Catalytic Processes in Biomass Gasification and Pyrolysis

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RTI International

Biomass Technical Advisory Committee Meeting

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RTI International

- Established in 1958 as collaboration between state government, area universities, and business leaders
- Mission: to improve the human condition by turning knowledge into practice
- Revenues >$750MM with13% average annual growth over the last 10 years.
- >4,200 professionals in >40 countries
- High-quality scientific staff with tremendous breadth
- >130 different academic disciplines

Notable Achievements:

- Taxol® and Camptothecin™
- Cochlear ear implants
- Wind shear avoidance system

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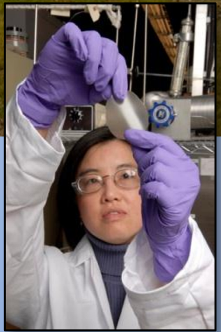
RTI's Center for Energy Technology (CET)

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

Discovery → Development → Demonstration


- 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

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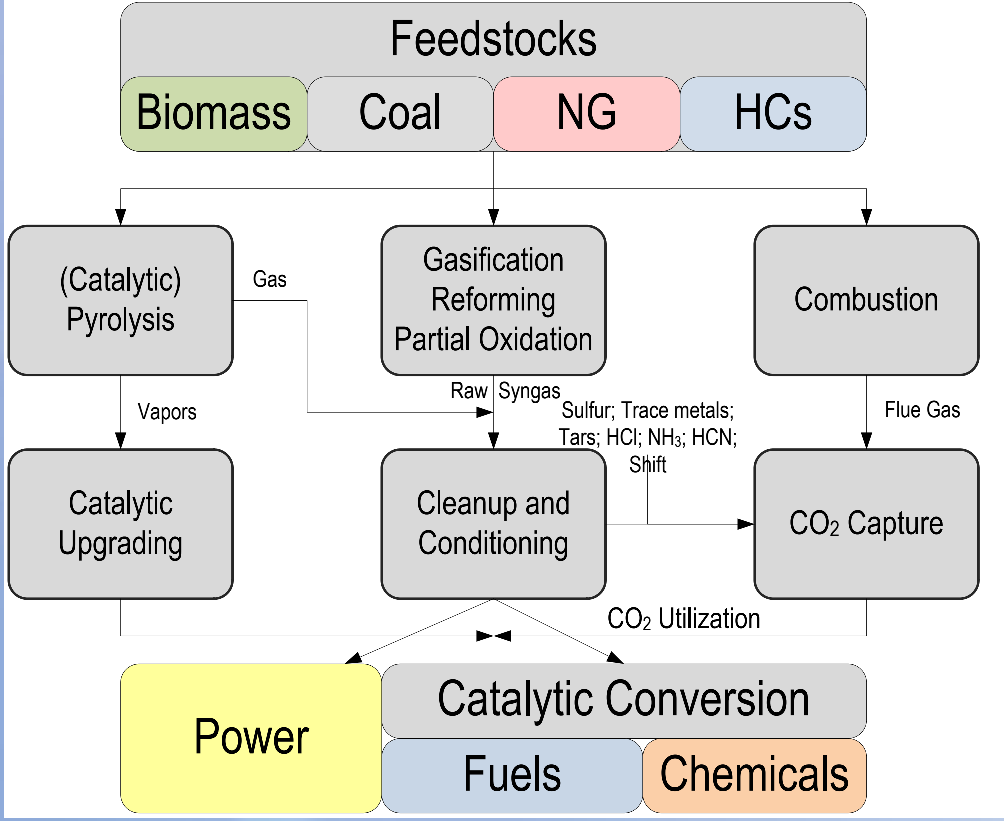
Energy R&D within CET



Program Areas

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

Biomass & Biofuels
- Biomass gasification
- Syngas cleanup/conditioning
- Pyrolysis to biocrude and conventional fuels

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

Core Competencies
- Catalyst & Sorbent Development
- Membrane Development
- Reaction Engineering
- Process Engineering & Design
- Bench-scale & Prototype Testing
- Techno-Economic Evaluations

