Catalytic Biomass Pyrolysis Technology Development for Advanced Biofuels Production

Workshop on Lignocellulosic Biofuels Using Thermochemical Conversion

Auburn University

June 15, 2012

Overview

- Overview of RTI International
- Background and Technology Overview
- R&D Status Update
  - Catalyst Development
    - Automated Microreactor tests
    - Catalyst Scale-up
  - Proof-of-Concept
    - Bio-crude production
    - Sample analyses
  - Bench-scale system design
    - Detailed Engineering
    - RTI Site Planning
  - Techno-economic Analysis
- Summary

What is RTI International

RTI is an independent, nonprofit institute that provides research, development, and technical services to government and commercial clients worldwide. Our mission is to improve the human condition by turning knowledge into practice.

Corporate Offices

Headquartered in North Carolina, with offices around the world

RTP, NC

Washington, DC

Rockville, MD

Atlanta, GA

Chicago, IL

Waltham, MA

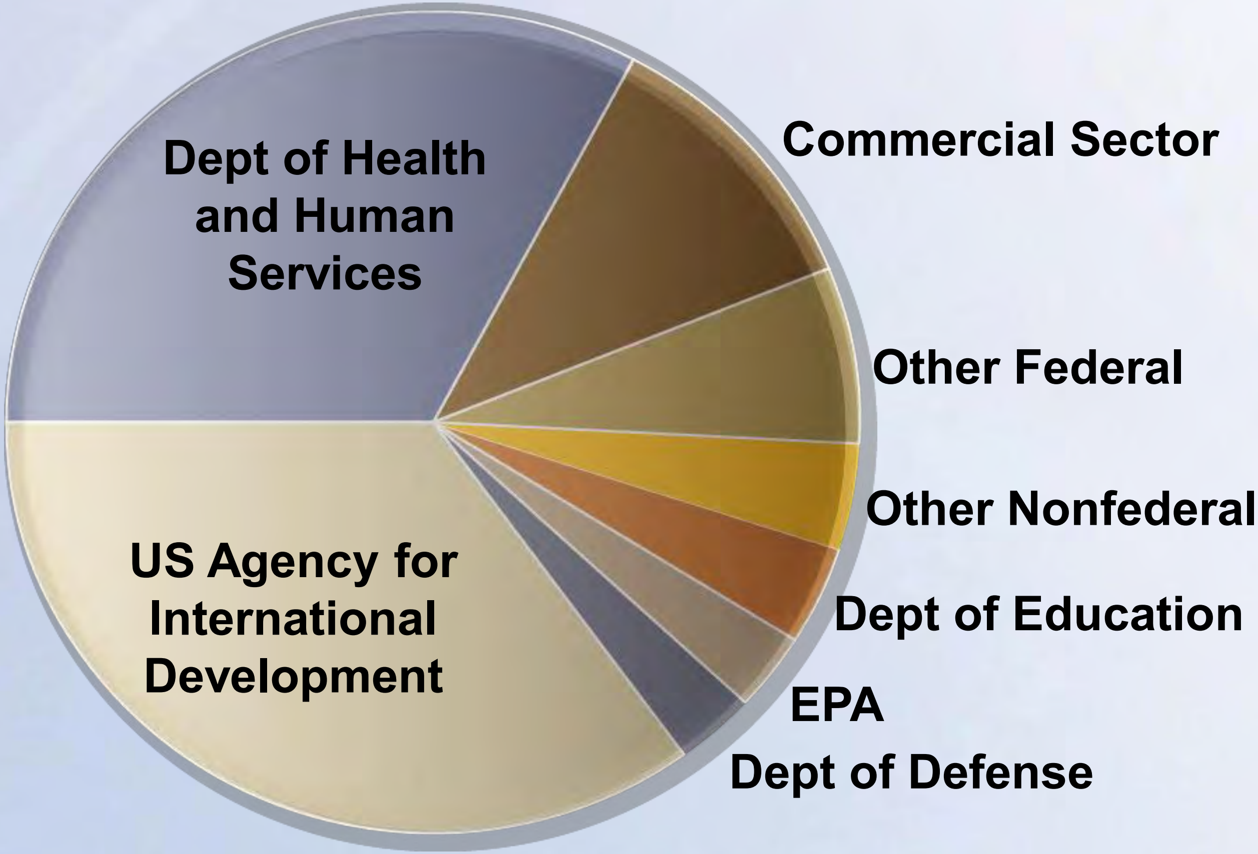
San Francisco, CA

Ann Arbor, MI

Our People

- 2,300 in North Carolina
- 500 in U.S. regional offices
- 1,000 supporting international development projects
- More than 130 disciplines
  - Statistics
  - Survey methodology
  - Public health
  - Epidemiology
  - Economics
  - Chemistry and life sciences
  - Engineering

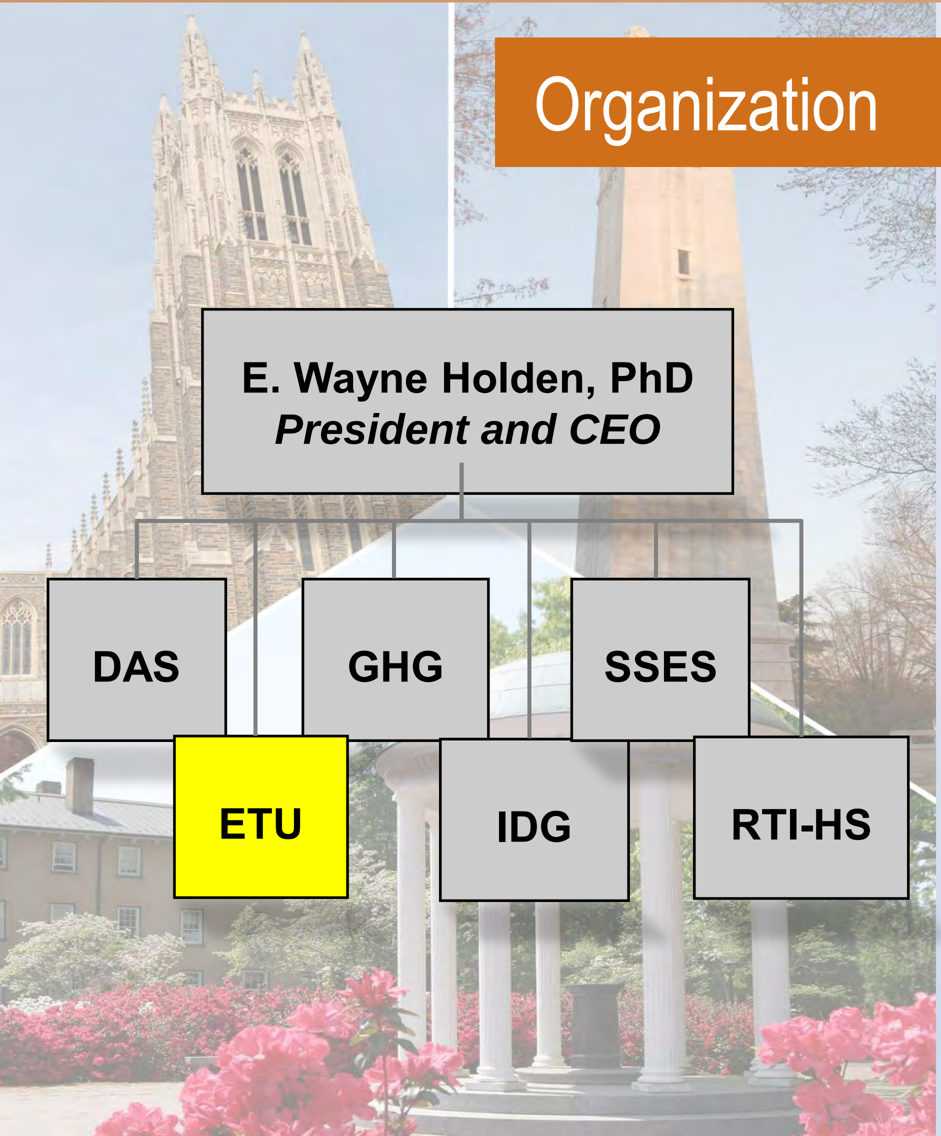
FY2011 Revenue – $777M



Research Focus

- Health
- Drug discovery and development
- Education and training
- Surveys and statistics
- International development
- Economic and social policy
- Energy and the environment
- Advanced technology
- Laboratory and chemistry services

Organization



- Discovery and Analytical Sciences
- Engineering and Technology
- Global Health
- International Development
- Social, Statistical, and Environmental Sciences
- RTI Health Solutions

RTI's Center for Energy Technology (CET)

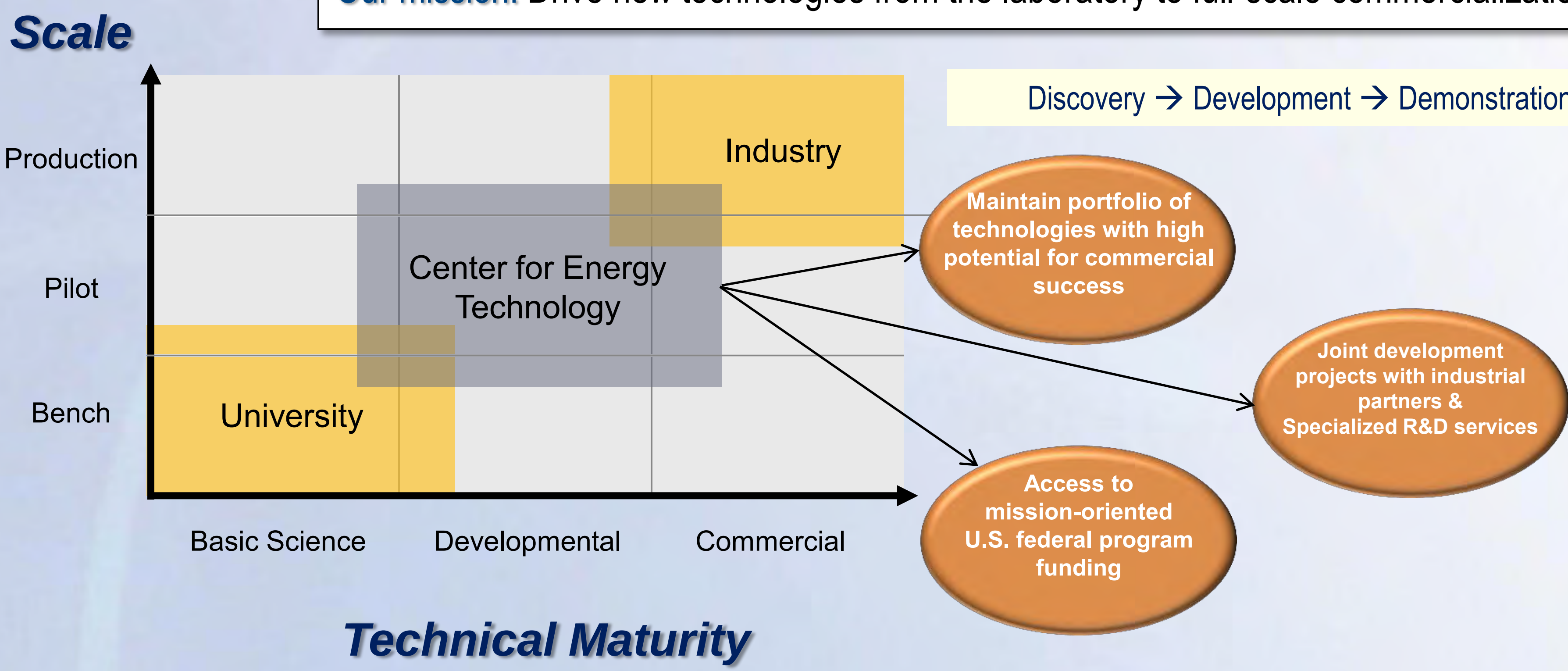

RTI's Johnson Science and Engineering Building
Home of the Center for Energy Technology

