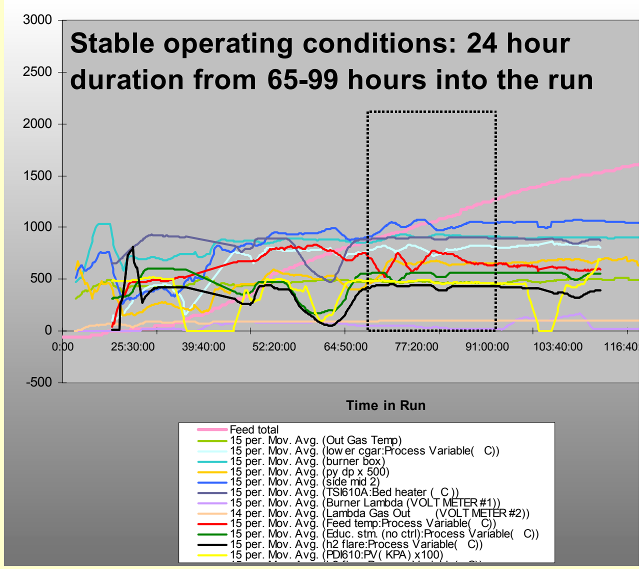
Steam Reformer Reactor

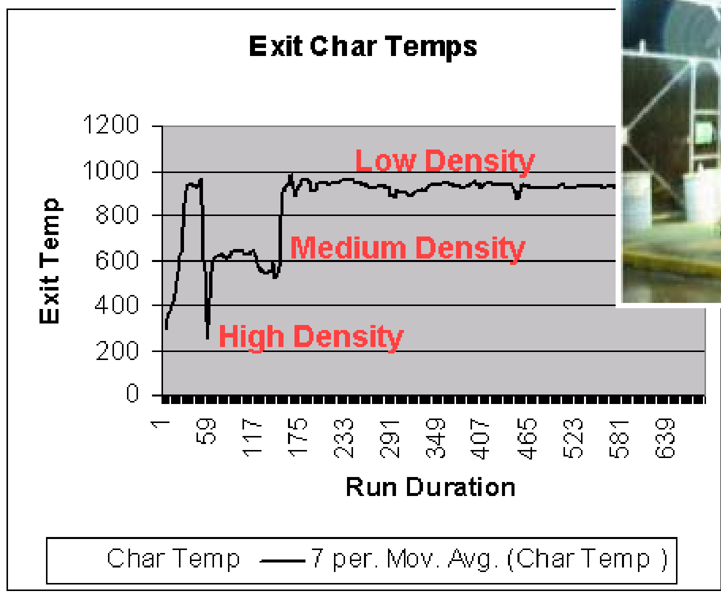
Demonstration Results

A 100 hour run was planned to insure that a stable 24 hour window of data was collected after processes had stabilized. Throughput was set at 50kg/hr of biomass with a moisture content of 13%. The online monitoring recorded by weight production rates of :

- 60% H_2
- 3% methane (giving the hydrogen a blue flare)
- 30% CO_2
- 7% CO

During this run the process also sequestered 20% of the biomass as fixed carbon. The variations in the run conditions produced three different types of char. An accidental discovery in start-up pointed toward a new application.