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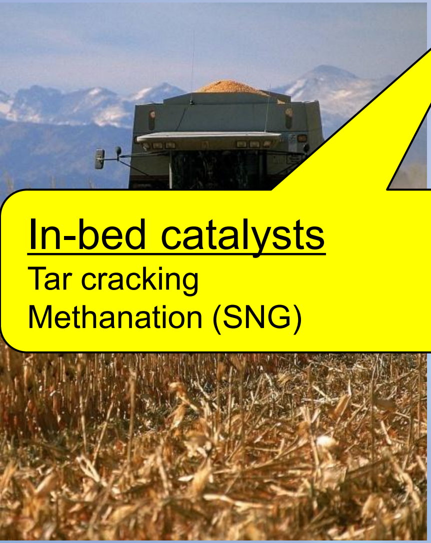
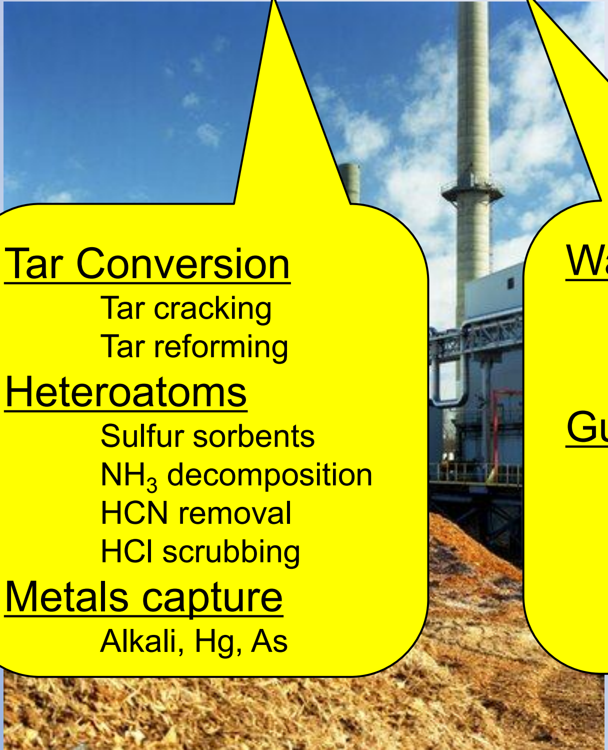
Catalytic Processes in Biomass Gasification

Feed Processing & Handling → Biomass Gasification → Syngas Cleanup → Syngas Conditioning → Catalytic Fuel Synthesis → Next Generation Biofuels



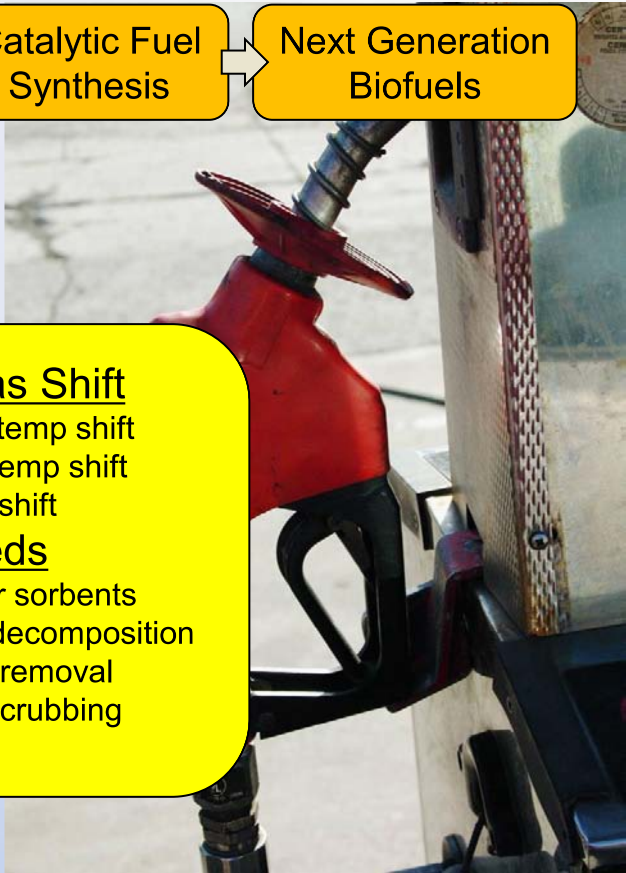
In-bed catalysts (Biomass Gasification)
- Tar cracking
- Methanation (SNG)