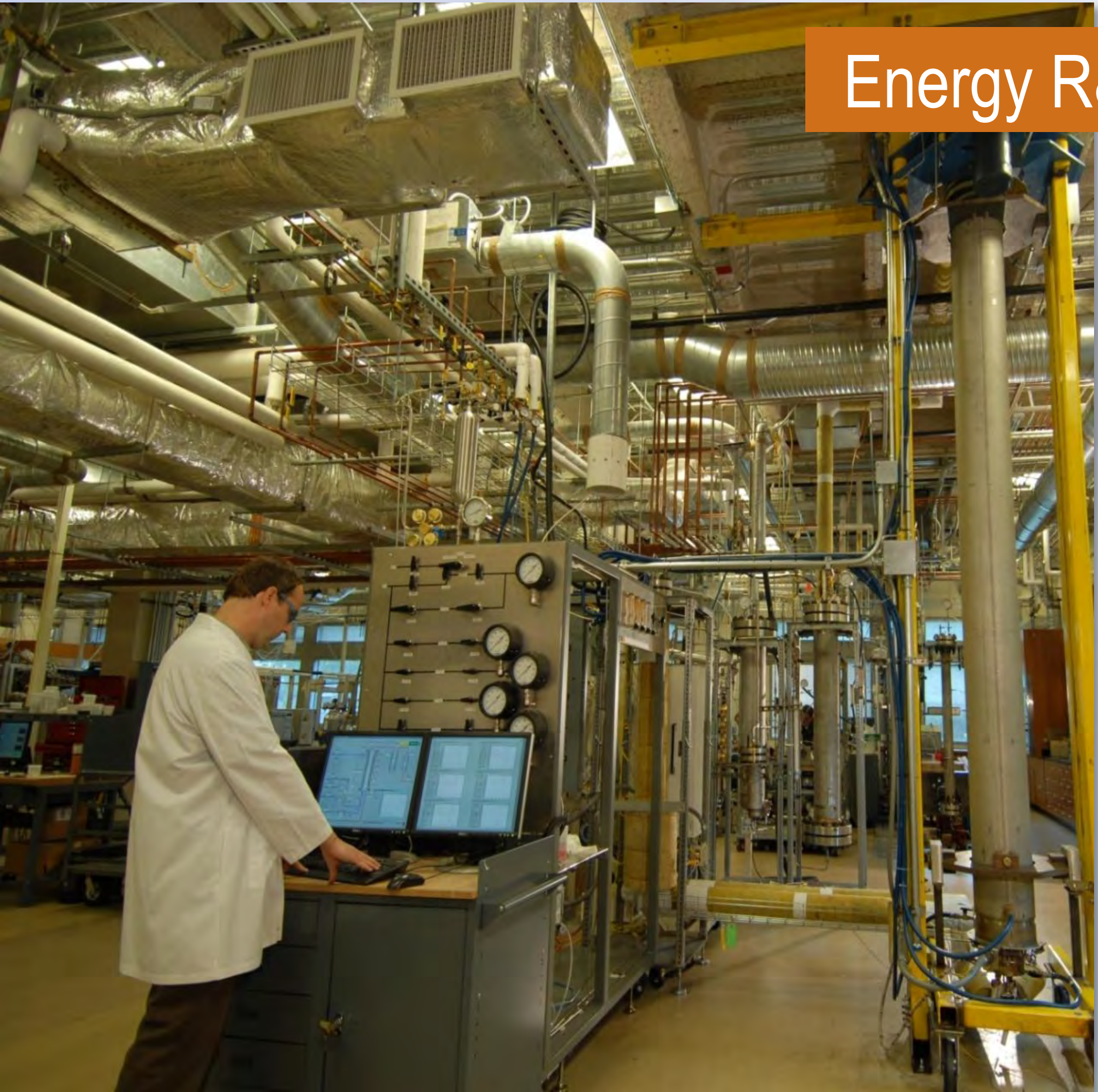
- CET develops **advanced energy technologies** to address some of the world's great energy challenges
- Leading-edge expertise in:
  - Advanced materials development
    - Catalysts
    - Membranes
    - CO_2 solvents
  - Process engineering & design
  - Scale-up & field testing
- Industries served by CET:
  - Power
  - Fuels & Chemicals
  - Gas Processing
  - Transportation
  - Cement

Translational Research

Our mission: Drive new technologies from the laboratory to full-scale commercialization

Discovery → Development → Demonstration





Energy R&D at RTI

Program Areas

Advanced Gasification
- Syngas cleanup/conditioning
- Substitute natural gas production
- Hydrogen production (Chemical Looping)

Biomass & Biofuels
- Biomass gasification
- Syngas cleanup/conditioning
- Catalytic Pyrolysis to biocrude
- Hydropyrolysis

Fuels and Chemicals
- Syngas to fuels and chemicals
- Hydrocarbon desulfurization

Carbon Capture & Reuse
- Post-combustion CO_2 capture
- Pre-combustion CO_2 capture
- CO_2 reuse for fuels chemicals

Industrial Water
- Industrial water reuse
- Energy recovery, waste heat utilization

Shale Gas
- Gas separation & processing
- Process water treatment

Core Capabilities

Catalysts, Sorbents, Solvents & Membranes
- Synthesis and development
- Characterization and testing
- Production scale-up

Lab-scale and Bench-scale Testing
- Micro-reactors (gas-solid reactions)
- Fixed- and fluidized-bed, bench-scale reactors

Process Simulation, Engineering & Design
- Process modeling
- Fluid-bed/Transport reactor design
- Process scale-up and integration
- Techno-economic assessments

Process Scale-up & Prototype Demonstration
- Pilot and demonstration units

RTI INTERNATIONAL

Background and Technology Overview

Catalytic Biomass Pyrolysis Technology Overview

Goal: Develop a process to convert lignocellulosic (non-food) biomass into a bio-crude oil that can replace petroleum crude in U.S. refineries

Technology: Catalytic pyrolysis of biomass into bio-crude

- Multi-functional catalysts maximize carbon efficiency, remove oxygen, and control bio-crude properties

Resulting bio-crude

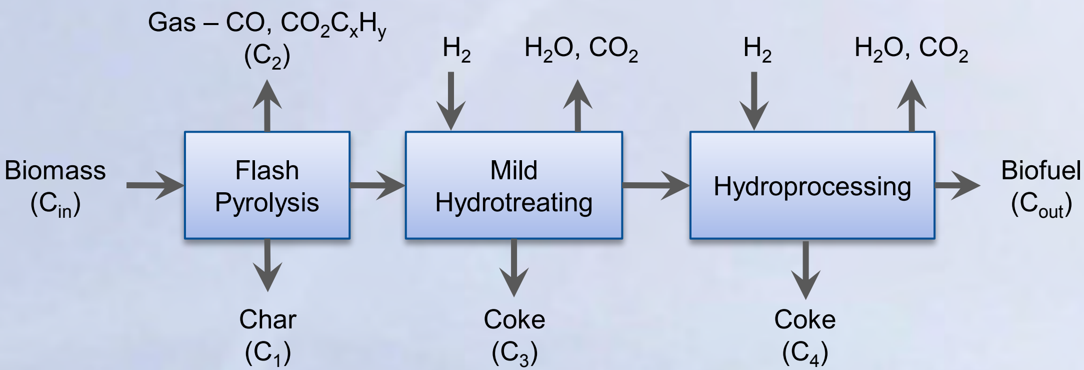
- Is highly energy efficient (maximize fuel yield)
- Can be integrated into existing refineries
- Requires less hydrogen to upgrade than bio-oil from conventional fast pyrolysis

Commercial Concept

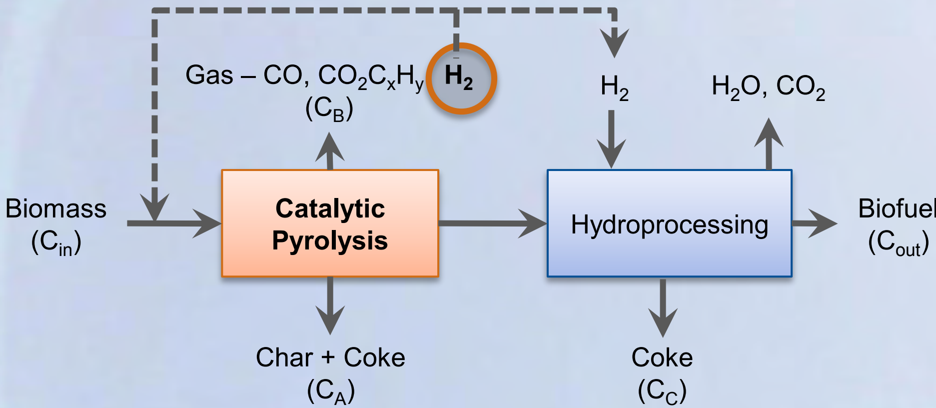
- Stand-alone integrated catalytic pyrolysis with hydroprocessing
- Distributed network of catalytic pyrolysis facilities process biomass
- Bio-crude sent to existing refineries for upgrading
- Refined fuel can be stored, pumped, and used exactly as petroleum-based fuels are today

Catalytic Biomass Pyrolysis State-of-Technology

Current State-of-the-Art



RTI's Translational Technology



Primary Technical Objectives

- Maximize biofuel output
- Minimize external H_2 consumption
- Reduce process complexity
- Maximize heat integration

Technical Barriers to Overcome

- Utilize H_2 produced *in-situ*
- Reduce oxygen content of biocrude
- Improve bio-crude thermal stability to maximize energy recovery
- Minimize coke formation
  - $C_B < C_2$
  - $C_A << C_1+C_3$
  - $C_C \approx C_4$

Technology Development Approach

Proposed Technology: A novel process that uses multi-functional catalysts to control biomass pyrolysis chemistry to produce a cost-effective refinery-compatible hydrocarbon intermediate

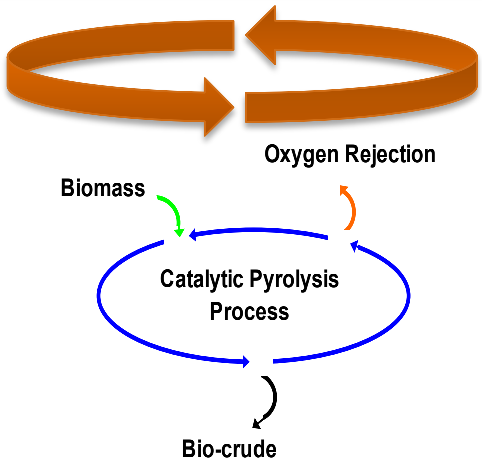
Catalyst Development

Catalyst Synthesis
Catalyst Characterization
BET, TPR, Surface Analysis
Model Compound Testing
Bench-scale Catalytic Pyrolysis

Identify key parameters for reactor design

- Deoxygenation
- Regeneration
- Coke yields/Energy efficiency
- Oxidation and reduction rates

Scale-Up and Commercialization

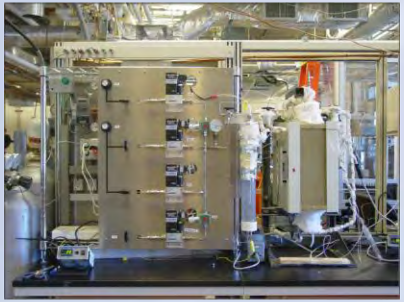


Process Development

Real Biomass Testing
Yields
Gas
Bio-crude
Char/Coke
Hydrogen demand
Bio-crude Analysis and Quality
Process Modeling
Heat and Material Balances
Reactor Design

- Focus on technology scale-up from the beginning
- Cover entire biomass to biofuels value chain
- Commitment and resources to commercialize new biofuels technologies

Technology Development Timeline



2010 – 2012

DOE/ARPA-E

Catalytic Bio-crude Production in a Novel, Short-Contact Time Reactor

DE-AR0000021 ($4MM)