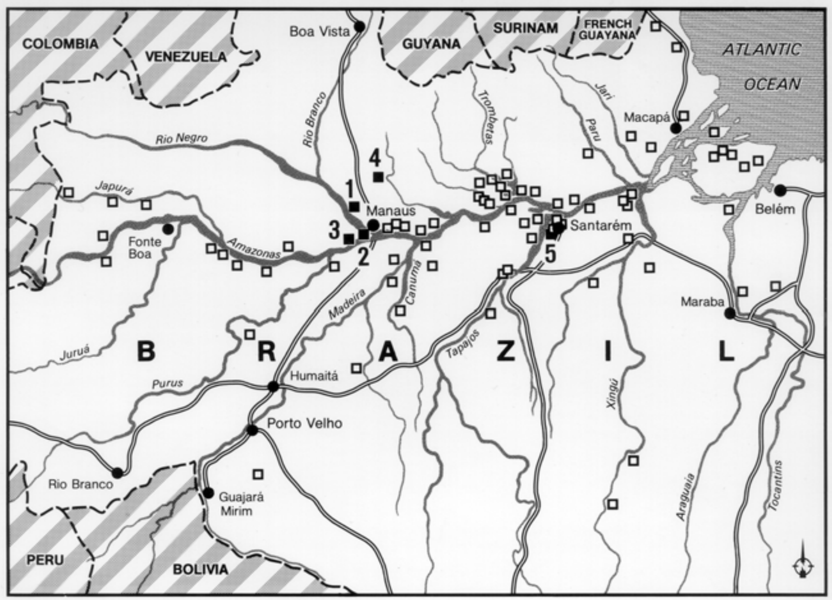




A Valuable Co-Product

We began to investigate the use of the material as a soil amendment and nutrient carrier after employees mentioned that a mound of char, used for start-up operations was covered in vegetation and more specifically turnips. Someone had tossed some turnip seeds, on the two year old, chest high, char pile. It was only char with no soil, yet on plants completely covered the mound. The plants appeared healthy with roots that enveloped each char particle. The turnips, unfortunately could not be inspected as they already had been eaten, but it was reported they were "Good!".

The Terra Preta Soil Experiment, 2000 Years Old



Terra Preta refers to black high carbon (9%) earth-like anthropogenic soil with enhanced fertility due to high levels of soil organic matter (SOM) and nutrients such as nitrogen, phosphorus, potassium, and calcium. Terra Preta soils occur in small patches averaging 20 ha. These man made soils are found in the Brazilian Amazon basin, also in Western Africa and in the savannas of South Africa. C14 dating the sites back to between 800 BC and 500 AD. Terra Preta soils are very popular with the local farmers and are used especially to produce cash crops such as papaya and mango, which grow about three times as rapid as on surrounding infertile soils.

(Map reprinted by permission: Steiner, 2002)

Background Research

With NPK and Charcoal | With NPK

Manaus, Brazil - Terra Preta Research, 2001
Christoph Steiner, University of Bayreuth
Institute of Soil Science and Soil Geography

(Taiwan, 2001)
Food and Fertilizer Technology Center for the Asian and Pacific Region

The images above were provided for this poster by Christoph Steiner, who has been recreating Terra Preta soils in Brazil since 1999.

•Amount of applied organic matter (25% increase of C_{org} in 0-10 cm

• Increased the soil C content ~ 0.75%

•Applied Charcoal 11 t / ha

•Mineral fertilizer: N (30), P (35), K (50), lime (2100 kg/ha)

International Workshop on Anthropogenic Terra Preta Soils, (July 2002 Brazil)

- Terra Preta soils contain 15-60 Mg/ha C in 0-0.3m but 1-3Mg/ha may be sufficient (GLASER et al.)
- Increased cation exchange capacity (GLASER)
- Char decreased leaching significantly (LEHMANN)
- Char traps nutrients and supports microbial growth (Pietikainen)
- Char experiments have shown up to 266% more biomass growth (STEINER) and 324% (Kishimoto and Sugiura)
- Available water capacity was 18% than surrounding soils (GLASER)
- Char stability measured in 1,000’s of years (SKJEMSTED)

