Hydrothermal Gasification of Biomass

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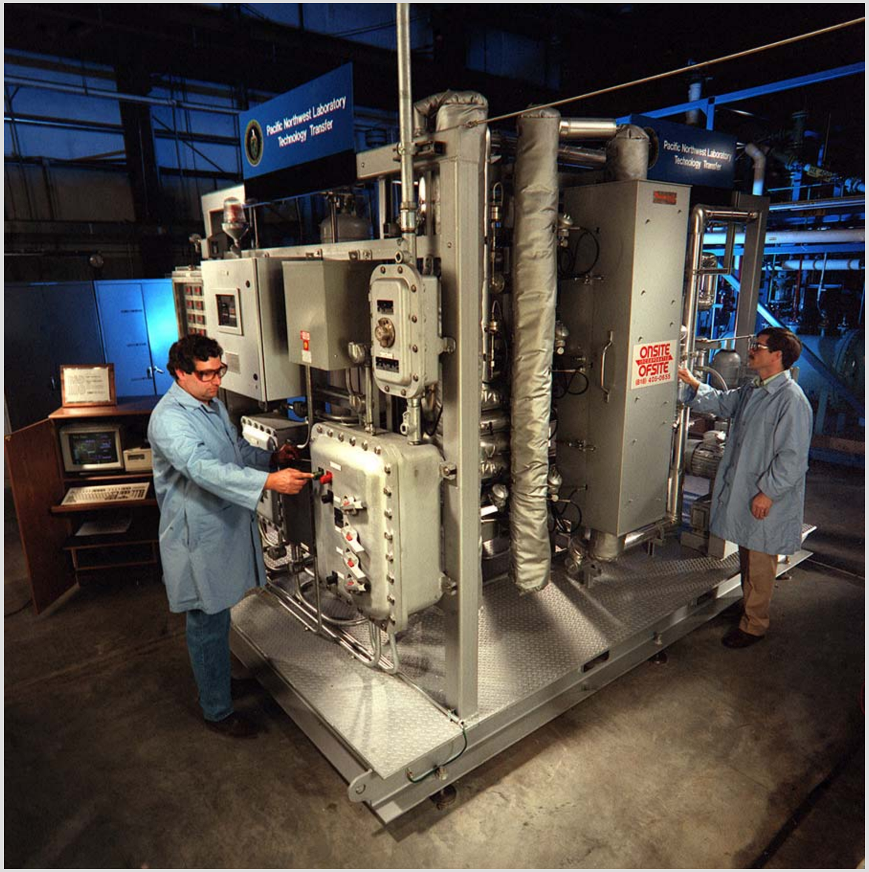
Outline

- Hydrothermal Processes
  - Catalytic Hydrothermal Gasification
  - Super-Critical Water Gasification
  - Low-Temperature Catalytic Gasification
  - Thermal Conversion

- Catalytic Hydrothermal Gasification
  - Technology Description
  - Status of Development
  - Gas Synthesis Integration
  - Current Barriers

Catalytic Hydrothermal Gasification

- 350°C, 3000 psig
- ruthenium (or nickel) catalyst
- methane/carbon dioxide product gas
- has been tested with real biomass slurries
- very high conversion of carbon
- currently in demonstration with biosludge at 7 liters/hr of 5% dry solids slurry



Super-Critical Water Gasification

- 450 to 600°C, 4000 to 6000 psig
- no (carbon?) catalyst
- hydrogen/carbon monoxide synthesis gas product
- moderately high conversion of carbon
- biomass work is limited to small bench-scale semi-continuous tests
- scaled-up plants for development in Germany and Japan
- capital costs are projected as very high

Low-Temperature Catalytic Gasification

- 225 to 265°C, 27-54 bar (400-800 psig)
- platinum-based bimetallic or nickel/tin catalyst
- hydrogen/carbon dioxide product gas
- glycerol, ethylene glycol, methanol
- less successful on glucose and sorbitol
- not tested with biomass

Virent Energy Systems, Inc.