Tar Conversion (Syngas Cleanup)
- Tar cracking
- Tar reforming

Heteroatoms
- Sulfur sorbents
- NH_3 decomposition
- HCN removal
- HCl scrubbing

Metals capture
- Alkali, Hg, As



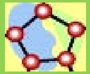
Water Gas Shift (Syngas Conditioning)
- High temp shift
- Low temp shift
- Sour shift

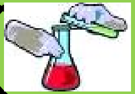
Guard beds
- Sulfur sorbents
- NH_3 decomposition
- HCN removal
- HCl scrubbing

Syngas Utilization

Clean Syngas

H_2, CO, CO_2





Building Blocks for Fuels and Chemicals

Chemicals

Steam Iron Process

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$

Hydrogen

Methanation

$CO + 3H_2 \rightarrow CH_4 + H_2O$

Methane (SNG)

Methanol Synthesis

$CO + 2H_2 \rightarrow CH_3OH$

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

$CO + H_2O \rightarrow CO_2 + H_2$

Dimethyl Ether Synthesis

$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$

LPG and Diesel Fuel

Transportation Fuels

Fischer-Tropsch Synthesis

$2nH_2 + nCO \rightarrow (\text{-}CH_2\text{-}) + nH_2O$

Gasoline and Diesel

Mixed Alcohol Synthesis

$2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$

Ethanol and Gasoline Additive

LPG and Gasoline

Tar Cracking Process Development at RTI

Feed Processing & Handling → Biomass Gasification → Syngas Cleanup → Syngas Conditioning → Catalytic Fuel Synthesis → Next Generation Biofuels

Technical Targets

Tar < 0.1 g/Nm³

NH_3 < 10 ppm

H_2S < 100 ppb

HCl < 10 ppb

Crystallized light tars in IC engine intake manifold (courtesy Dahlman)

Heavy tar accumulation (courtesy ECN)

Technical Goals

- Reduce syngas cleanup process complexity
- Validate technology with biomass-derived syngas

Economic Target

- Reduce syngas cleanup/conditioning capital and operating costs to achieve biofuel production cost goals

Process Advantages

- Thermally efficient
- Cleaner and reduced-volume water product
- Process intensification (i.e., fewer unit operations)