Drivers for Food and Energy Production from Pyrolytic Production of Hydrogen

- Food and Energy Independence
- Dwindling Oil and Topsoil Reserves
- Global Warming Impacts from Agriculture
- Distributed Socio-Agro-Economic Impacts
- Ability to co-locate and integrate unrelated business, symbiotic processing for food, and energy
- Carbon Negative Energy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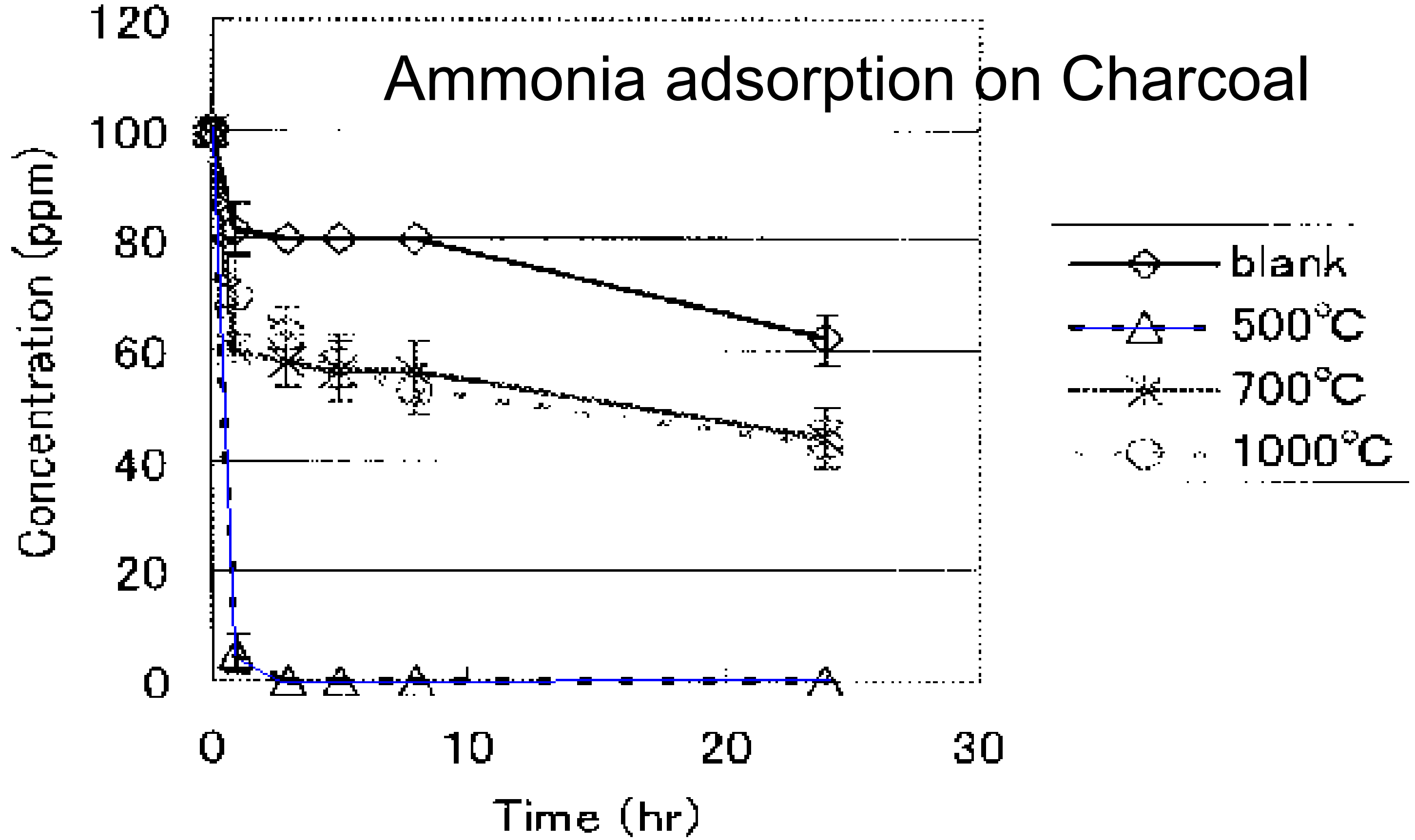
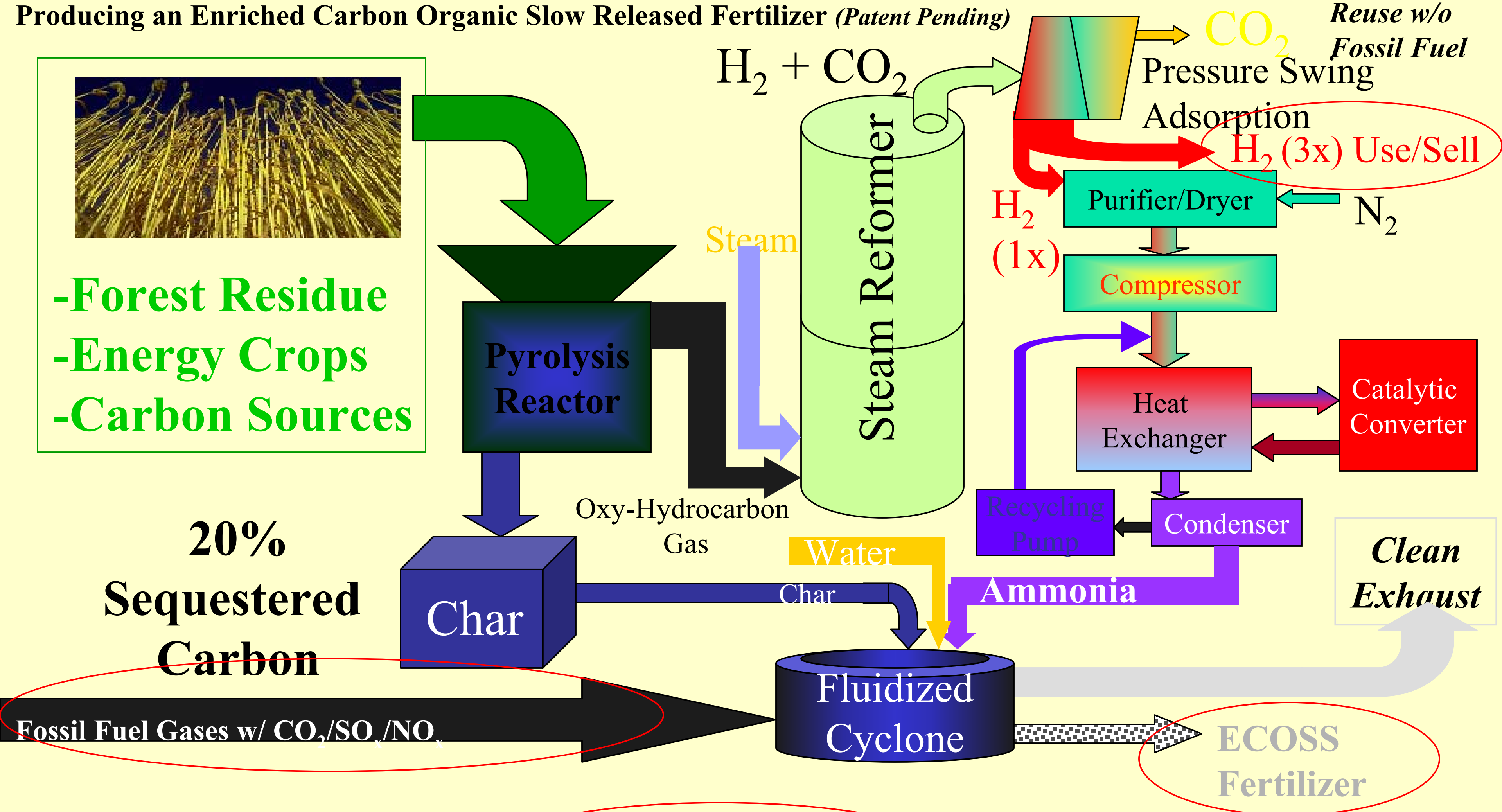
Low Temp Charcoal Advantage