2007 **2008** **2009** **2010** **2011** **2012** **2013** **2014** **2015**

2007

RTI Internal R&D

Funds ($200k)

2009 – 2011

DOE/OBP

Catalytic Deoxygenation of Biomass Pyrolysis Vapors to Improve Bio-Oil Stability

DE-FG36-08GO18208 ($1.875MM)

2012 – 2015

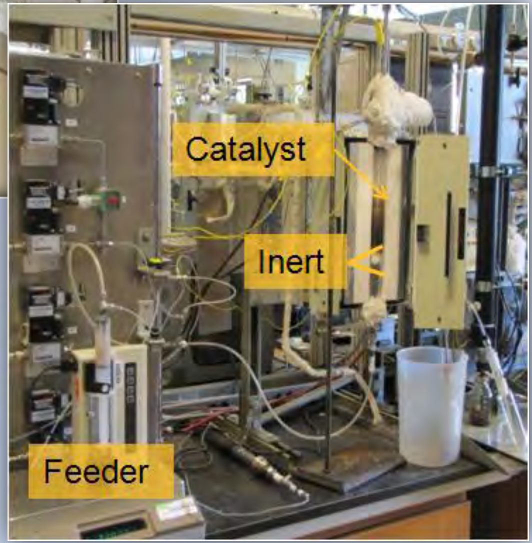
DOE/OBP

Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons

DE-FOA-0000467 ($5MM)

Catalyst Development

Catalyst Development



- Screened catalyst formulations for deoxygenation activity in multiple reactor systems
- Automated Medium Throughput Microreactor (MTP)
  - Programmed reaction sequence for unattended operation
  - Rapid screening to evaluate deoxygenation activity with model compounds
  - Quantitative real-time product analysis
  - Measure regeneration products for coke yield
- Bench-top fluidized bed reactor for catalytic biomass pyrolysis
  - Correlate deoxygenation activity with bio-crude oxygen content
  - On-line gas analysis
  - Liquid and solid product collection and analysis
  - > 95% mass closure for bio-crude yield and energy recovery
  - Over 100+ trials of catalytic fast pyrolysis in the bench-top fluidized bed reactor

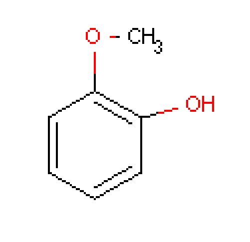
Medium Throughput Catalyst Microreactor System

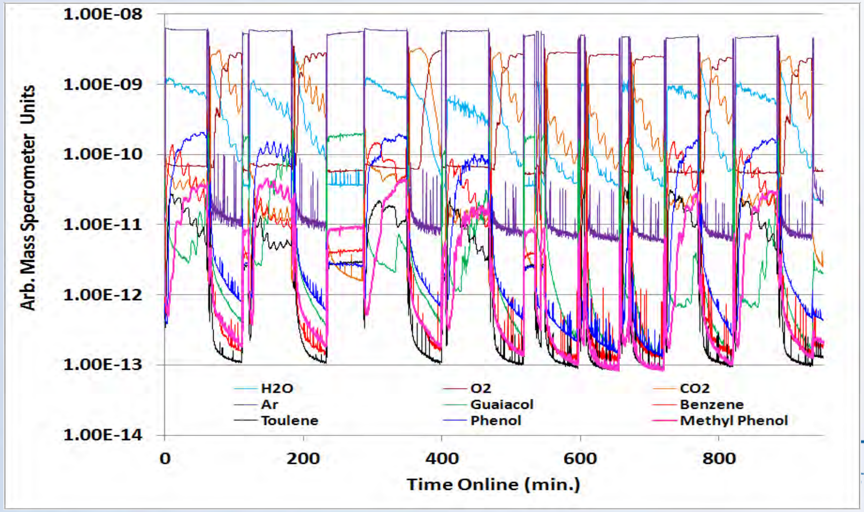
- Fully automated to increase catalyst testing throughput
- Real-time, quantitative product sampling
- Develop reaction mechanisms and kinetics for model compounds

Supported catalyst development

- Evaluating long-term activity of RTI-A9
- Screening formulations
- Testing effect of promoters

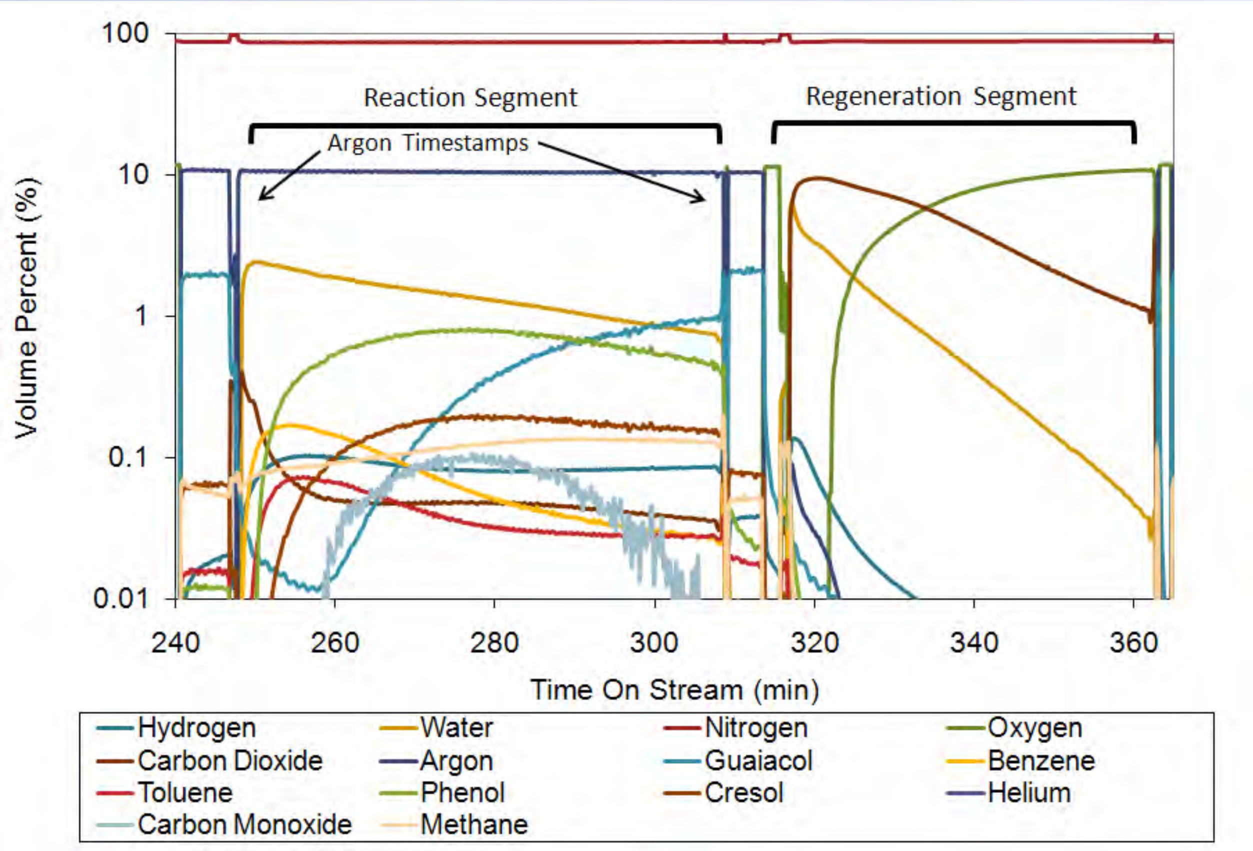
Guaiacol Deoxygenation with RTI-A9





MTP Reactor Data Analysis

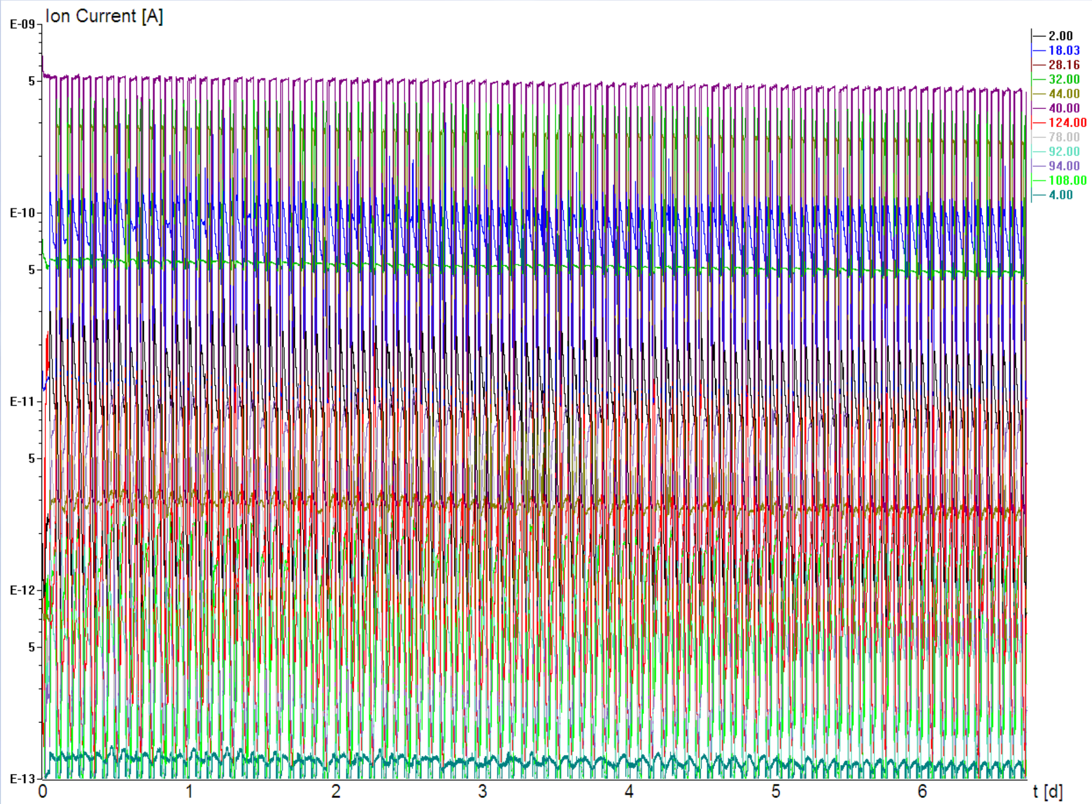
Guaiacol flow rate adjusted for 90% or less conversion to evaluate time-dependent deoxygenation activity



Real-time, online MS analysis

- Products correlated with specific ions (m/z)
- Products quantified by calibration and integration under curve
- Provides time resolved product composition
- Measure both reaction and regeneration