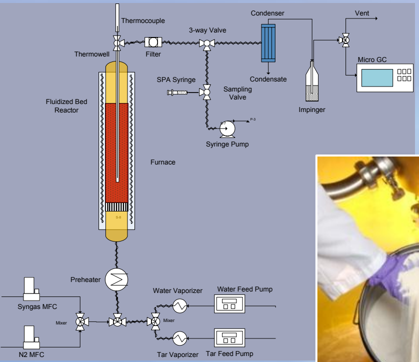
Technology Development Approach

Catalyst Development

- Productivity
- Attrition resistance
- Stability

Process Development

- Reaction kinetics
- Integration strategy

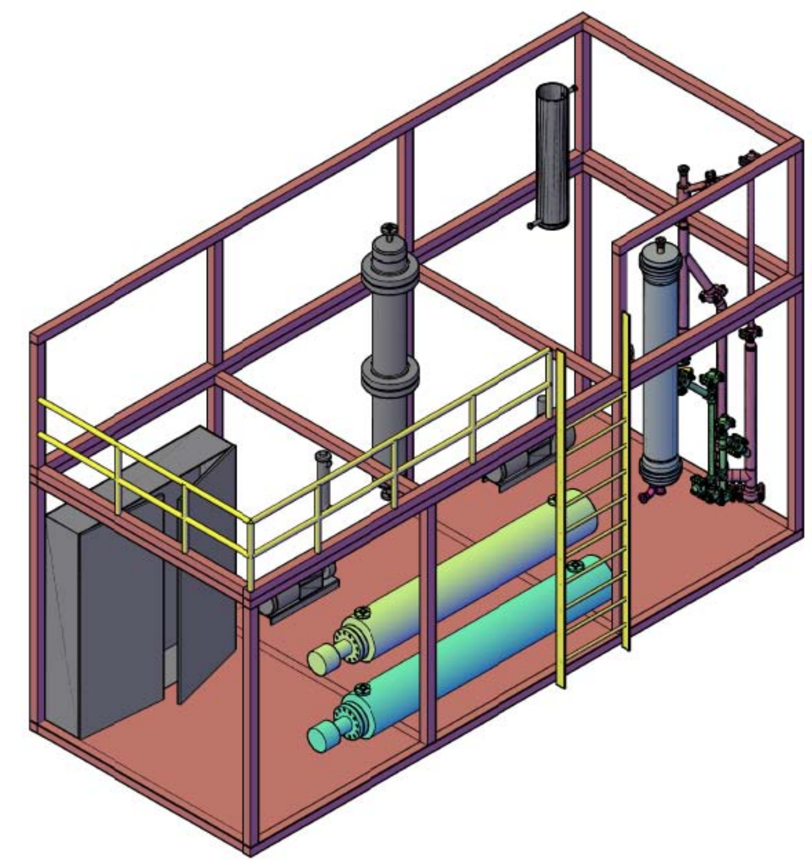


Catalyst Development

- Catalyst scale-up

Process Development

- Reactor scale-up
- Process modeling and design
- Detailed engineering
- Continuous operation
- Performance evaluation
- Pilot-plant testing



Tar Cracking Technology - Summary

Tar cracking catalyst screening

- Use sorbent for sulfur removal
- FCC has promising tar cracking activity

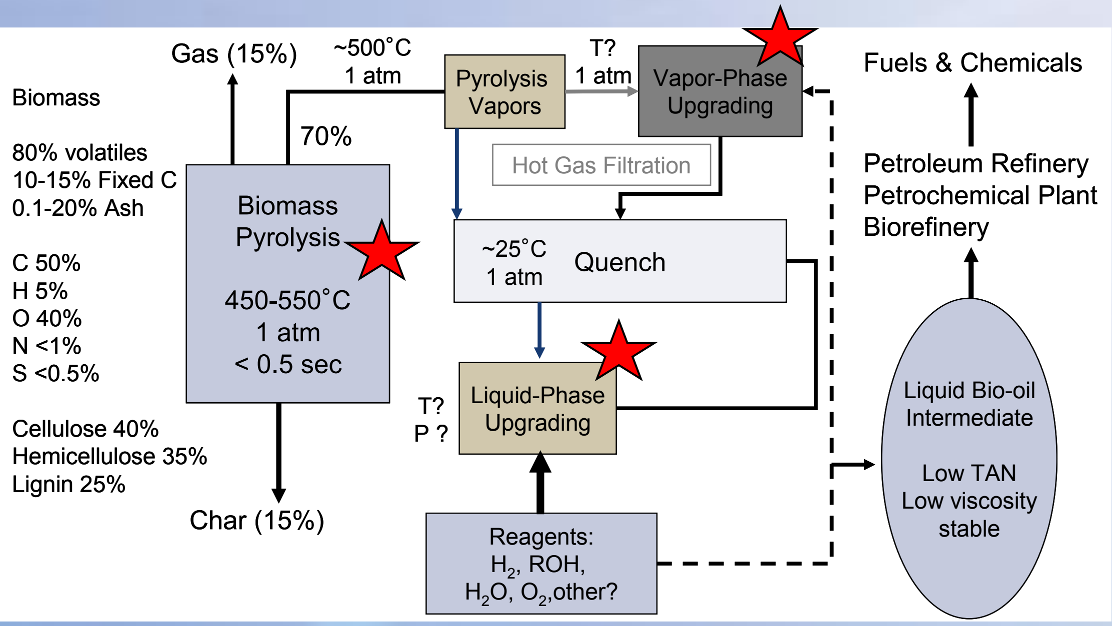
Biomass Gasification Testing

- Successful operation of integrated biomass gasification system (gasifier, feeder, filter)
- Syngas quality (composition, HHV) sensitive to steam flow and O_2 addition

Tar cracking reactor design, fabrication, and installation complete

Integrated Testing just starting

Biomass Pyrolysis Technology Development



Potential catalytic processes

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 Options:

- Catalytic upgrading of fast pyrolysis oils
  - 2-stages: mild hydrotreating for stabilizing bio-oil followed by traditional hydroprocessing for biofuel production
- Catalytic upgrading of biomass pyrolysis vapors for bio-crude oil production
  - Inline catalytic upgrading prior to condensation
- Catalytic Biomass Pyrolysis
  - Multi-functional catalysts maximize carbon efficiency, remove oxygen, and control bio-crude properties

What are the target bio-crude physical properties and the desired chemical composition that make it valuable as an intermediate for fuels and chemicals production?