Asada 2002

Process Flow : Hydrogen Production and CO_2 Sequestration

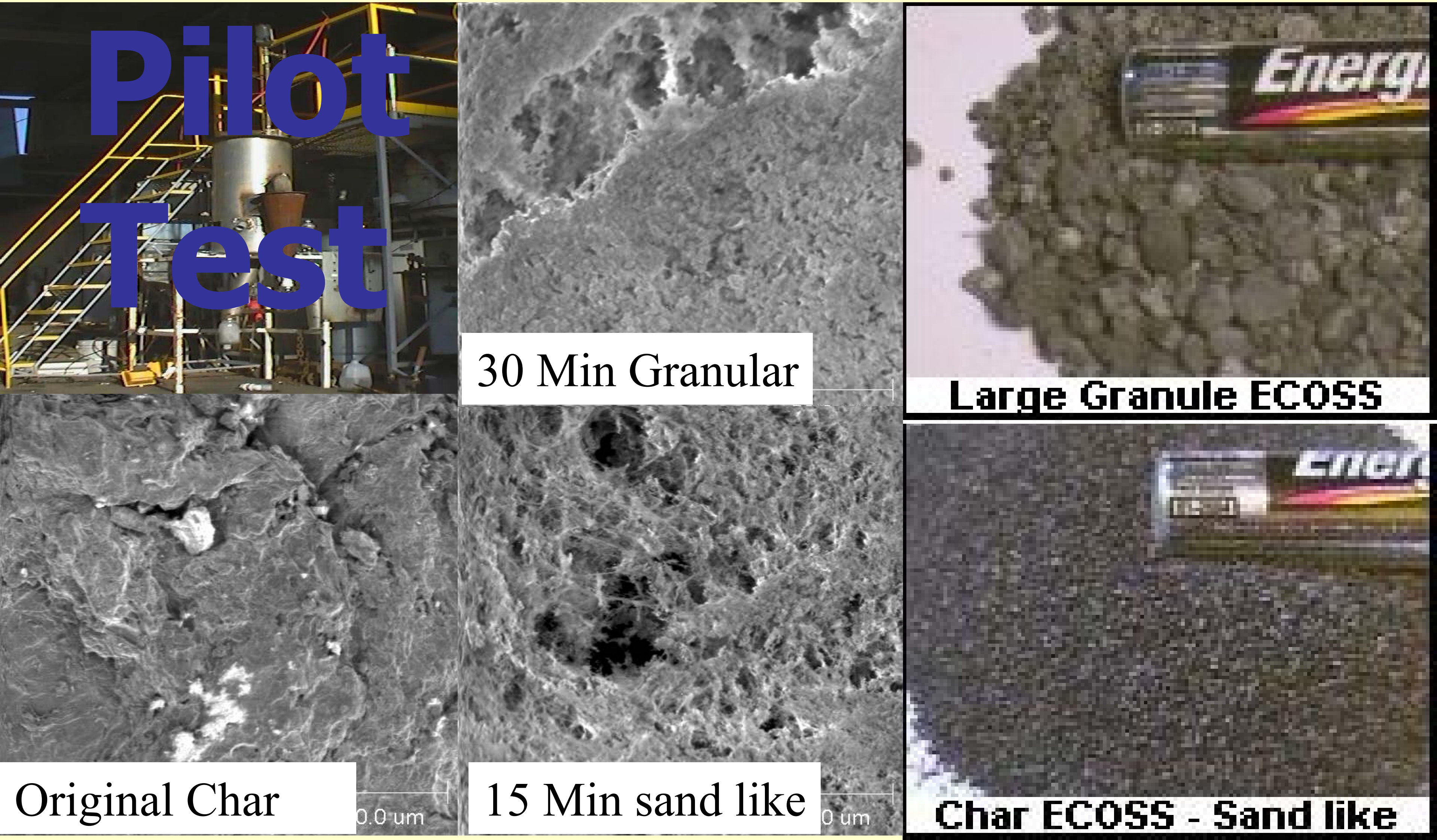
Producing an Enriched Carbon Organic Slow Released Fertilizer ***(Patent Pending)***