- small-scale application for conversion of glycerol to hydrogen for power production (ICE genset) is being tested
- 3kg/h = 10 kW

http://www.virent.com/apps-genset.htm

Changing World Technologies

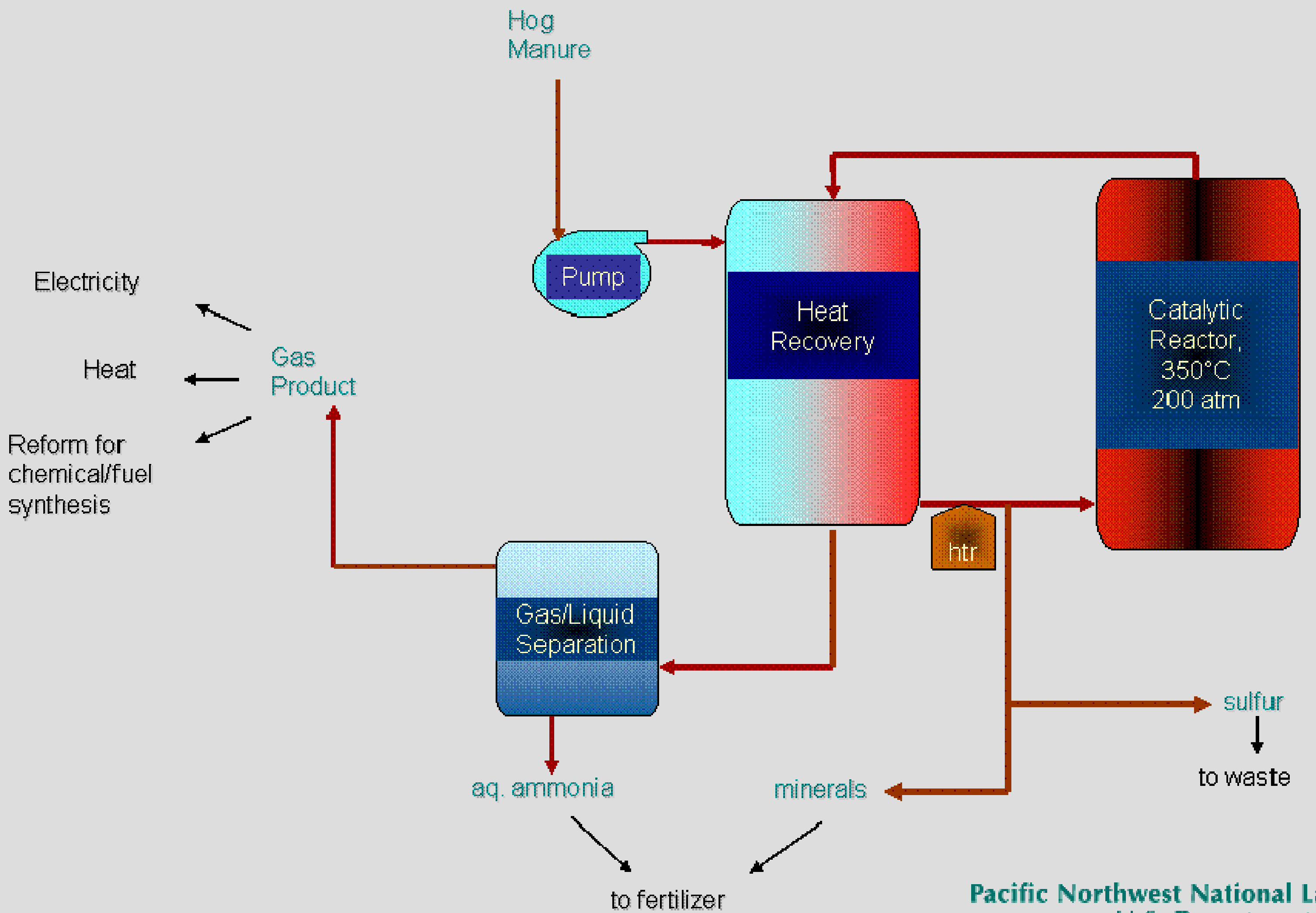
- two stage
  - low-temperature hydrolysis
  - higher temperature thermal treatment of organics
- 260°C, 600 psig, 20 minutes
- distillate fuel oil product
- liquid fertilizer (NH_4 aq) and solid fertilizer (Ca)