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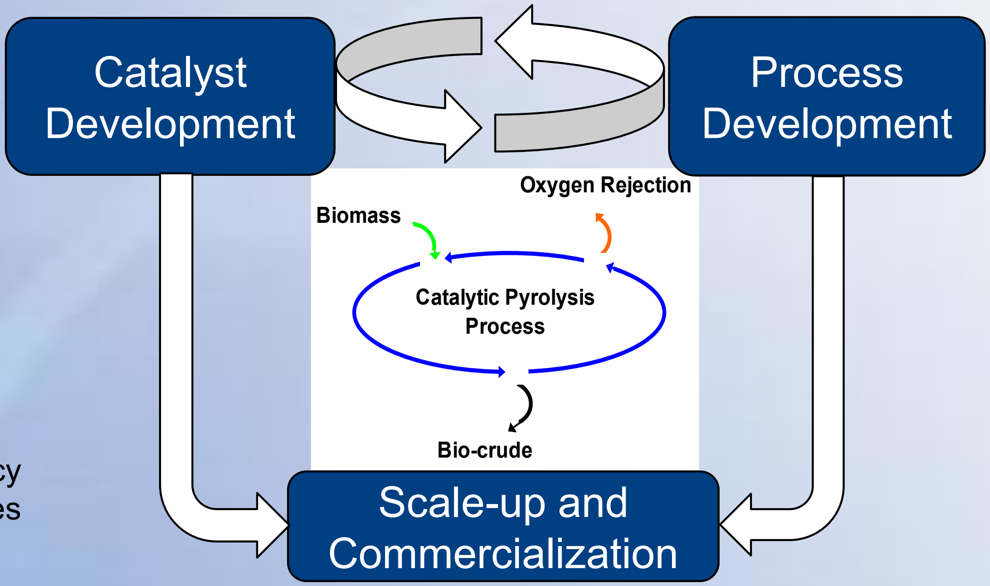
Technology Development Approach

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 Synthesis
Catalyst Characterization
- BET, TPR, Surface Analysis

Model Compound Testing
Bench-scale Catalytic Pyrolysis
Proof-of-concept

Identify key parameters for reactor design
- Deoxygenation
- Regeneration
- Coke yields/Energy efficiency
- Oxidation and reduction rates



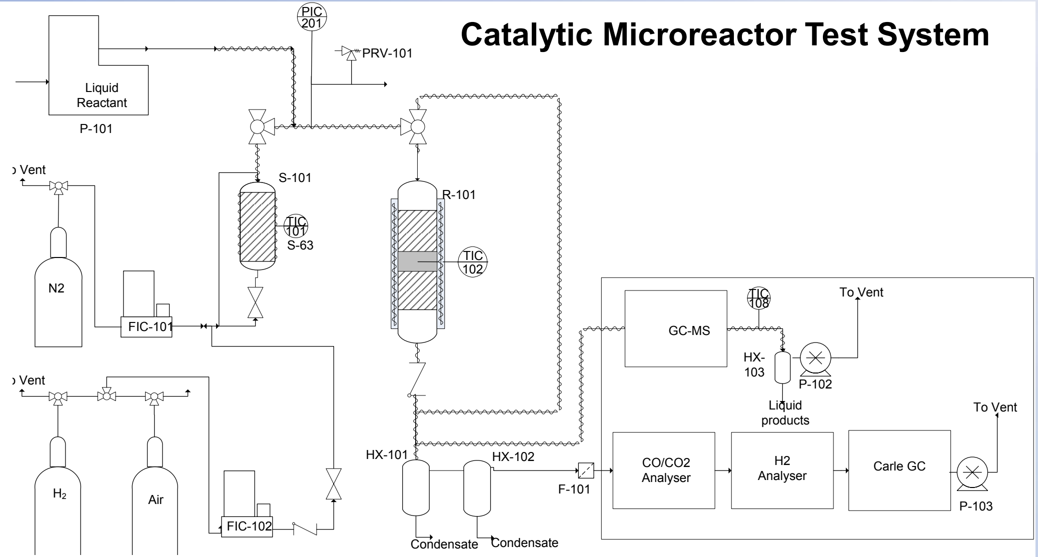
Reactor design/prototypes
Real Biomass Testing
Yields
- Gas
- Bio-crude
- Char/Coke