Revenue Sources

Profit Centers

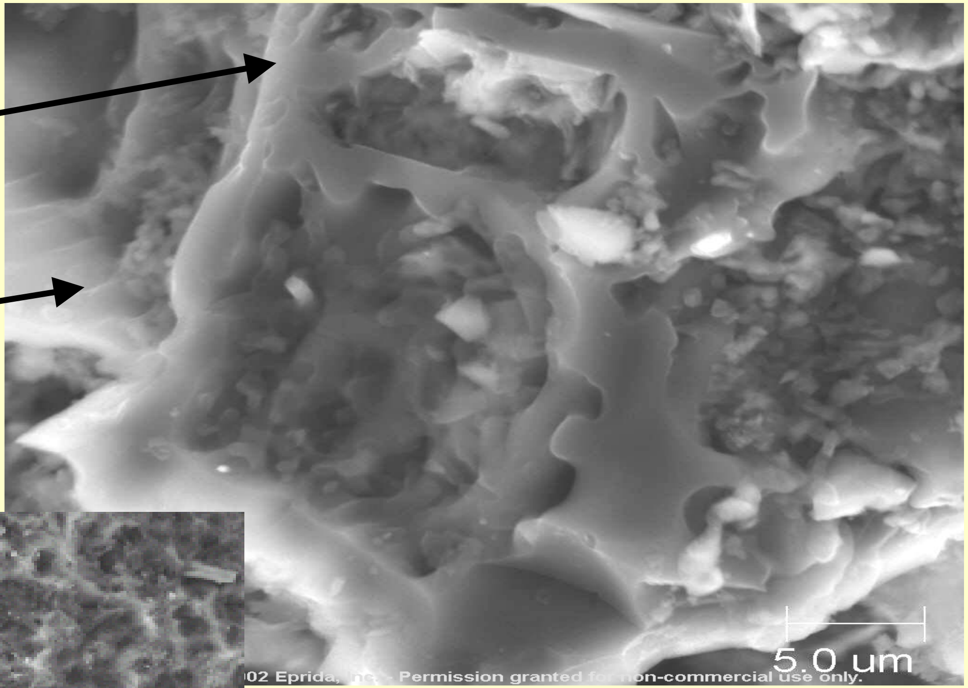
- **Operated at ambient pressure and temperature**
- **CO_2 separation is not required**