Changing World Technologies

- turkey offal and pig fat
- 270 ton and 20 ton yields 500 bbl of #2 fuel oil
- $42 million capital $80/bbl cost ($42/bbl subsidy)

http://www.changingworldtech.com

Low-Temperature Catalytic Gasification in Pressurized Water



Gasification of Wet Biomass

- Low-temperature (~350 ºC) gasification of wet biomass
  - Pressurized liquid water environment
  - Metal catalyst
  - High-pressure steam reforming & methanation
- Intended for biomass feedstocks not suitable for conventional gasification
  - Examples include fermentation wastes, biosludge, dairy manure and others
  - An alternative to anaerobic digestion or combustion of wet wastes

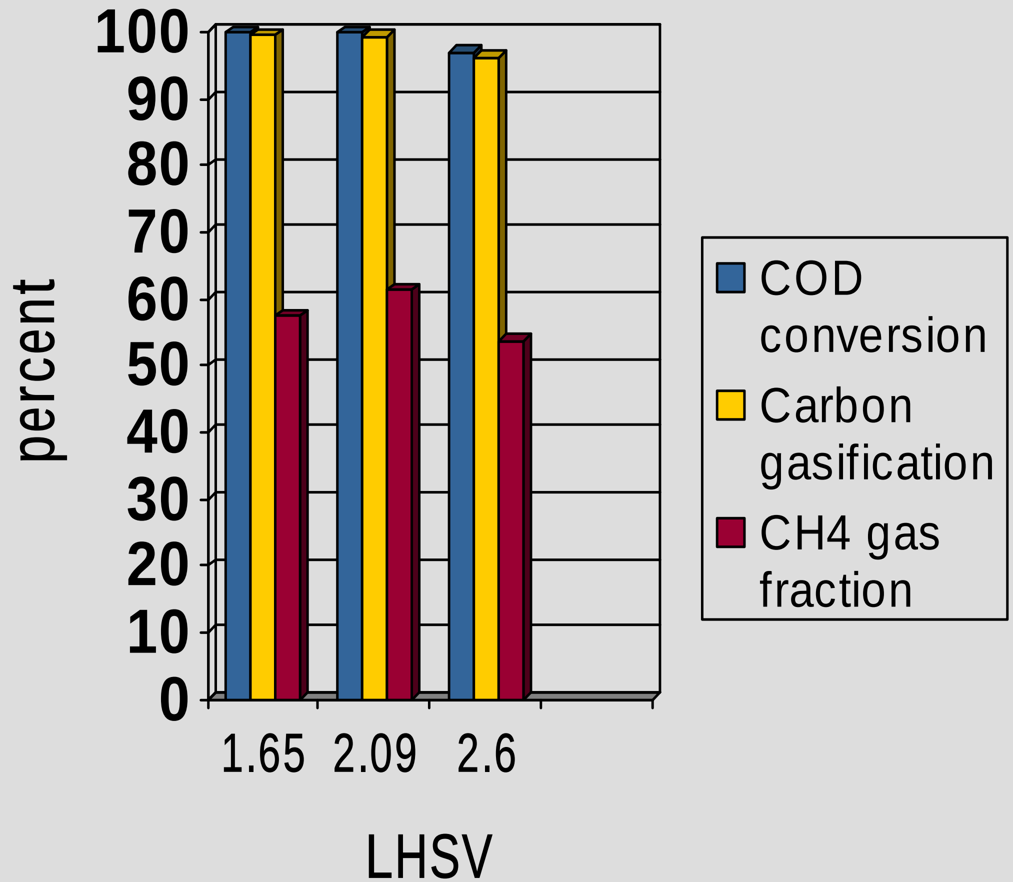
Status of Technical Feasibility

- Concept was invented during fundamental gasification studies for Gas Research Institute
- Initial process tests for DOE Fuels from Biomass
  - The concept showed promise as a method to gasify wet biomass feedstocks
  - The catalysts available at the time were not sufficiently durable for aqueous phase processing
  - Effect of feedstock contaminants on long-term catalyst activity was identified
- PNNL has since developed robust catalysts and supports for use in aqueous solution as part of DOE-OIT sponsored Chemical IOF research