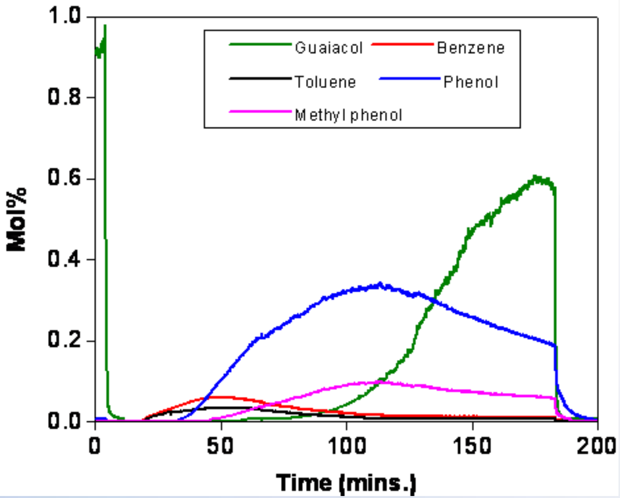
Hydrogen demand
Bio-crude Analysis and Quality
Process Modeling
- Heat and Material Balances
- Reactor Design

Focus on technology scale-up from the beginning

Catalyst Development – Model Compounds

Catalytic Microreactor Test System





Guaiacol deoxygenation over RTI-A9 at 450°C with 3 vol% steam

Reaction Conditions:

Temperature: 300-500° C
Catalyst loading: 5 g
Liquid feed rate: 0.02-0.05 ml/min.
Carrier feed rate: 50 ml/min.
LHSV: 0.1 h^{-1}
GHSV: 1831 h^{-1}

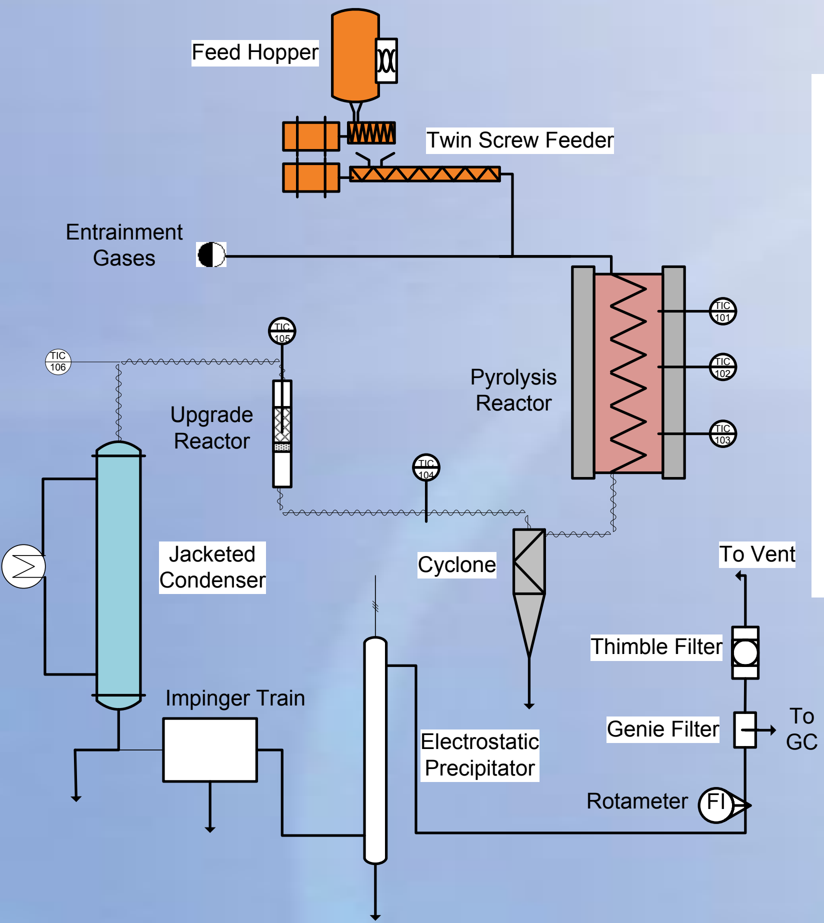
- Convenient & effective approach to understanding complex reaction chemistries
- Enables fast & relevant screening of catalysts
- Helps develop understanding of deoxygenation pathways (mechanism)
- Provide insights for catalyst optimization and development of novel catalyst composition