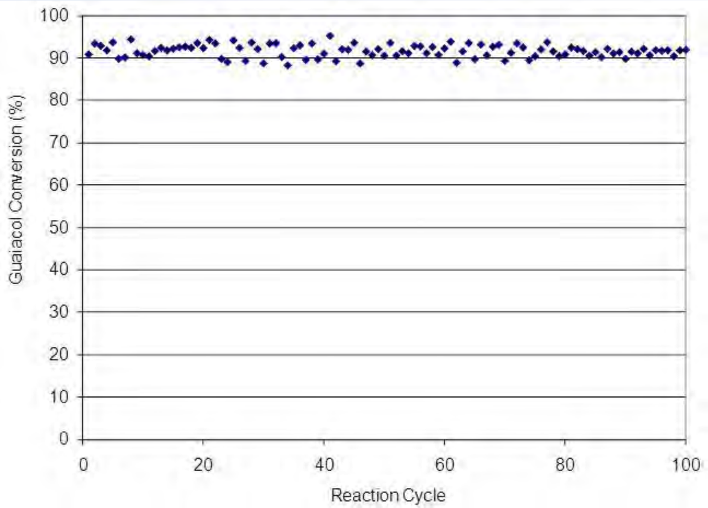
RTI-A9 Long-term Activity



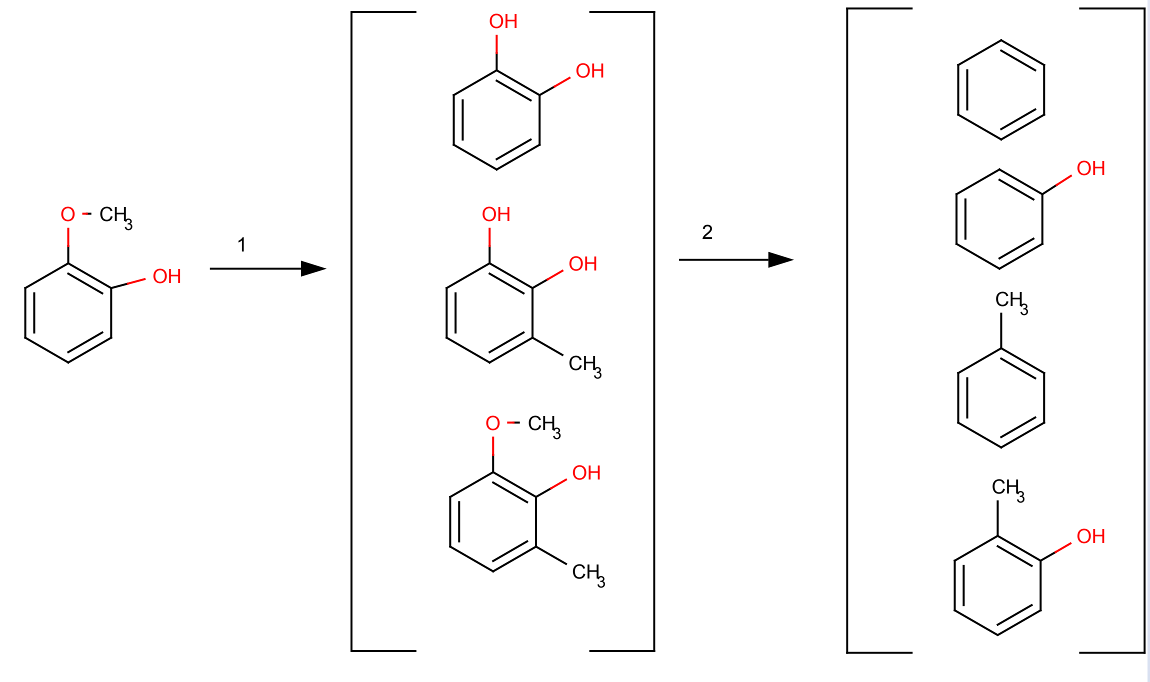
6 days (75 reaction/regeneration cycles) of guaiacol deoxygenation with RTI-A9 at 450 C.

Long-term activity of RTI-A9 measured over 100 cycles

- Negligible change in 92% conversion
- Negligible change in product distribution



Catalyst Development Summary

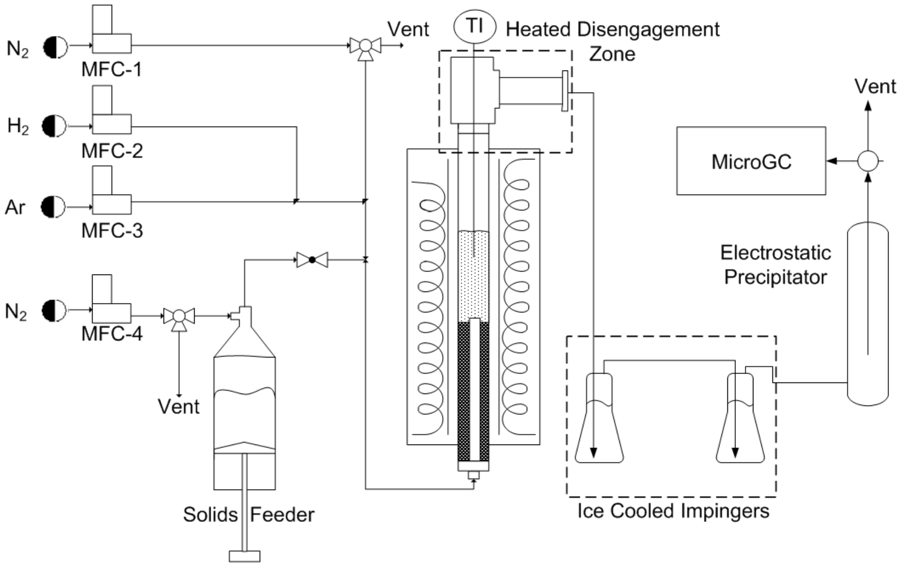


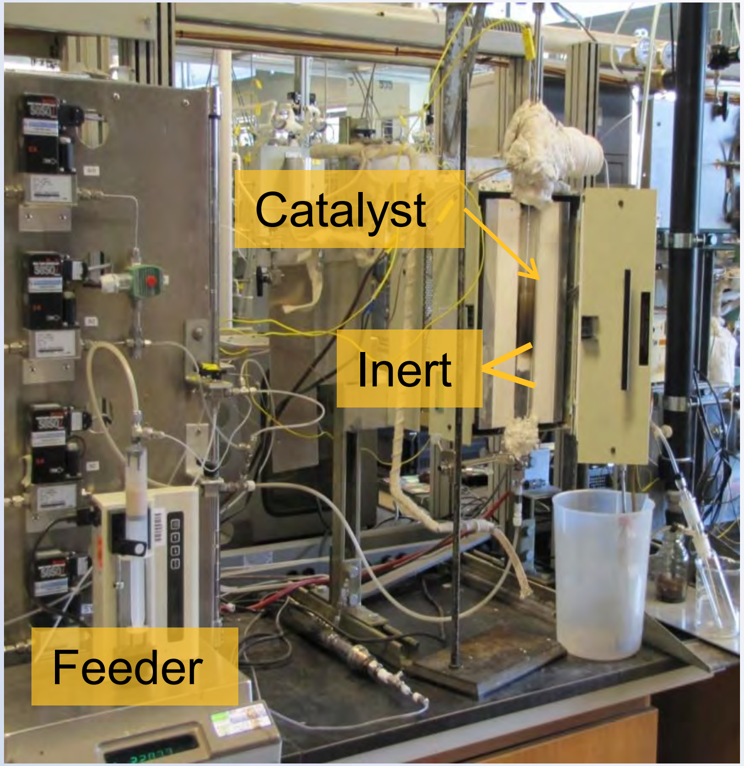
Transalkylation (1) and Hydrodeoxygenation (2) are possible reaction paths for deoxygenation of guaiacol over RTI-A9 and its derivatives

- Key material properties (independent of preparation method)
- MTP will be used to test catalyst formulations to validating performance of material from scale-up procedures
- RTI-A9 stable for 100 cycles
- Explore using MTP results to develop deoxygenation mechanisms and Arrhenius rates to predict catalyst performance

Catalytic Biomass Pyrolysis Proof-of-Concept

1”-diameter Fluid Bed Reactor System





- Catalytic pyrolysis studies in a bench-top fluidized bed reactor
- Rapid catalyst screening
- Biomass injected directly into fluidized catalyst bed
- Mass closures > 90%
- On-line gas analysis
- Liquid and solid product collection and analysis

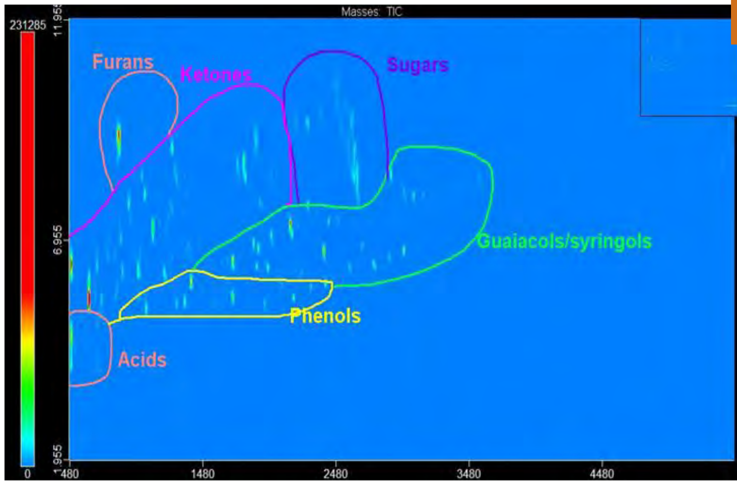
Bio-crude Properties

	Baseline	RTI-A9
Solids (wt%)	14.3	19.8
Gas (wt%)	11.6	23.9
Water (wt%)	18.4	28.7
Bio-crude, dry (wt%)	49.4	24.8
Bio-crude Composition (wt%)		
C	56.6	72.8
H	5.8	7.2
O	37.7	19.9
Gas composition (vol%)		
H_2	1.5	7.7
CO	25.4	37.1
CO_2	42.1	32.6
CH_4	3.5	10.6
C_{2+}	27.4	12.0

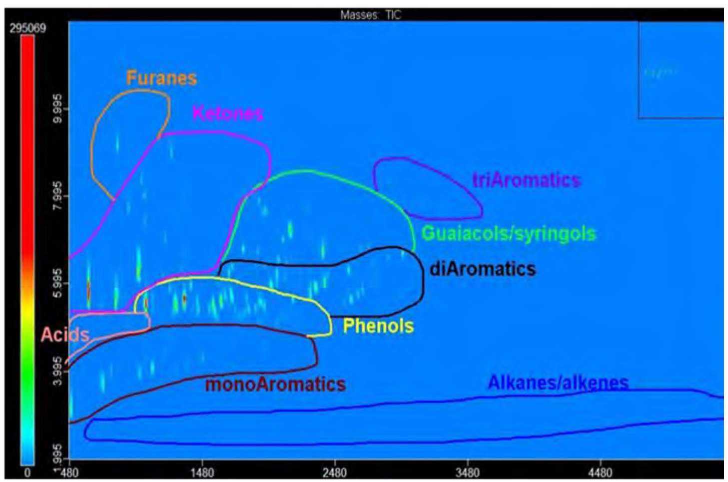
Bio-crude Properties	Baseline	RTI-A9
TAN (mg KOH/g bio-crude)	193	70
KF water Content (wt%)	27	54
Kinematic Viscosity at 40 C (cSt)	53.2	56
Revaporization Efficiency at 350 C	48%	82%

Catalytic Effect on Bio-crude Composition

White oak fast pyrolysis oil



White oak bio-crude produced with RTI-A9 catalyst

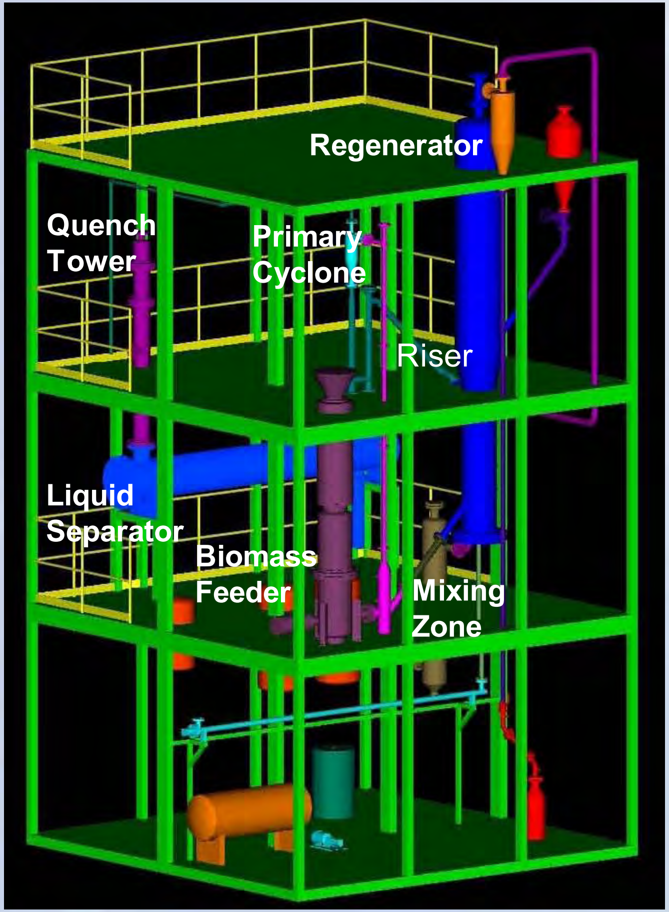


Quantified Content (Area-%) of Identified Compound Classes in Pyrolysis Oil.