Wide Range of Feedstocks Evaluated

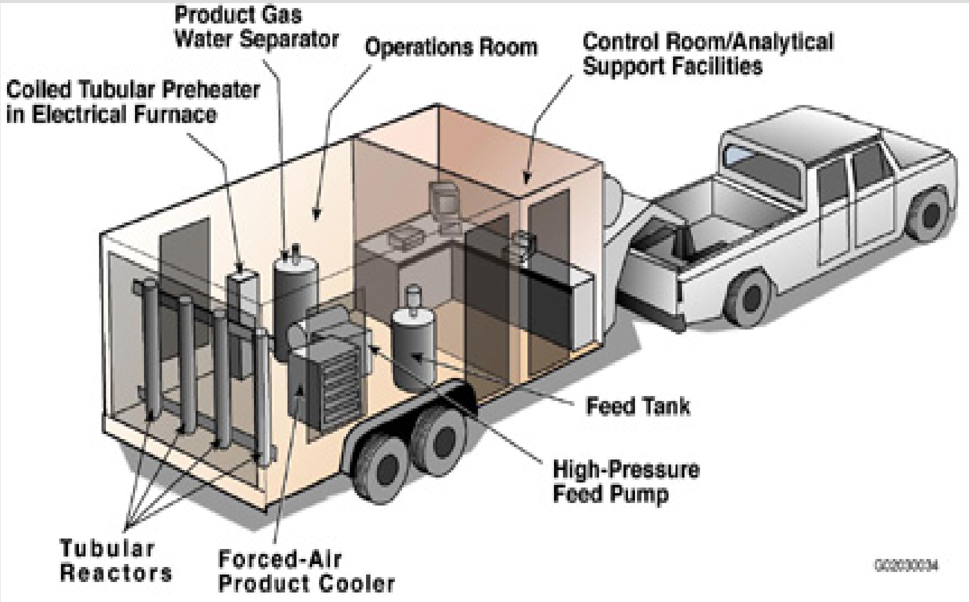
- Byproducts from biobased product conversions
  - EtOH stillage from lignocellulosic feeds
  - extracted product from destarched corn fiber and wheat millfeed
- Animal wastes
  - dairy cattle manure solids
- Chemical manufacturing wastes
  - chemical models of many chemical functional groups
  - listed wastes
  - on-site demonstrations

Manure Conversion Results
bench-scale continuous flow reactor @350°C and 200 atm



Current CRADA Project

- Eastman Chemical wastewater biosludge
- Extended analytical effort
- Bench-scale process development
- Scaled-up reactor modifications and on-site operations



Scope of the Project

Phased research to evaluate concept

- 2005:
  - Biosludge analysis and batch reactor testing
  - Modification and operation of bench-scale continuous-flow reactor
- 2006:
  - Modification and operation of 20 kg/hr continuous-flow facility
- 2007:
  - Completion of R&D and detailed process design and analysis
  - Scale-up design with Eastman
- 2007-8?:
  - Pilot plant construction with Eastman

Economics for Catalytic Gasification of Biosludge -- 350 wet ton/day

- Capital Costs (TCI) $5.3M
  - Equipment, Installation, Site
  - Working Capital, Contingency, Contractor
- Operating Costs
  - Utilities, Labor, Net Catalyst Charges
  - Capital Depreciation, 20 yr straight-line
  - Other Overheads & Directs

  Annual Operating Costs $1.3M/yr
- Product gas value ($7/MMBtu) $1.8M/yr
- Product gas amount 1.3M SCF/day
- Potential H_2 production 2.0M SCF/day