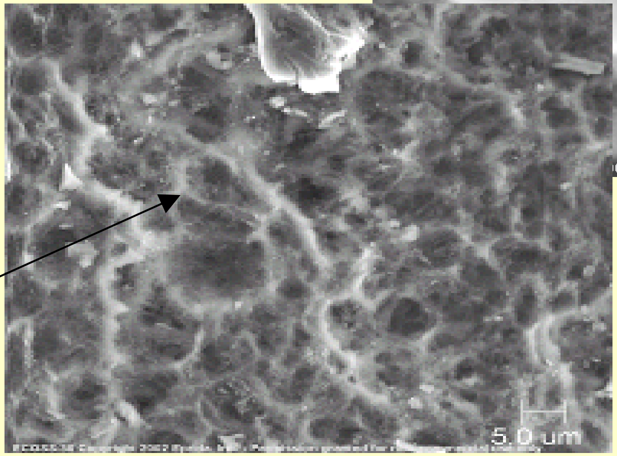
Crushed Interior 2000x SEM

The residual cell structure of the original biomass is clearly visible

The ABC fibrous buildup has started inside the carbon structure

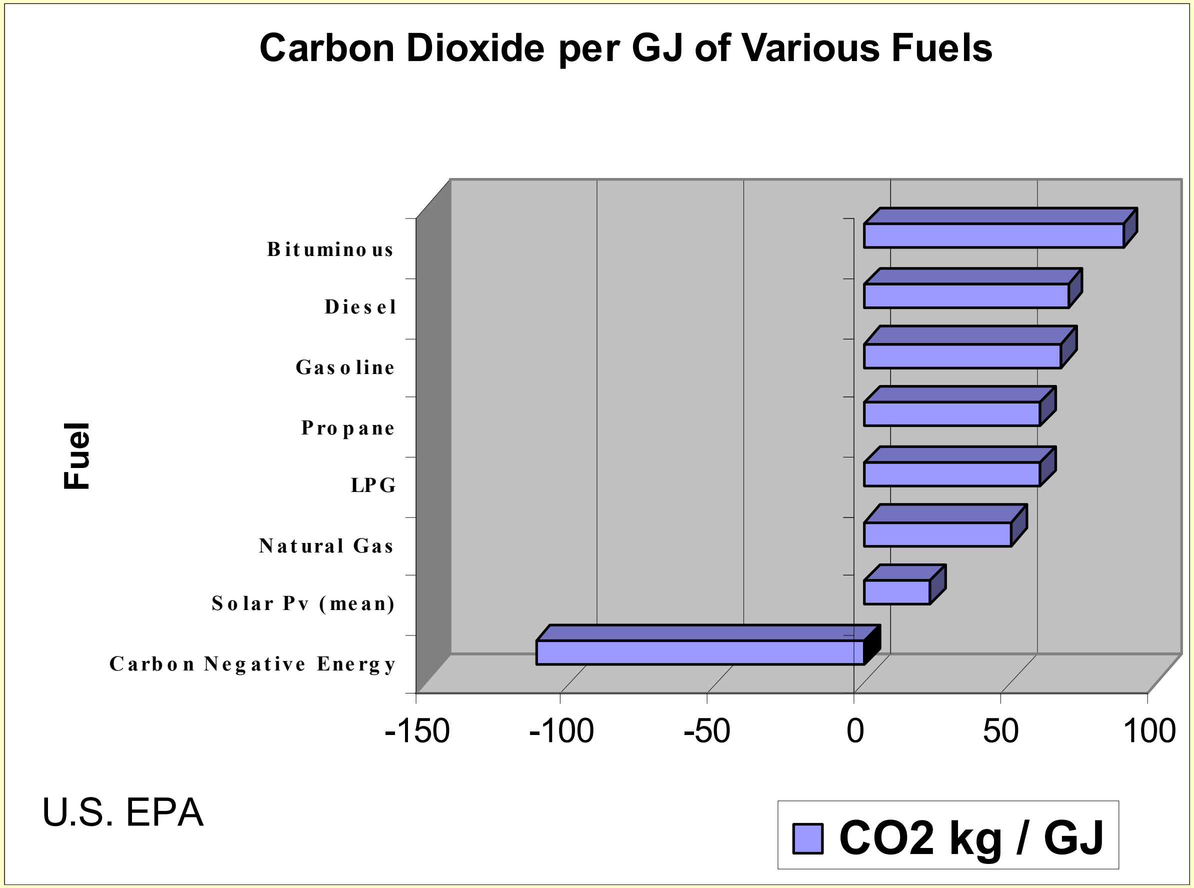


After complete processing, interior is full

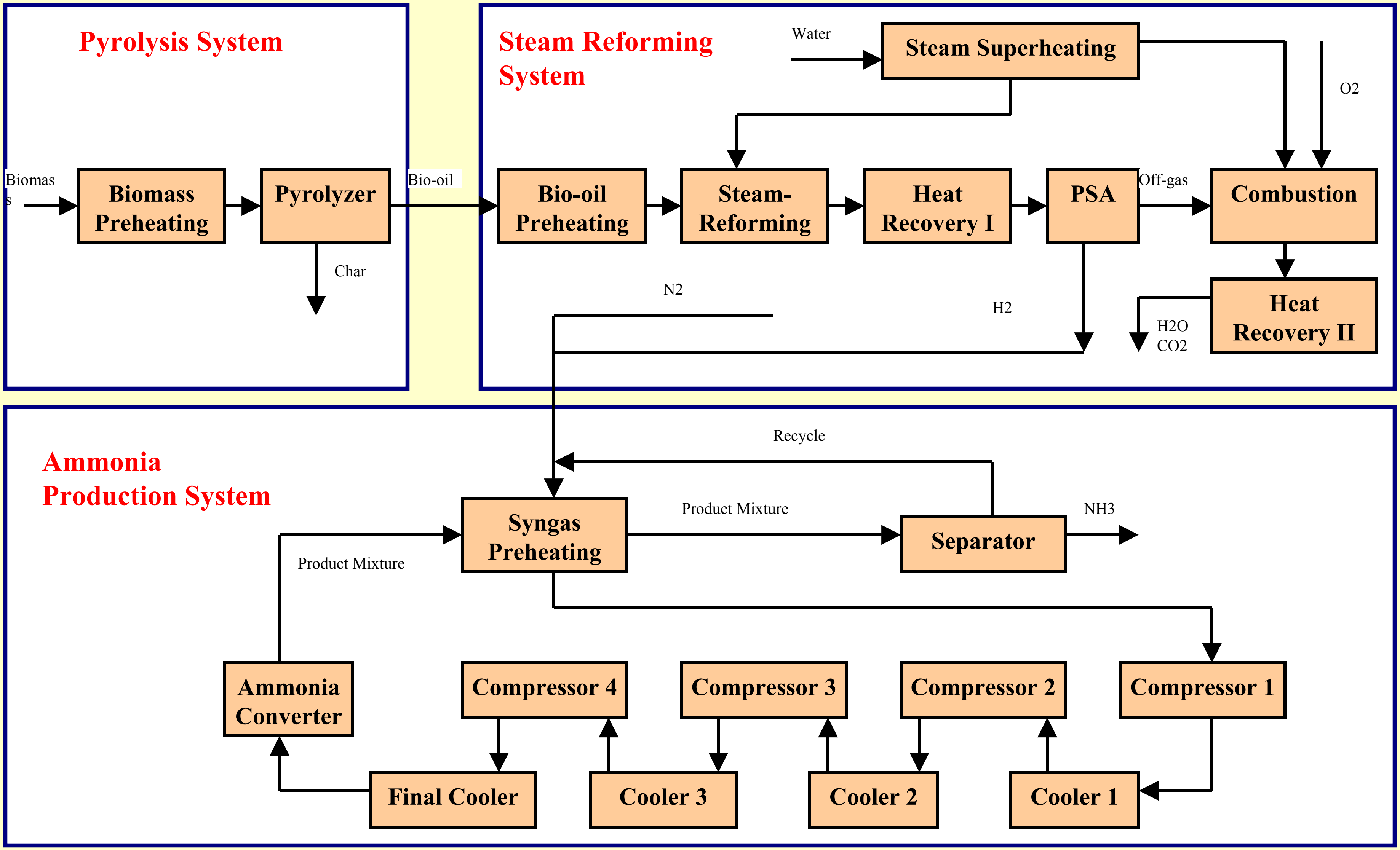


Trace minerals are returned to the soil along with essential nitrogen.

Carbon Negative Energy



Integrated System with H2 and Ammonia from Biomass



Energy Balance

Heat Requirement	Total Amount Required (kJ)	Heat Sources to Provide the Heat	Heat Provided (kJ)	Contribution (%/100)	Note
Biomass Preheating	75.96	Heat Recovery I	13.93	0.183	Biomass from 27 to 100C
		Heat Recovery II	12.02	0.158	Biomass from 100 to 163C
		Cooler 1	48.73	0.642	Biomass from 163 to 418.3C
		Cooler 2	1.27	0.017	Biomass from 418.3 to 425C
Pyrolysis	86.89 – 145.06	Cooler 2	27.41	0.189 – 0.315	
		Cooler 3	28.69	0.198 – 0.330	
		Final Cooler	15.75	0.109 – 0.181	
		External	15.03 – 73.20	0.505 – 0.173	
Bio-oil Preheating	37.81	External	37.81	1	Bio-oil from 425 to 850C
Reforming	101.63	External	101.63	1	850C
Steam Superheating	673.92	Heat Recovery I	232.46	0.345	Water from 27 to 163C
		Heat Recovery II	350.84	0.521	Water from 163 to 571.5C
		External	90.62	0.134	Water from 571.5 to 850C
Syngas Preheating	49.66	Reaction Heat	17.63	0.355	Syngas from 27C to 126.7C
		Product Stream	32.03	0.645	Syngas from 126.7C to 309.5C
Total Heat	1025.87 – 1084.04				
Total Work Required	137.40				
Total Energy Required	1163.27 – 1221.44				