Compound Classes	White Oak Pyrolysis Oil	RTI-A9 Bio-crude	Observed Changes (↑/↓)
acids	11.3	Not detected	↓
Furans	11.6	1.0	↓
Aldehydes/Ketones	9.0	10.0	≈
Phenols	2.9	23.1	↑
Aromatic polyols	38.4	37.2	≈
Sugars	16.5	0.2	↓
Paraffins	0.6	0.5	≈
Monoaromatics	1.2	5.3	↑
Di- to tetraaromatics	Not detected	15.9	↑
Unknown	3.4	2.9	≈

Bench-scale Catalytic Biomass Pyrolysis System

1 TPD Catalytic Biomass Pyrolysis Unit Overview



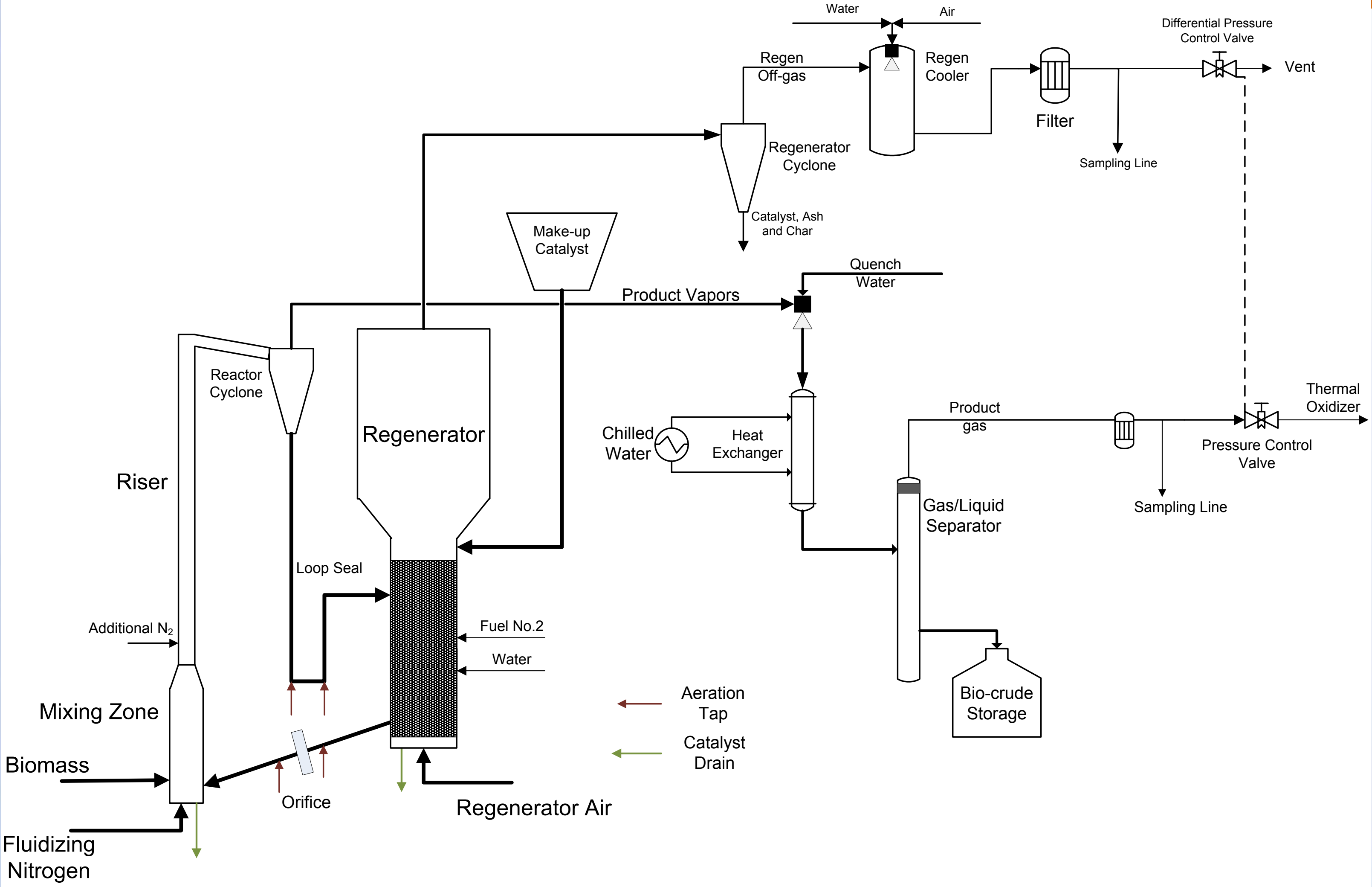
Objectives:

- Demonstrate RTI's catalytic biomass pyrolysis process at pilot-scale with a biomass feed rate of 100 lb/hr
  - Bio-crude with less than 20 wt% oxygen
  - At least 50% energy recovery
  - Mass closure at least 90%
- Understand the effect of operating parameters on product yields and quality
  - Pyrolysis temperature (350-500 ºC)
  - Residence time (0.5-1.0 s)
  - Regenerator temperature (500-700 ºC)
  - Catalyst circulation rate
  - Type of biomass

Design based on single-loop transport reactor system

- Catalyst undergoes continuous reaction and regeneration
- System can be operated autothermally with heat of regeneration (and char combustion) carried over by the catalyst to the reaction zone

1 TPD Catalytic Biomass Pyrolysis System PFD



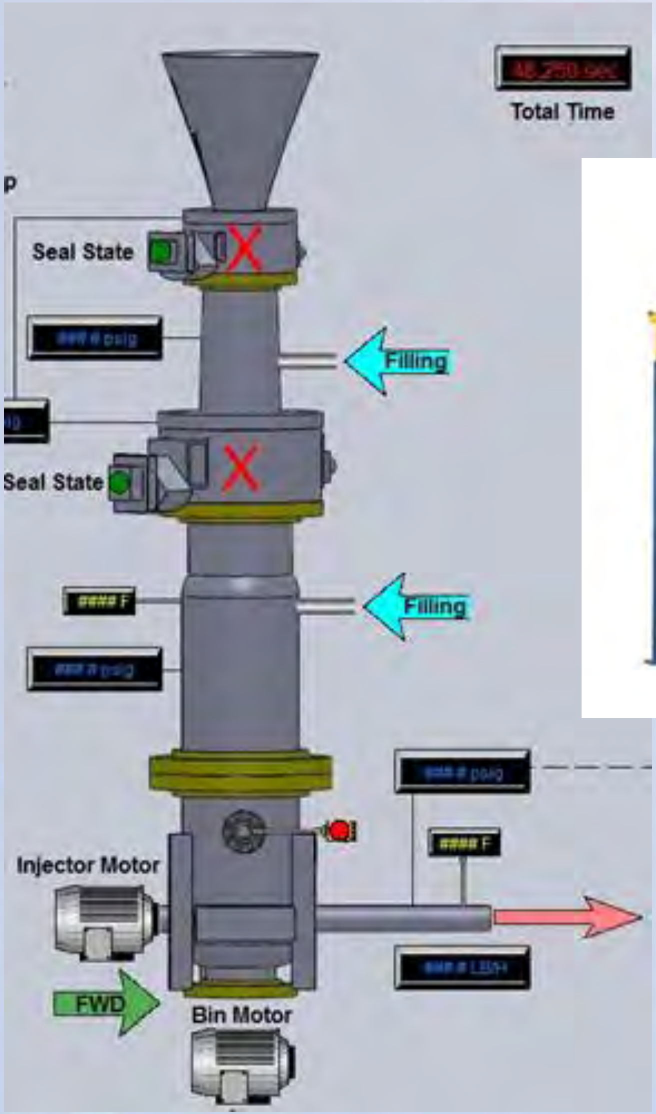
Design Basis and System Overview

	Design Basis	Range
Pyrolysis temperature, ˚C	500	350-500
Regeneration temperature, ˚C	700	500-700
System pressure, psia	20	20-30
Biomass feed rate, lb/hr	100	25-110
Residence time, s	0.5	0.4-1.2

Process Sub-systems

- Biomass Feeder
  - – Bulk bag discharge
  - – Double lock hopper
- Reactor System
  - Transport reactor
  - Make-up catalyst storage
  - Quench system for pyrolysis products recovery
    - – Spray column
    - – Separation vessel
    - – Heat exchanger
- Product Collection and Storage
- Regenerator Off-gas Cooler
- Thermal Oxidizer and Vent

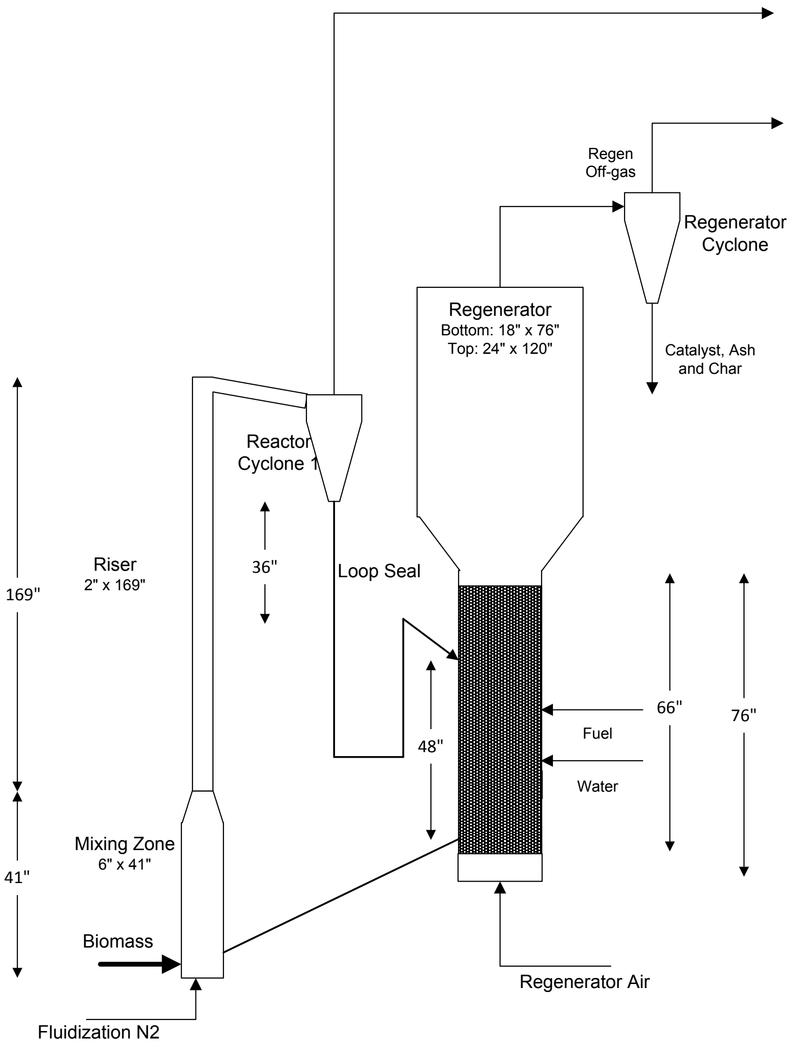
Biomass Feed System Design – T.R. Miles



Feedstock Preparation

- Biomass received in super sacks (0.5” top size, 10% moisture, 15-30 lb/ft^3 bulk density)
- Bulk bag discharger for loading the feeder hopper