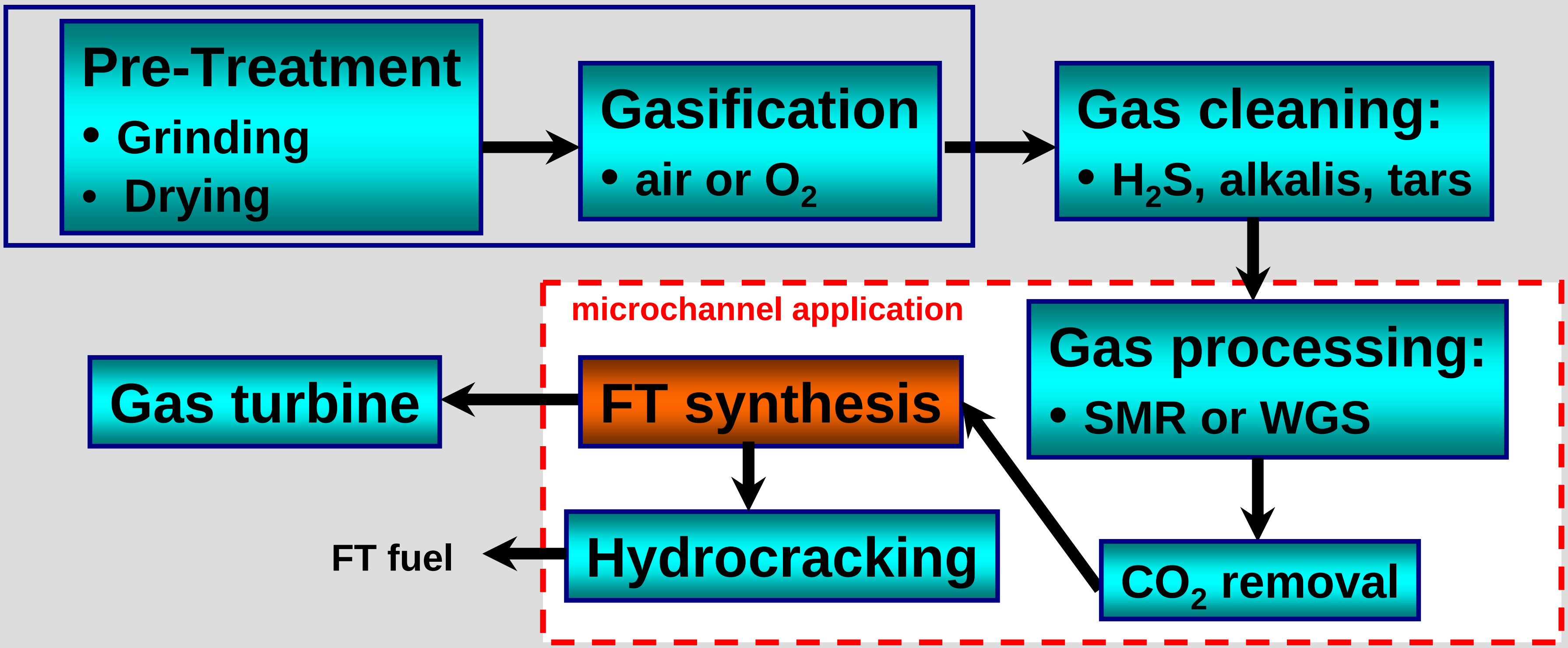
Wet Gasification of Hog Manure

- Evaluate the use of hydrothermal gasification for hog manure treatment with the ARS Coastal Plains Research Center, Florence, SC staff
- PNNL effort funded by USDA Interlaboratory Agreement
- Tasks
  - Develop biomass resource information
  - Develop plant cost data
  - Identify technology barriers

Utilization of Product Gas for Fuel

- Clean, water-washed, product gas
- Methane requires reforming to synthesis gas
- Membrane separation development may be required for CO_2 recovery and efficient methane utilization
- Small-scale operation will require innovative reforming and synthesis methods in order to be cost competitive for liquid fuels production