Catalytic Biomass Pyrolysis Proof-of-Concept

	Baseline	**RTI-A9**
Solids (wt%)	**14.3**	**21.2**
Liquid (wt%)	**67.8**	**45.6**
Bio-crude Composition (Wt%)		
C	43.9	65.9
H	6.74	6.77
O	44.9	23.4
N	0.09	0.07
S	0.006	0.015
Gas (wt%)	**11.6**	**25.8**
Gas composition (vol%)		
H_2	1.7	12.7
CO	28.1	36.6
CO_2	46.5	34.6
CH_4	3.8	9.9
C_{2+}	19.9	6.3

- Catalytic pyrolysis studies in micro-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

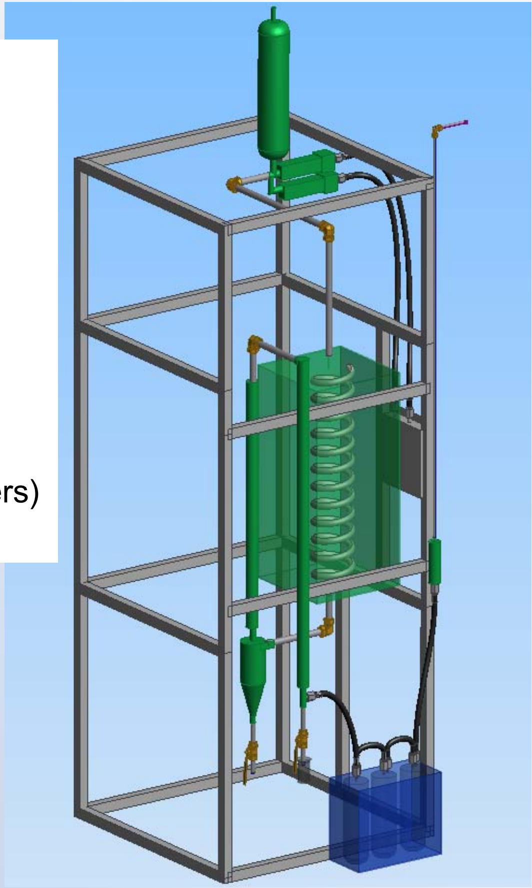
RTI'S Bench-Scale Pyrolysis System



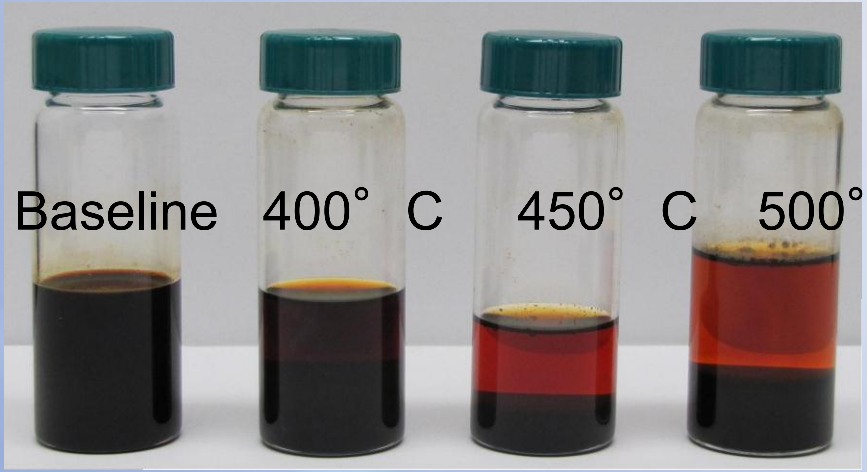
Biomass Pyrolysis – Vapor Phase Upgrading