- Biomass Feeder
  - Double lock hopper design to purge and pressurize feed
  - Design feed rate: 100 lb/hr based on volumetric flow rate
  - Bottom bin capacity above level switch: 1.8 ft^3
  - Cycle time every 15-30 minutes
- Cooling water jacket surrounding the feeder screw
- P.O. for feed system has been placed
- Delivery - August 2012



Transport Reactor Operation

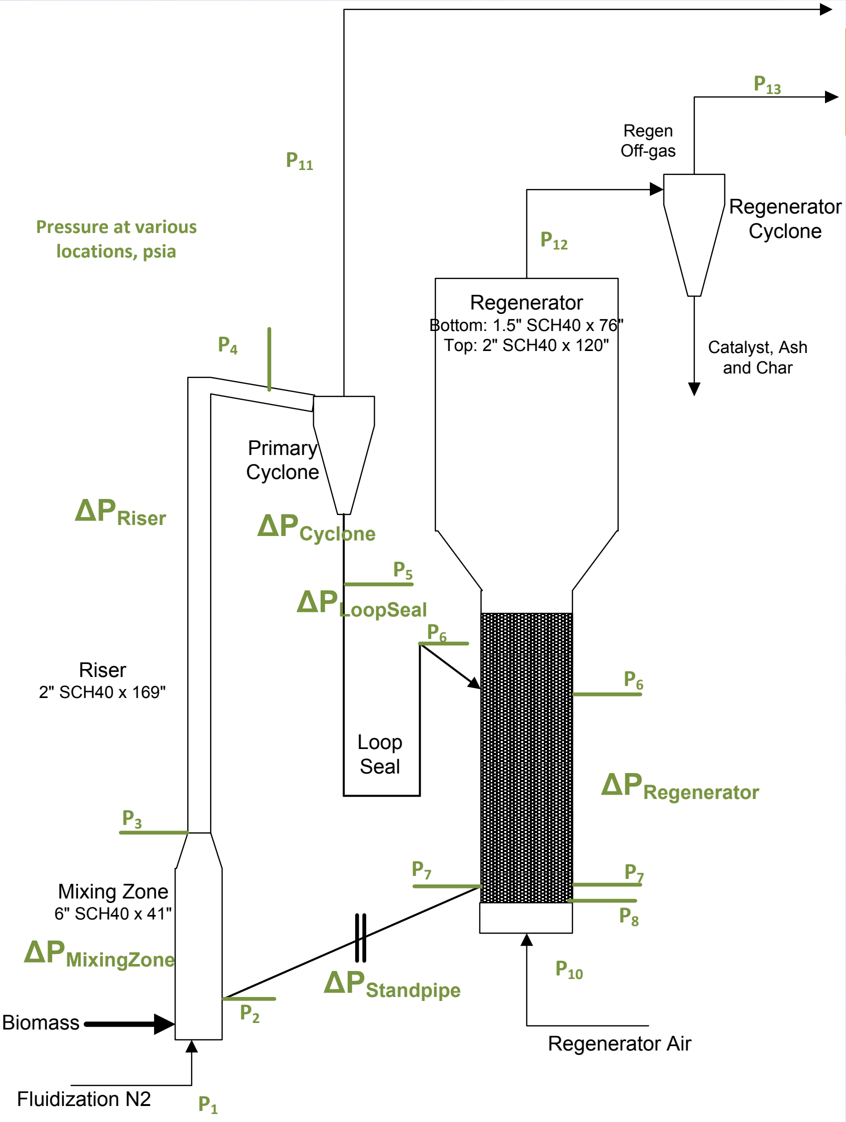
Reactor

- Biomass and catalyst are fluidized with N_2 in the mixing zone
- Biomass and regenerated catalyst fed just above gas distributor
- Fluidizing gas velocity is expected to be 1 ft/s
- Reactor cyclone separates coked catalyst, char, ash and unconverted biomass from pyrolysis vapors and permanent gases

Regenerator

- Char and coke oxidize in the regenerator
- Water or diesel can be added to the regenerator to control the bed temperature
- Air velocity is maintained at 1.4 ft/s in the bottom zone and is lowered to 0.8 ft/s in the top section
- Ash and catalyst fines are expected to entrain out of the regenerator at the operating gas velocity of 0.8 ft/s
- Make-up catalyst can be added if solids level in the regenerator drops below a certain level

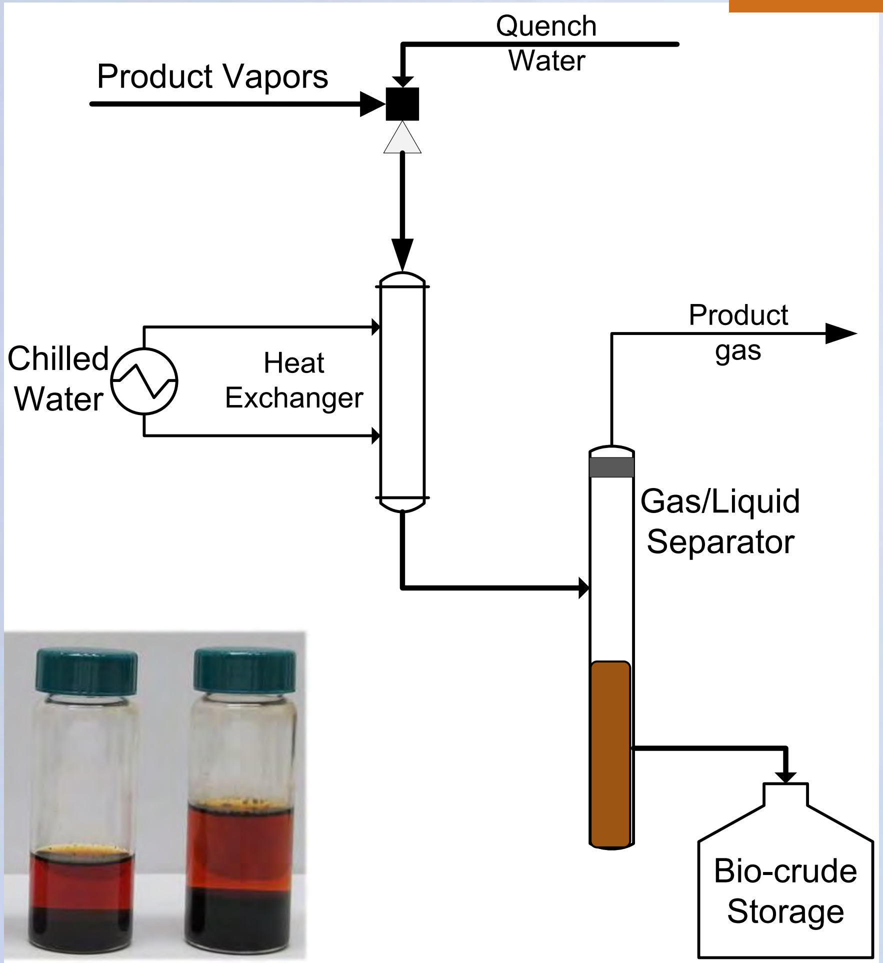
Pressure Profile and Control



$$\Delta P_{Regenerator} = \Delta P_{Standpipe} + \Delta P_{MixingZone} + \Delta P_{Riser} + \Delta P_{Cyclone^*} + \Delta P_{loopseal}$$

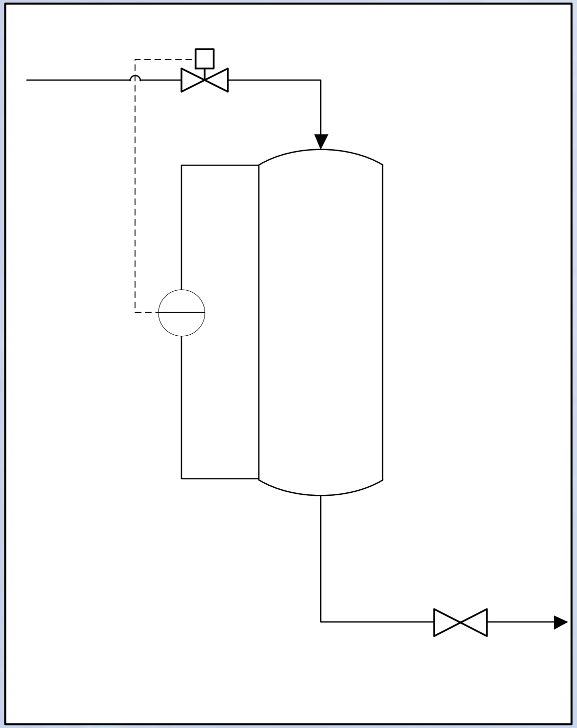
- Balancing pressure throughout the transport loop is critical to achieving desired catalyst circulation
- Reactor loop seal to adjust against pressure fluctuations and not to effect any pressure change
- Reactor loop controlled using a pressure control valve downstream of the quench system
- Regenerator loop controlled using a pressure difference control valve relative to the reactor side pressure

Quench System Operating Philosophy



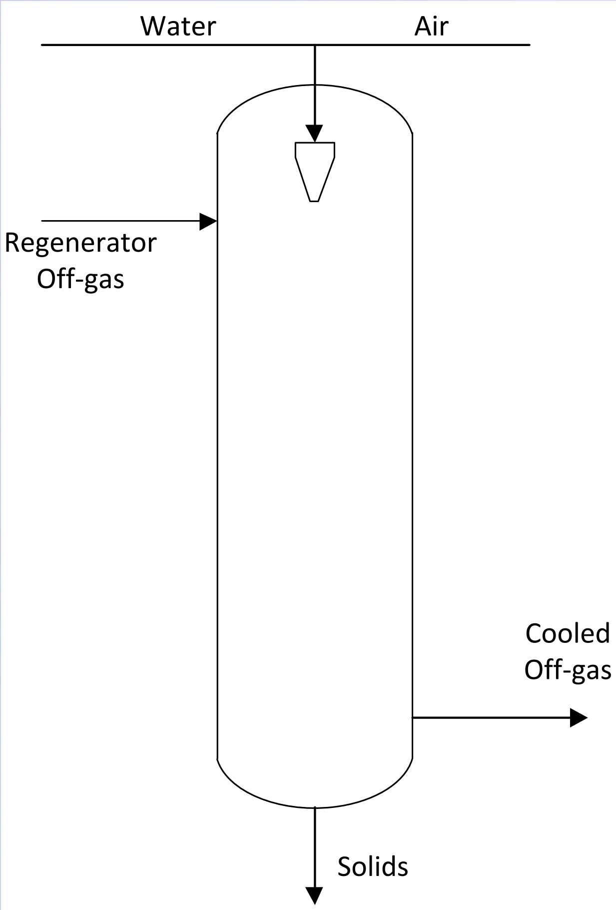
- Pyrolysis vapors and gas contacted with a spray of quench water
- Bio-crude vapors and water cooled in a heat exchanger
- Bio-crude liquid and permanent gases separated
- Demister pad to remove any entrained aerosols
- Interface level transmitters control bio-crude collection
- Bio-crude and water drained to a storage/settling tank
- Organic and aqueous phases separate and collected in drums

Product Collection and Storage



- Total liquid products transferred to vessels with level transmitters
- Each vessel consists of a on-off switch in the feed line and a manual drain valve
- Products will be collected in storage vessels, allowed to phase separate, and transferred to storage area
- If vessel is not drained in time, a “high level” trip will close the on-off valve (and stop product addition)

Regenerator Off-gas Cooler



- Regenerator off-gas: 3700 scfh, 1100 ºF
- Regenerator off-gas cooled down to ~250 ºF
    - Heat duty: ~70,000 Btu/hr
    - Direct contact with water sprayed through air atomizing nozzle
    - Temperature set point will control water flow
    - Outlet stream must always be above boiling point of water (at the process pressure)
- Co-current feed at the top of the vessel
    - Enables separation of any entrained solids
    - Solid outlet at the bottom
    - Gas outlet 8” above the bottom on vessel wall

