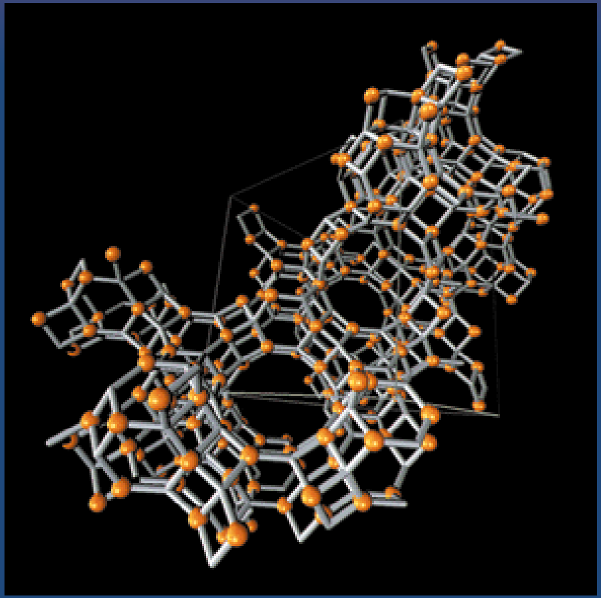
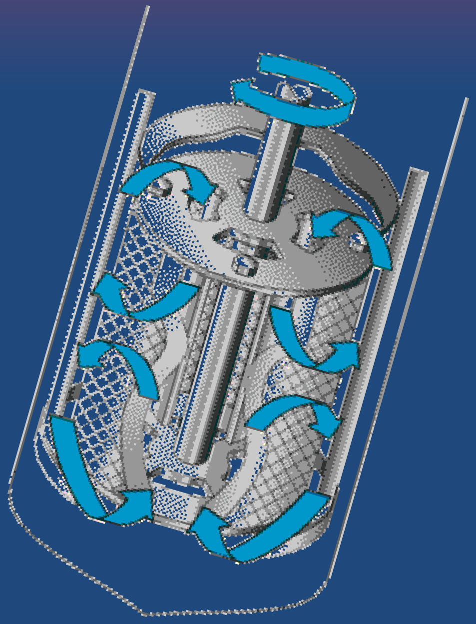
Fast Pyrolysis for Biomass Conversion to Fungible Fuels





UNIVERSITY OF OKLAHOMA

Lance Lobban
School of Chemical, Biological, and Materials Engineering
Center for Biomass Refining (www.ou.edu/cbr)
Oklahoma Bioenergy Center

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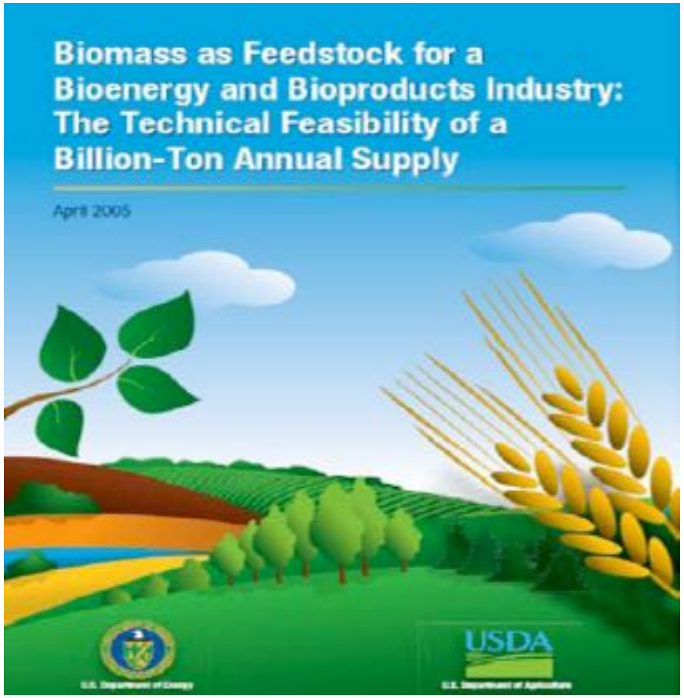
Availability of Biomass Resources



2005 US DoE/USDA "Billion Ton Report"

Lignocellulosic biomass (grasses, trees, MSW, agricultural residue): over 1 billion tons/year can be *sustainably* available in the US