Fischer-Tropsch Fuels From Biomass

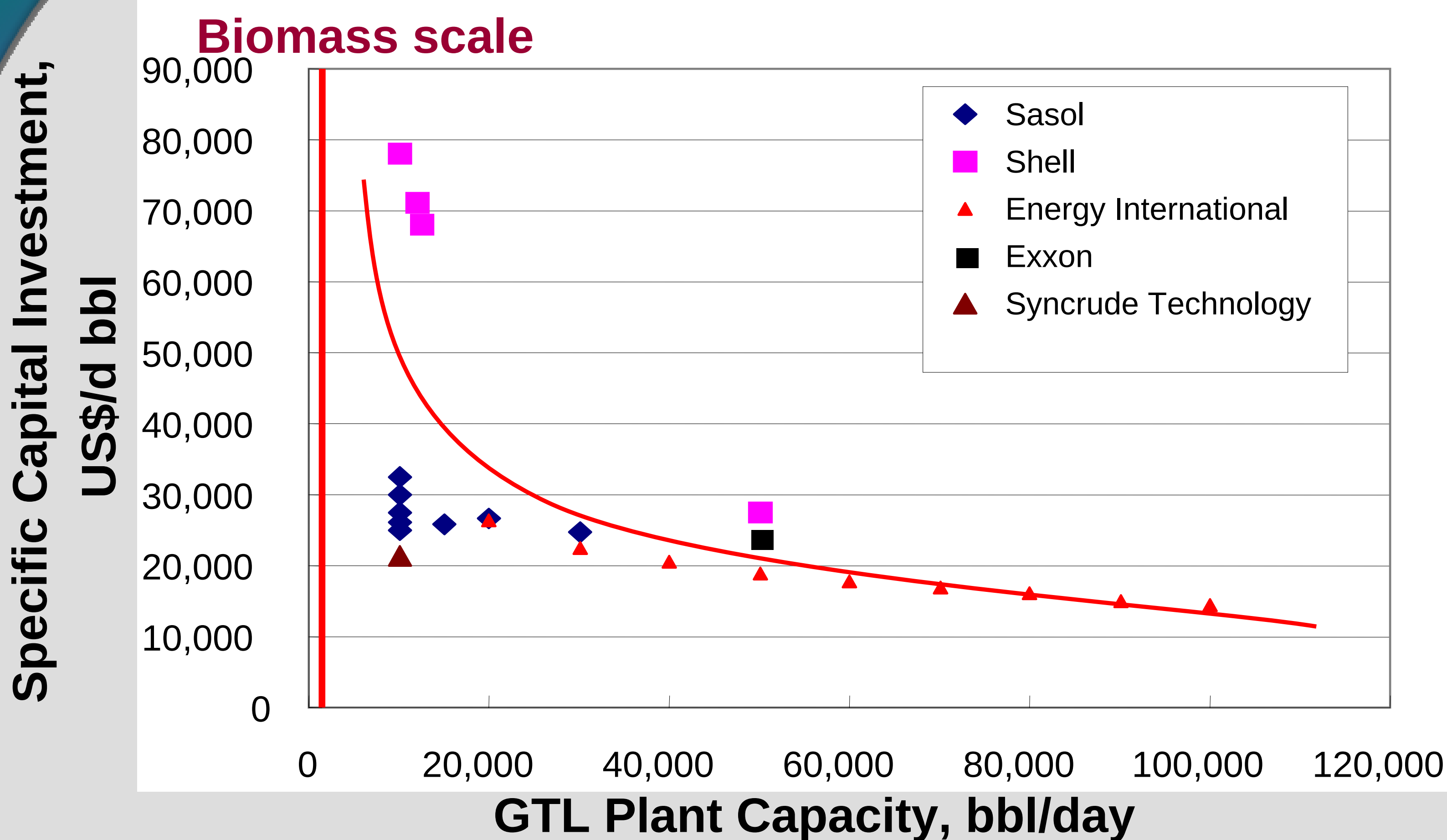


Challenges of Biomass Syngas to Fuels

- Stranded feedstock
  - No existing pipelines to move syngas to large central facilities
- Conversion facilities are small in scale: <1000 tons biomass/day
  - Equivalent to <~1100BPD liquid FT fuels
  - Not economic to convert to fuels using conventional technologies
- Costly CO_2 clean up
- Low Pressure, ~14bar

Microchannel reaction technology provides the potential to cost effectively convert syngas to fuels