Biomass feed rate: 100-350 g/h
Carrier gas: 2-20 SLPM N_2
Residence time: 0.3-5 s
Temperature: 350-900 ° C
Mass closure - >95 wt%
- On-line microGC gas analysis
- Liquid yield: 50-70 wt%
- Char yield: 5-15 wt%

Bio-oil Collection
- Heat Exchanger (~13° C)
- Condensation Train (dry ice impingers)
- Electrostatic Precipitator



Commercial Catalyst - Summary



Liquid Yield (g)	Baseline	400° C	450° C	500° C
Total	389 (22%)	16.8 (31%)	13.2 (42%)	21.3 (44%)
Light Fraction	na	8.2 (49%)	7.8 (62%)	12.7 (67%)
Heavy Fraction	na	8.6 (14%)	5.4 (12%)	8.6 (10%)

- Gas yields increase with temperature
  - Hydrogen yields with catalyst are much higher than baseline (useful in process for regeneration)
  - CO_2/CO increases with temperature
- Coke deposits on the catalyst and at the entrance to the upgrading reactor
- Bio-crude phase separates
  - Water content increases with temperature (more cracking and dehydration)
  - Light fraction also increases with temperature
  - Water content of heavy fraction relatively constant

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Acknowledgments

- RTI Team in CET
- Industrial and University Partners
- Funding from the U.S Department of Energy (Office of Biomass Programs and ARPA-E)

Some Perspectives on RTI

We are one of the world's leading research institutes

- Exceptional depth and a continuously evolving knowledge base
- Unique ability to create high-performing teams to solve the most complex problems

We are an applied research organization

- Little basic research or true consultancy
- Dependant upon competitively awarded contracts

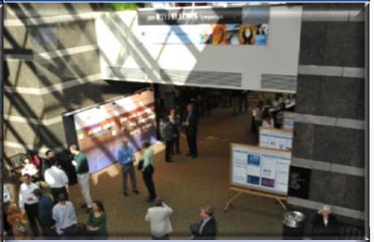
We are an institute, not a university

- 100% professional, dedicated staff
- Experienced project managers, many from industry

We are a non-profit organization

- Very conducive to true "win-win" scenarios
- Independent, objective work on complex scientific challenges
- We have a pragmatic, flexible approach to IP

We have a diverse client base



- Extensive network of relationships with industrial, academic, and government clients.
- When appropriate, we can provide access to mission oriented federal programs

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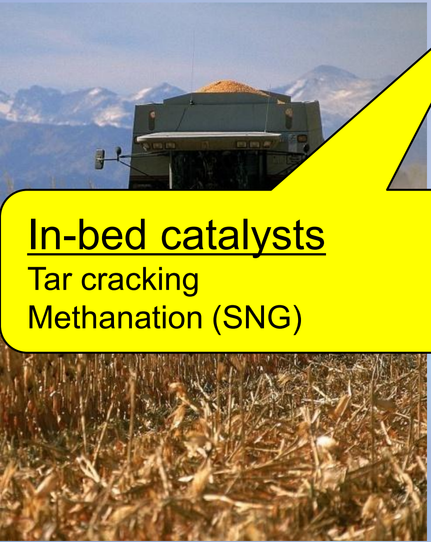

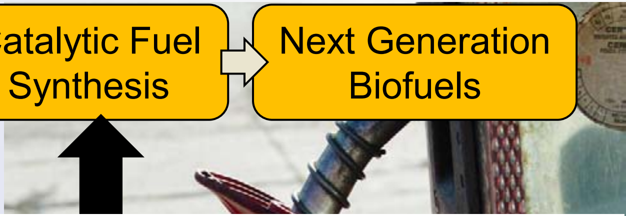

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Tars Removal
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Metals capture
- Hg, As, alkali