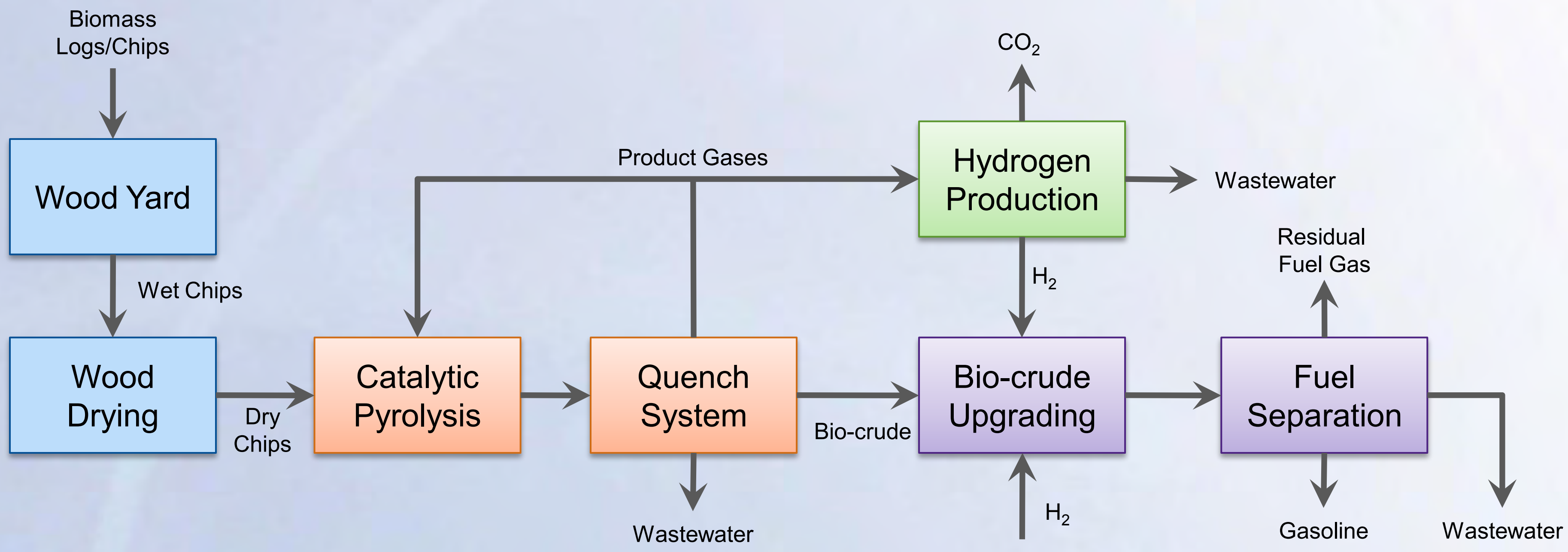
Site Preparation - RTI Satellite Field

Energy Technology Research Facility

Energy Technology Research Facility

Techno-economic Analysis

2000 tpd Preliminary Commercial Design Concept



Wood Yard and Drying

- Logs and chips storage
- Wood chipping
- Wood chips drying
- Dry chips storage

Biomass to Bio-crude

- Catalytic pyrolysis reactor
- Coolers and quench column
- Electrostatic precipitator
- Bio-crude/water separation

Bio-crude Upgrading

- Bio-crude pump and heater
- Hydrotreater
- Multi-stage H_2 compressor
- Gasoline/water separation

Hydrogen Production

- Steam reformer
- Shift reactor
- Amine scrubber
- Gas furnace

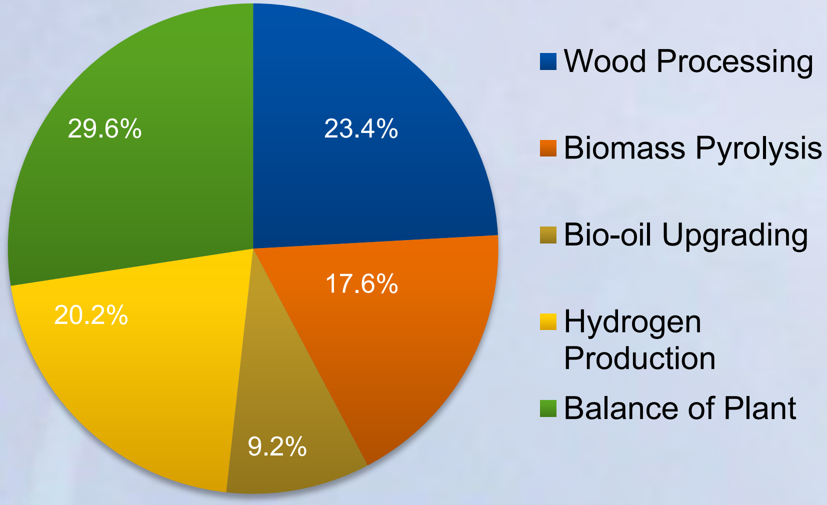
Financial Assumptions

- Debt Rate – 7.5%
- Debt Term – 20 years
- Percent Debt – 60%
- Availability
  - Year 1 – 80%
  - Year 2 – 85%
  - Year 3 – 90%
  - Year 4 – 95%

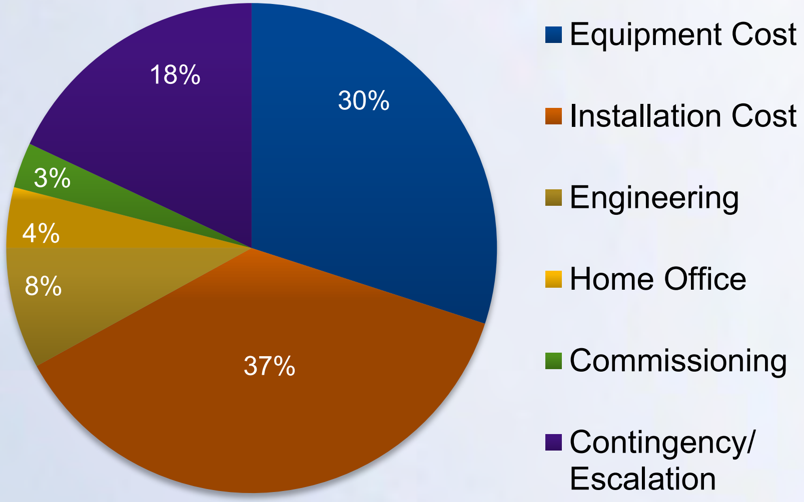
Escalation	Per Year
Feedstock	2.0% (Price BioStock)
Product	0.95% (EIA AEO2010)
Electricity	2.1% (EIA AEO2010)
Natural Gas	1.6% (EIA AEO2010)
Maintenance	0.5% (Industry standard)
Operations	0.5% (Industry standard)
Personnel	3% (Industry standard)