Conventional GTL Plant Capital Investment

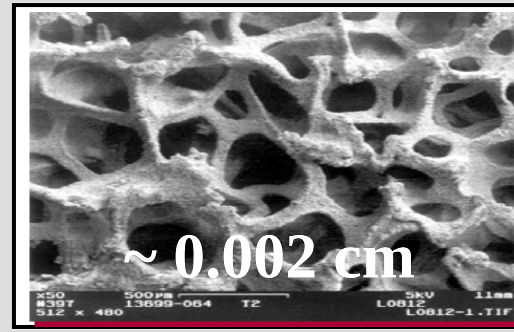


- Conventional GTL plant is not cost competitive at the capacity typical of biomass feedstocks

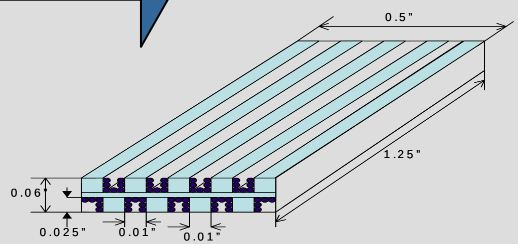
Engineered Catalysts

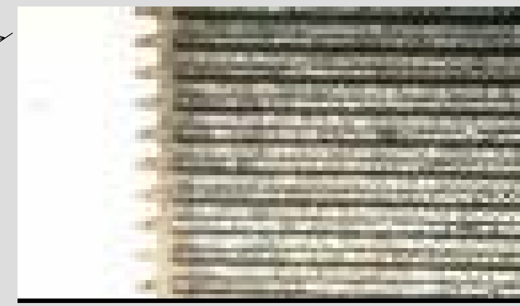
Catalyst tailored for microchannel reactor

Microchannel



Conventional





Support	Porous Ceramic	Porous Metal and Metallic Structured Monolith
Heat Transport Efficiency	Low	High
Mass Transport Efficiency	Low	High
Activity	Limited	High

Accomplishments to Date

- High throughput: 60 $\times$ greater than conventional (GHSV = 60,000hr^{-1} at 15 atm, H_2/CO = 1-2.5)
- Demonstrated tailored product distribution in gasoline and diesel slates -- potentially eliminate hydrocracker
- Preliminary results indicate the potential of no costly CO_2 separation
- Promising economics – low capital cost

Competitive Advantages

- Efficient use of wet biomass without drying
- Effective conversion of biomass components to high yields of fuel gas with minimal residuals, typically >98% conversion
- Intensified process for smaller footprint, 300 times rate of anaerobic digestion
- No added reagents or nutrients (catalyst required)
- Medium-Btu gas product, ~600 Btu/SCF
- Potentially cost competitive conversion technology

Technical Barriers to Utilization

- High-Pressure Aqueous Processing System
  - Feeding systems for wet biomass
  - Scale-up of effective heat exchange systems
- Gasification Catalysts
  - Methods for protecting catalysts from impurities
- Impact of Process Integration
  - Utilization of gas product for synthesis
  - Scale of operation

Technology Focus

- Near-Term --
  - Biosludge is Eastman-Kingsport target
  - Gas product could be used for synthesis
  - Disposal of sludge is constrained
- Long-Term --
  - Wet residues will be widely available
  - Effluent elimination will be important
  - Energy requirements for operations

Legal/Regulatory

- Right to practice
  - 2 relevant process patents
  - 2 additional catalyst formulation patents

- Process effluents
  - Wet gasification cleans waste streams
  - Does not generate residual organic byproducts
  - Byproduct inorganic materials need outlet

Representative Processing Results:

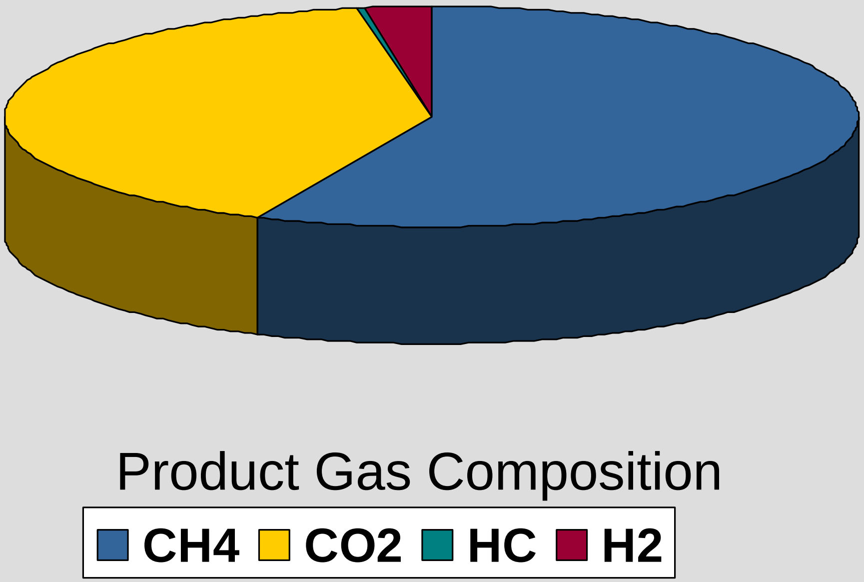
7.8% DDG&S @ 350°C, 200 atm

- COD reduced from 126,000 ppm by 99.9%

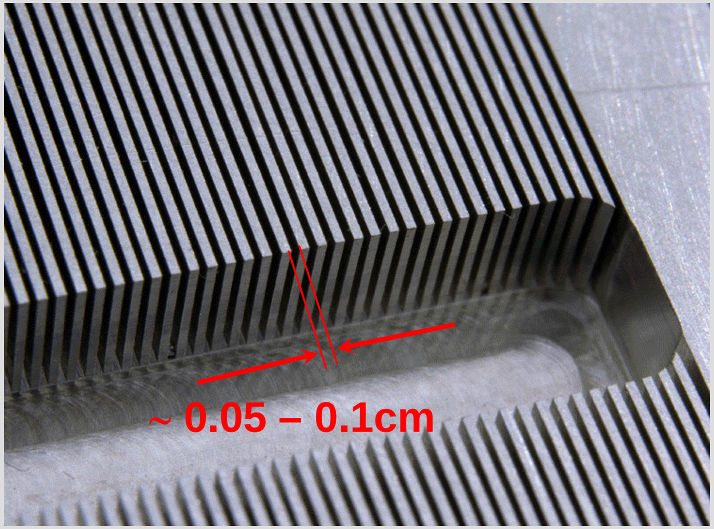
  (125 ppm effluent)

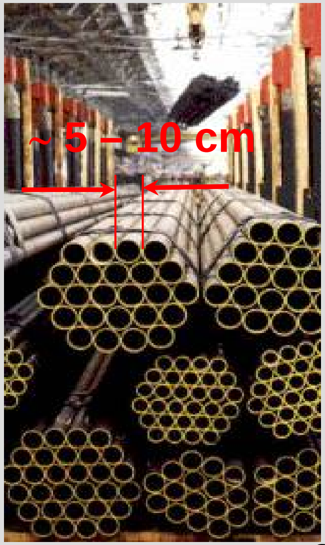
- 0.74 L / g DDG&S solids of a medium-Btu gas

  (590 Btu/SCF)



Characteristics of Microchannel Reactor





- Heat and mass transfer advantages -- Intensifies syngas-to-fuel process
  - Enhances productivity
  - Improves product selectivity
  - Minimizes catalyst deactivation
- Provides a potential cost-competitive solution at the scale relevant to biomass
- Allows potential integration of unit operations (simplification of reforming with synthesis step
- Achieves advanced performance through
  - Microchannel reactor
  - Engineered catalyst

Economics for Wet Gasification of DDG&S
45 million gal/yr EtOH

- Capital Costs (TCI) $35.0M
  - Equipment, Installation, Site
  - Working Capital, Contingency, Contractor
- Operating Costs
  - Raw Materials $ 0
  - Utilities, Labor, Net Catalyst Charges
  - Other Overheads & Directs

  Annual Operating Costs (AOC) $6.3M

- Break-Even gas cost (AOC/Btu/yr) $3.58/MBtu

- 10% ROI gas cost $5.58/MBtu

Cost Sensitivities