Heat Recovery/ Total system

Heat Sources	Total (Kj)	Heat Sinks to Obtain the Heat	Amount of Heat Obtained (Kj)	(%/100)	Note
Heat Recovery I	328.323	Steam Superheating	232.46	0.708	Provide the heat with temperature from 850 to 50C
		Biomass Preheating	13.93	0.042	Provide the heat at 100C
		Waste	81.93	0.250	Provide the heat at 100C
Heat Recovery II	644.19	Steam Superheating	350.84	0.545	Provide the heat with temperature from 1220 to 163C
		Biomass Preheating	12.02	0.019	Provide the heat from 163 to 119.5C
		Waste	281.32	0.437	Provide the heat from 119.5 to 60C
Cooler 1	48.73	Biomass Preheating	48.73	1	Provide the heat from 591.9 to 309.5C
Cooler 2	48.73	Biomass Preheating	1.27	0.026	Provide the heat from 591.9 to 584.4C
		Pyrolysis	27.41	0.563	Provide the heat from 584.4 to 425C
		Waste	20.04	0.411	Provide the heat from 425 to 309.5C
Cooler 3	48.73	Pyrolysis	28.69	0.589	Provide the heat from 591.9 to 425C
		Waste	20.04	0.411	Provide the heat from 425 to 309.5C
Final Cooler	15.93	Pyrolysis	15.93	1	Provide the heat from 591.9 to 500C
Reaction Heat	17.63	Syngas Preheating	17.63	1	
Ammonia Mix	32.03	Syngas Preheating	32.03	1	
External Heater	245.09 – 303.26	Pyrolysis	15.03 – 73.20	0.061 – 0.241	Provide the heat at temperature above 425C
		Bio-oil Preheating	37.81	0.125 – 0.154	Provide the heat for bio-oil from 425 – 850C
		Steam Superheating	90.62	0.299 – 0.370	Provide the heat for steam from 571.5 to 850C
		Reforming	101.63	0.335 – 0.415	Provide the heat at temperature above 850C
Char Cooling	6.28	Waste	6.28	1	Provide the heat from 425 to 27C

Total Heat Released	1435.66 – 1493.83
Total Work Provided	137.40
Total Energy Provided	1523.40 – 1581.57
Total Energy Wasted	409.61

Hydrogen with Carbon Utilization The Opportunity

- The economic value of utilizing hydrogen to enhance the value of charcoal as scrubbing agent, trace mineral source, fertilizer carrier and topsoil amendment can significantly exceed the energy value of its combustion.
- Hydrogen use ties back to farm productivity
- Establishment of sustainable energy and agricultural systems
- Charcoal in a modified SCR strategy can scrub CO_2, SO_x, and NO_x from fossil fuel exhaust producing valuable nitrogen fertilizers.

Technical Barriers: Hydrogen from biomass via pyrolysis and steam reforming

- Feedstock cost and availability
- Efficiency of pyrolysis and reforming technologies
- Durable, efficient and impurity tolerant catalysts
- Hydrogen separation and purification
- Market and delivery

Benefits

- Locally produced hydrogen yields locally produced fertilizer which can provide the highest crop yields and return harvested soil nutrients
- Mutually beneficial business structures form in a organic and symbiotic fashion
- Groups form which have a much stronger natural competitive defense against imported goods and power. Long-term contracts mutually support financing needs.
- Income opportunities stabilize local economies and balance the influence of large manufacturing firms
- For each ton of CO_2 captured \$179 of fertilizer and hydrogen will be generated at \$54 paid for the biomass.
- 1 million BTU of hydrogen used or sold, ~112 kg of CO_2 will be removed from the atmosphere.
- Nitrogen yields additional energy crop productivity from biomass growth.

Conclusion

- This solution allows agricultural and forestry to join in a mutually beneficial relationship with renewable hydrogen producers and fossil fuel users. This synergy supports the restoration of our soils and represents limitless carbon storage options.

- Hydrogen with carbon co-products allow "capture and utilize" technology to help reduce energy costs

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Final Note: A Limiting Factor

- **Material Balance and Production Limits (Energy is not the limiting factor)** *At theoretical maximum H_2 –CO_2 conversion there would only be enough CO_2 to convert 61% of H_2 to ABC and since our target nitrogen content for the pyrogenic carbon is 10%, (requiring 45% carbon by weight), our limit becomes the 20% carbon char (wt. 12) vs the 56% of ABC (mol.wt. 79). The limit is therefore the carbon char as a carrier utilizing only 31% of available hydrogen but sequestering 112kg of carbon dioxide (as measured experimentally) per million BTU of hydrogen utilized for energy. In addition, there is more than 112kg-150kg when the carbon sequestered in the form of additional plant growth and CO_2 equivalents from reduced greenhouse gas emissions from lower power plant and fertilizer NOx release.*