-Forest: 368 million tons

-Agricultural: 998 million tons*

-Total: 1,366 million tons

***includes 87 million tons grain, ~800 million tons energy crops and residues**

Cellulosic Liquid Biofuel Process Options

Cellulosic biomass (cellulose, hemicellulose, lignin)

Gasification → **Syngas** ($CO + H_2$)

- Fermentation → **Ethanol**
- FT synthesis → **Diesel**
- Metals/zeolite → **Gasoline**

Fast pyrolysis, solvolysis → **Bio-oils** (Sugars, acids, aldehydes, aromatics)

- Hydrodeoxygenation
- Zeolite upgrading
- Emulsion processing

→ **Gasoline, Diesel, chemicals**

Pretreatment & hydrolysis → **Sugars**

- Fermentation → **Ethanol**

Advantages of Hydrocarbon Biofuels

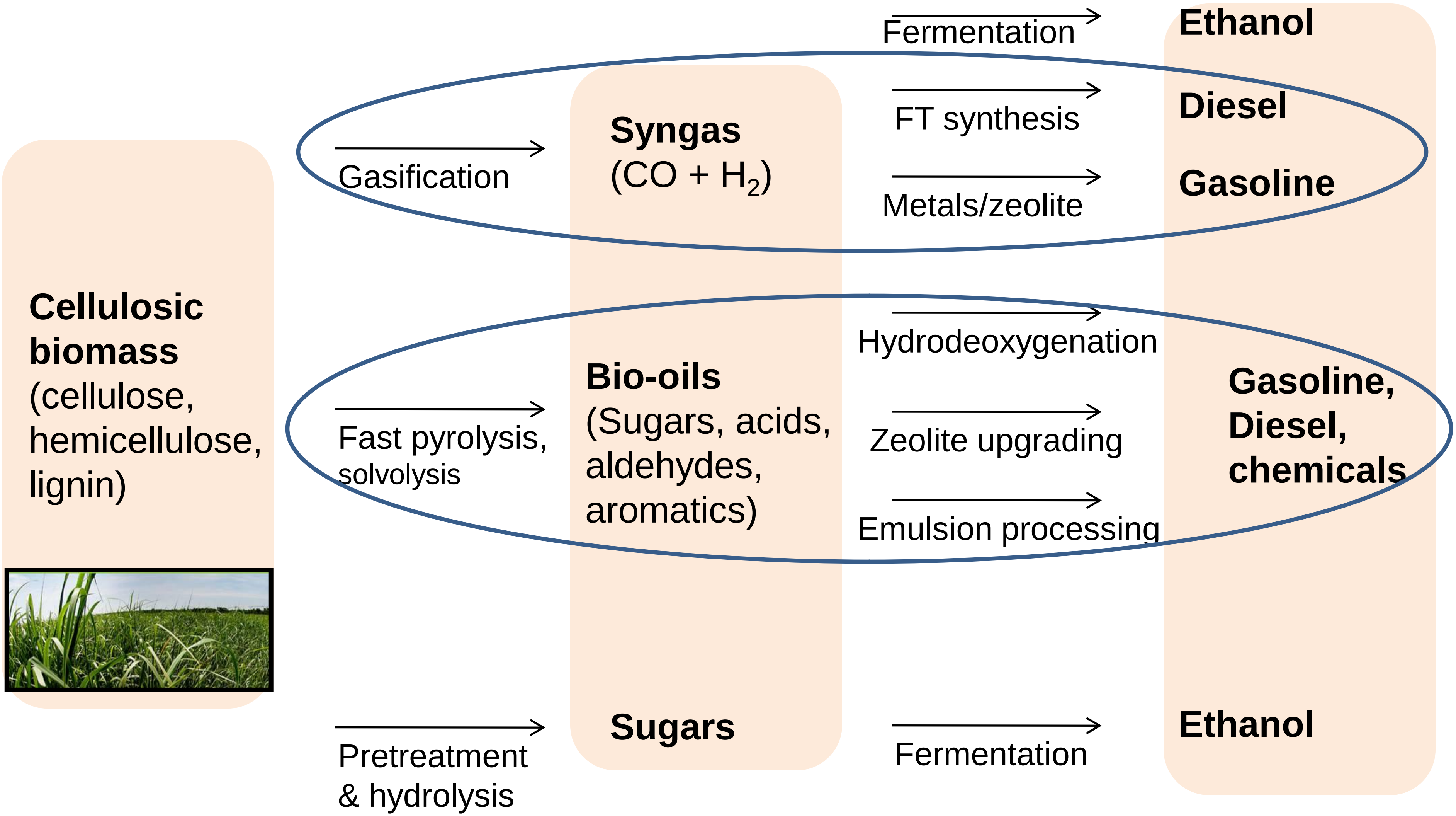
- Self-separate, eliminating the expense of distillation
- ~40% greater energy density than ethanol; consumers won't suffer loss of gas mileage
- Reduced process water usage
- Green fuels (gasoline, diesel, jet fuel) fit into current infrastructure (FUNGIBILITY); no need for modification of engine, distribution, storage
- Facilitates creative use of existing infrastructure as new biorefinery infrastructure develops