Capital Cost Summary

Equipment Cost By Area

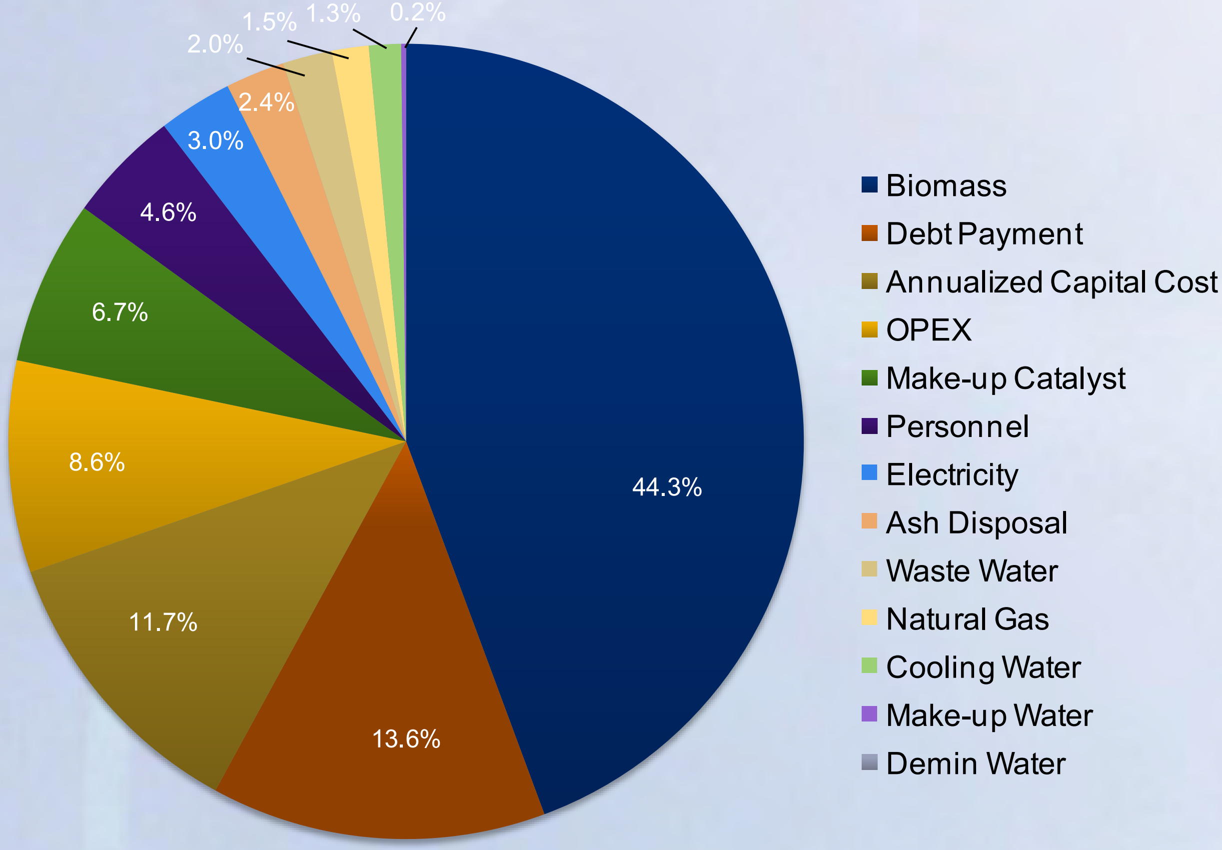


Total Cost By Category



Process Economics Assumptions

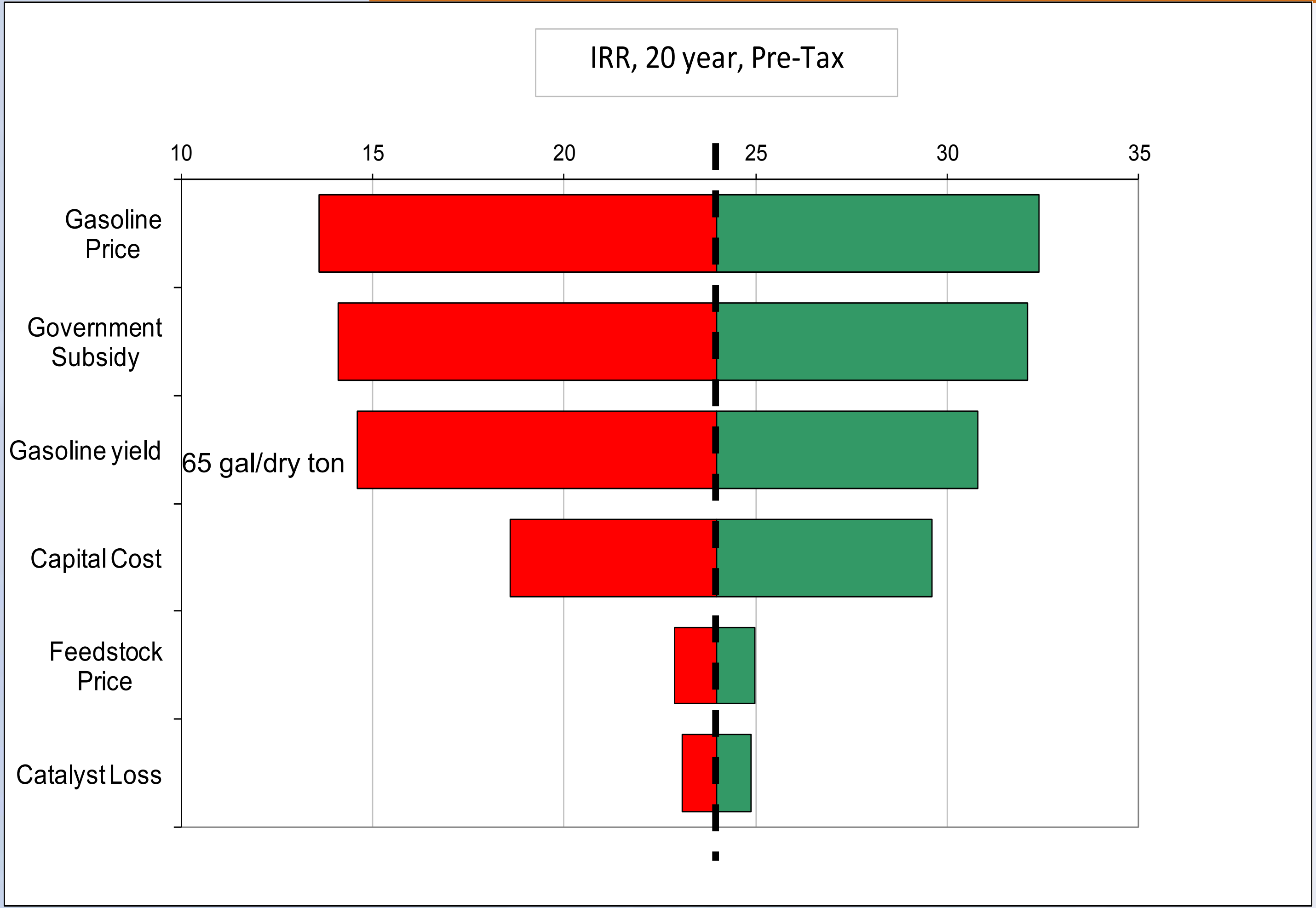
Annualized Production Cost Distribution



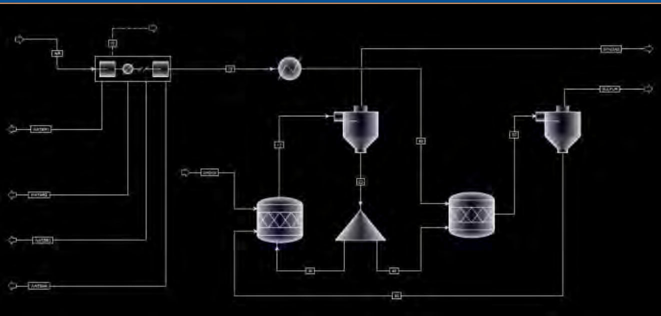
Base Case

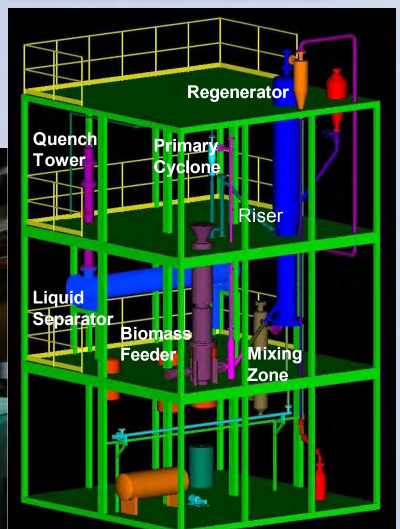
- Feedstock: $65/dry-ton
- Gasoline Price: $3.13/gal
- Govt. Subsidy: $1.01/gal
- Natural Gas: $4.50/MMBtu
- Electricity: $0.06/kWh
- No CO_2 credit

Sensitivity Analysis



Summary of Technology Status





- Catalyst development included model compound screening and bench-top (~ 1 g/hr) biomass conversion
  - Suitable catalyst identified for scale-up
  - Working with catalyst partners for bench-scale batches
- Catalytic biomass pyrolysis in a 1”-dia fluidized bed reactor
  - Organic and aqueous phases
  - 20 wt% oxygen content
  - 42% energy recovery
- Laboratory data provides the basis for a 1 TPD bench-scale unit
  - HMB and process design complete
  - Detailed engineering completed June 1, 2012
  - Fabrication
  - Installation and commissioning late 2012
- Catalyst Scale-up
- Preliminary Techno-Economic Analysis
- Bio-crude Upgrading

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Critical Validation Matrices

- Pilot plant representative of a commercial engineering design
- Pilot plant operated for long-enough duration to get design data for a commercial plant and operational experience
- Multiple biomass feedstocks tested
- Catalyst scaled-up and physical/chemical properties confirmed
- Long-term durability of the catalyst demonstrated
- Oil yields and oil quality validated
- Final product certified as a “drop-in” fuel
- Production of other value-added products explored (BTX, ethylene, propylene, etc.)

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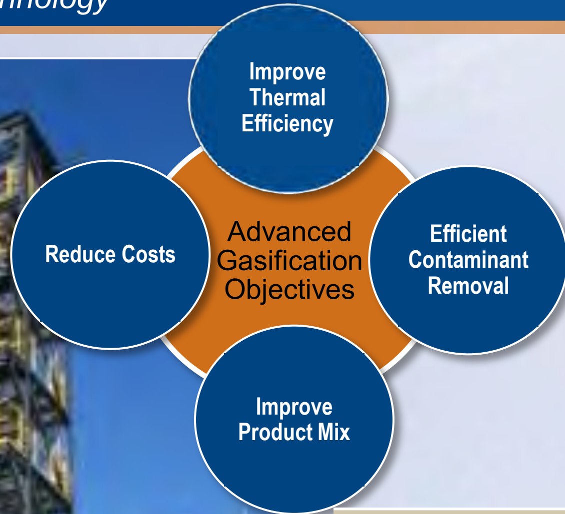


Advanced Gasification Program

Maximizing the potential of gasification for power and chemical applications

Technology	
High Temperature Syngas Clean-up Technology Platform	**Increased thermal efficiency and lower capital cost for IGCC and syngas-to-chemicals applications** • Syngas contaminant removal at high temperatures (> 200 C) • 50 MW_e demonstration at Tampa Electric's Polk Power Station IGCC with carbon capture and sequestration
High Temperature Desulfurization	▪ Transport reactor based syngas desulfurization
Multi-Contaminant Syngas Cleaning	▪ Fixed-bed catalysts and sorbents for high temperature removal of contaminants such as Hg, NH_3, Cl, arsenic, cadmium, selenium, and CO_2
Co-Production Processes	**Convert low-rank carbonaceous feedstocks to valuable products** ▪ Developing process technology to convert feedstocks to combinations of substitute natural gas, hydrogen, electricity, and CO_2

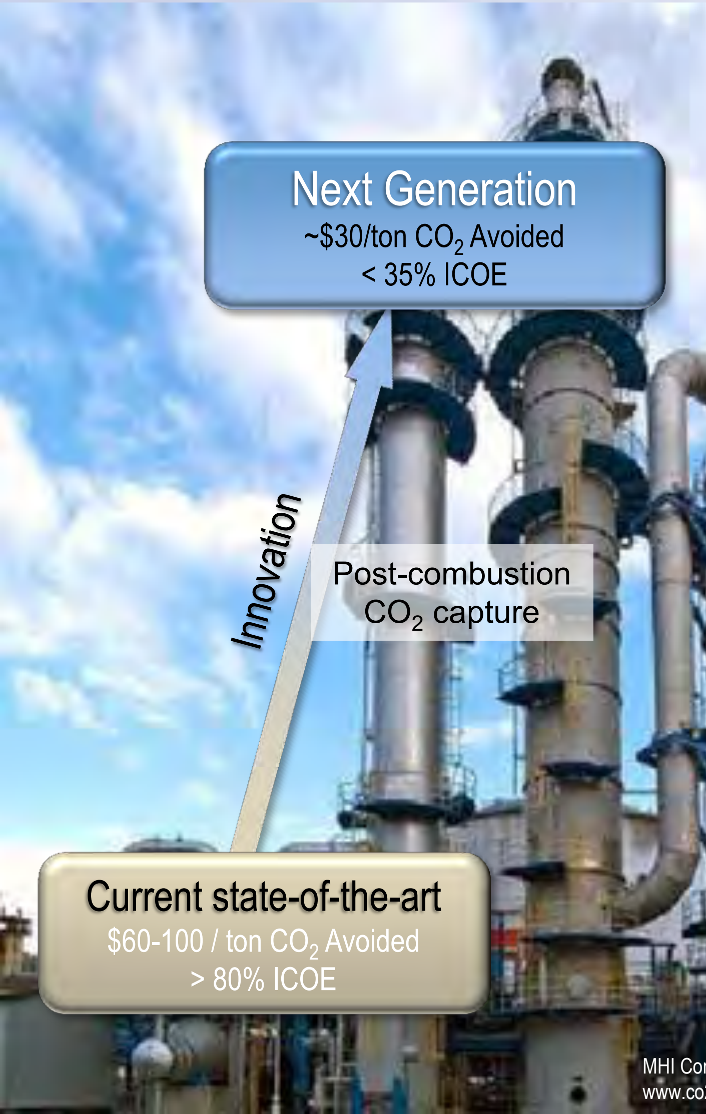
Biomass and Biofuels Program

U.S. Energy Independence and Security Act of 2007 establishes new renewable fuel targets

- Produce 36 billion gpy by 2022 ; 21 billion must be cellulosic
- Biofuels must deliver a 20% lifecycle greenhouse gas reduction

Technology	
Catalytic Biomass Pyrolysis	**Optimize biomass pyrolysis chemistry and catalysis** ▪ Developing a novel biomass pyrolysis process to produce an intermediate that is compatible with existing transportation fuel production and distribution
Biomass Hydropyrolysis	**National Advanced Biofuels Consortium (Lead: NREL)** ▪ Developing novel process for catalytic conversion of biomass in the presence of high pressure hydrogen
Biomass Syngas Cleanup & Fuel Synthesis	**Reduce costs to remove tars, NH_3, and sulfur from biomass syngas** ▪ Syngas clean-up technology can be used to produce cost-competitive biofuels
Biomass Syngas Contaminant Effects	**Determine effects that syngas contaminants have on catalysts** ▪ Evaluating the effects coal/biomass-derived syngas contaminants have on Fischer-Tropsch and water gas shift catalysts

CO_2 Capture and Utilization Program



Technology	
Solid Sorbents	**Reduce energy penalty** ▪ Develop sorbent materials with lower heats of absorption and improve energy efficiency of process through heat integration
Membrane Processes	**Reduce compression energy** ▪ Membrane materials with improved CO_2 permeance and CO_2/N_2 selectivity
Liquid Solvents	**Reduce regeneration energy and capital cost** ▪ Develop solvents with lower regeneration energies, milder regeneration conditions, and reduced corrosivity
Hybrid Processes	**Reduce regeneration energy and capital cost** ▪ Integrated processes that capitalize on benefits of individual technologies
CO_2 Utilization	**Breakthrough ideas for converting CO_2 to value-added products** ▪ Identify readily available reducing agents with small CO_2 footprint ▪ Developing technologies to convert CO_2 to methanol, dimethyl ether, or gasoline and electrochemical conversion of CO_2 to fuels

MHI Commercial KS-1 CO_2 Capture Plant (Japan)
www.co2management.org/proceedings/Masaki_Iijima.pdf