Thermochemical Process Advantages

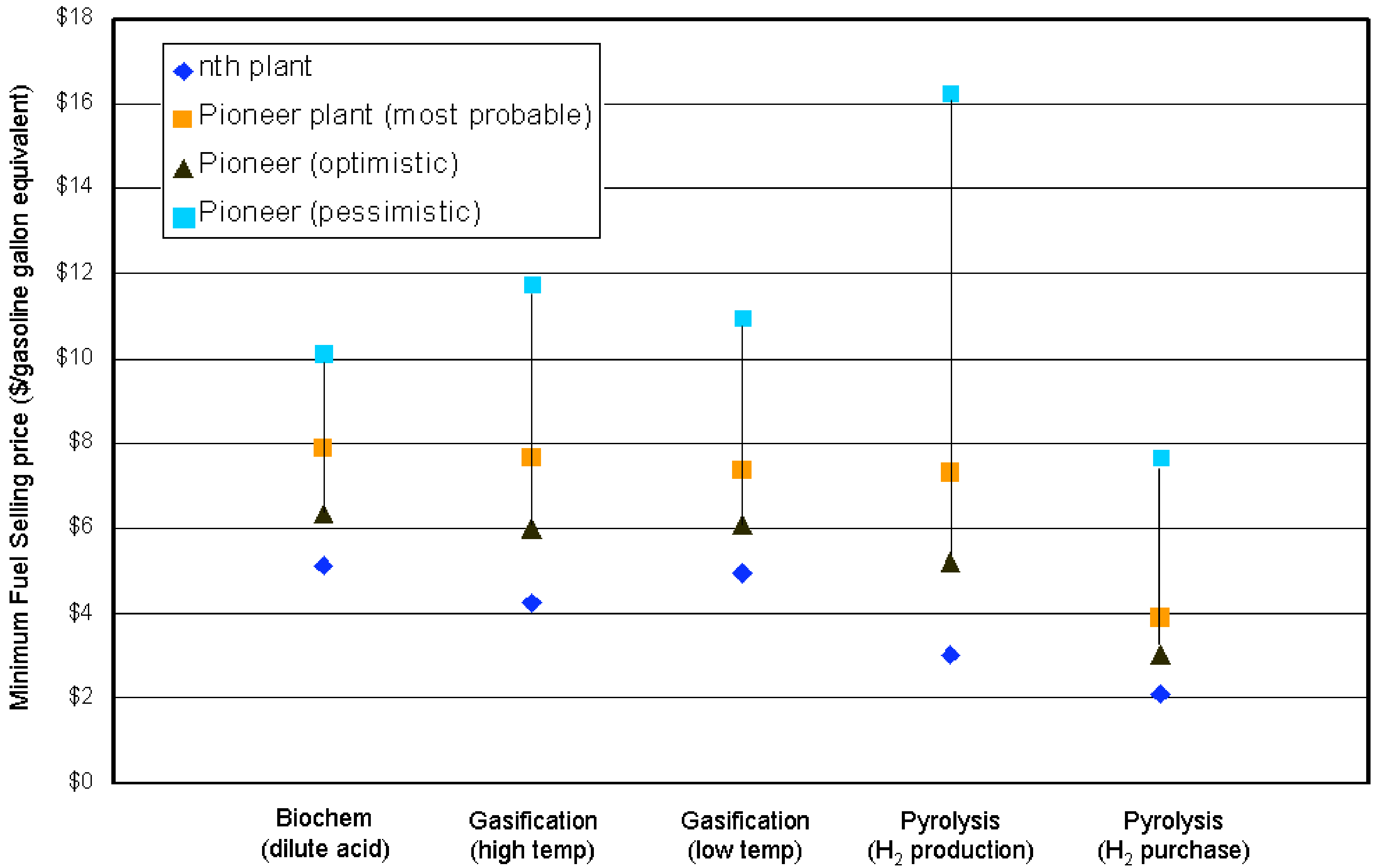
	Biological Catalysts	Chemical Catalysts
Products	Alcohols	Wide range of hydrocarbon fuels
Reaction conditions	<70ºC, 1 atm	100-1200ºC, 1-250 atm
Residence time	1-5 days	0.01 second to 1 hour
Selectivity	>95%	Can be selective (>95%) depending on catalyst
Catalyst cost	~$0.50/gallon ethanol	$0.01/gallon gasoline (based on petroleum industry)
Sterilization	Feeds must be sterilized	Unnecessary
Recyclability	Not with present catalysts	Yes (solid catalysts; may require regeneration)
Size of cellulosic plant	2000-5000 tons/day	100-2000 tons/day (est.)

*From "Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels"

Cellulosic Liquid Biofuel Process Options

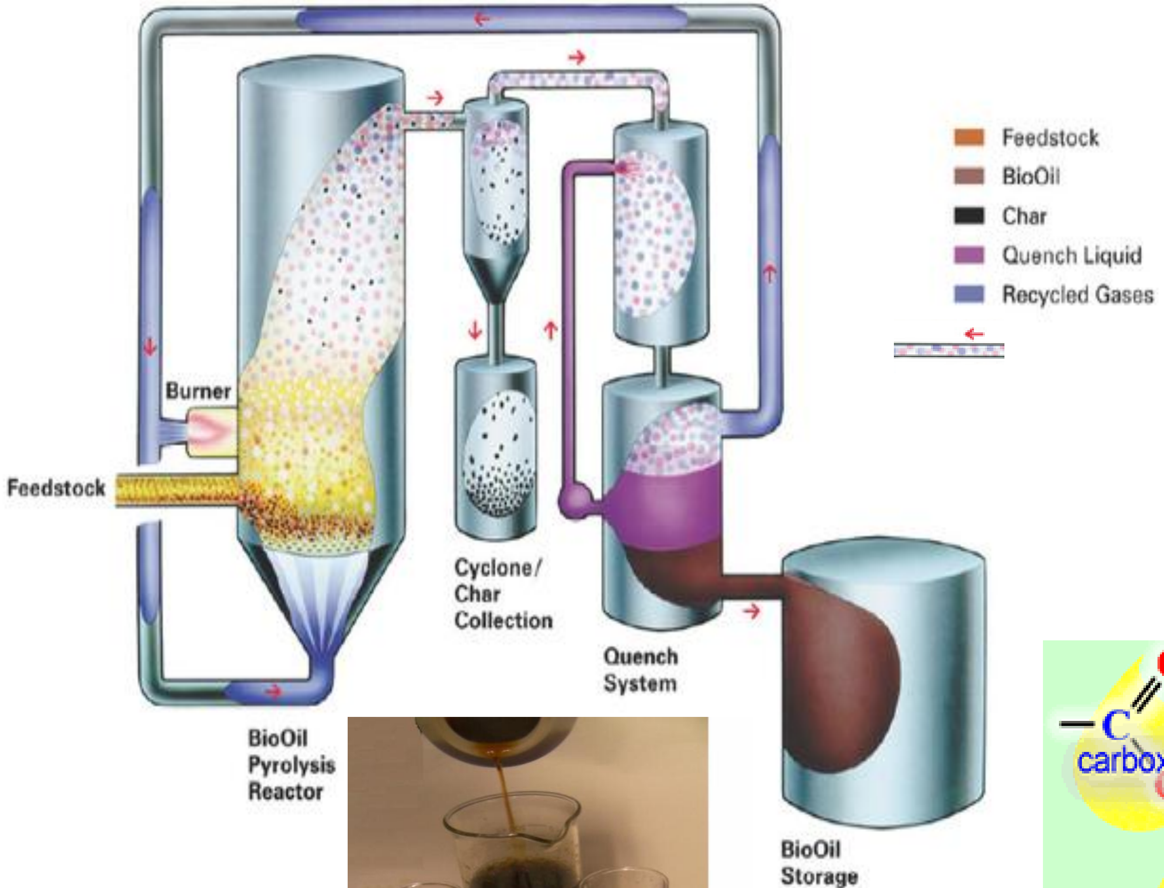


Technoeconomic comparison

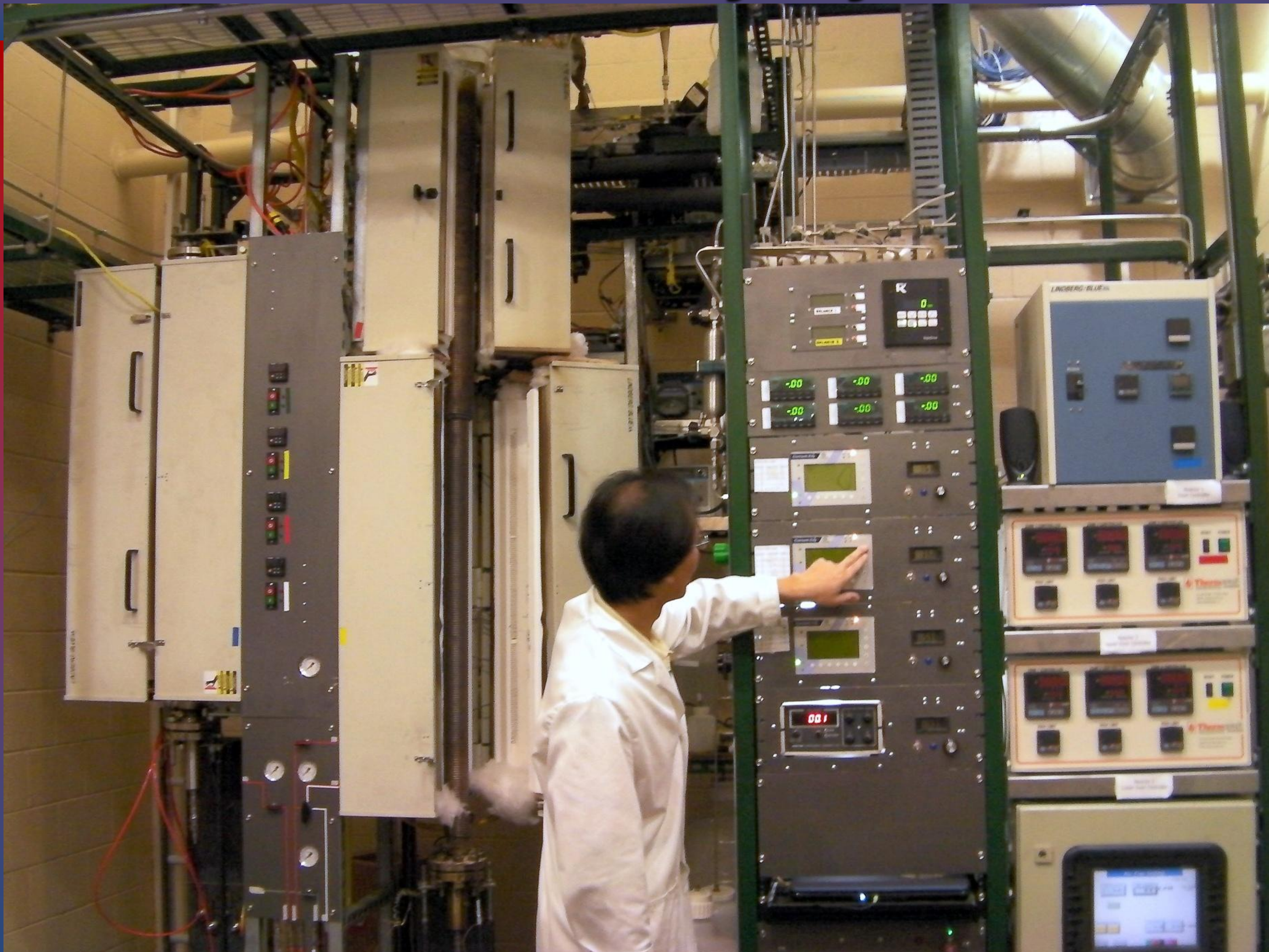


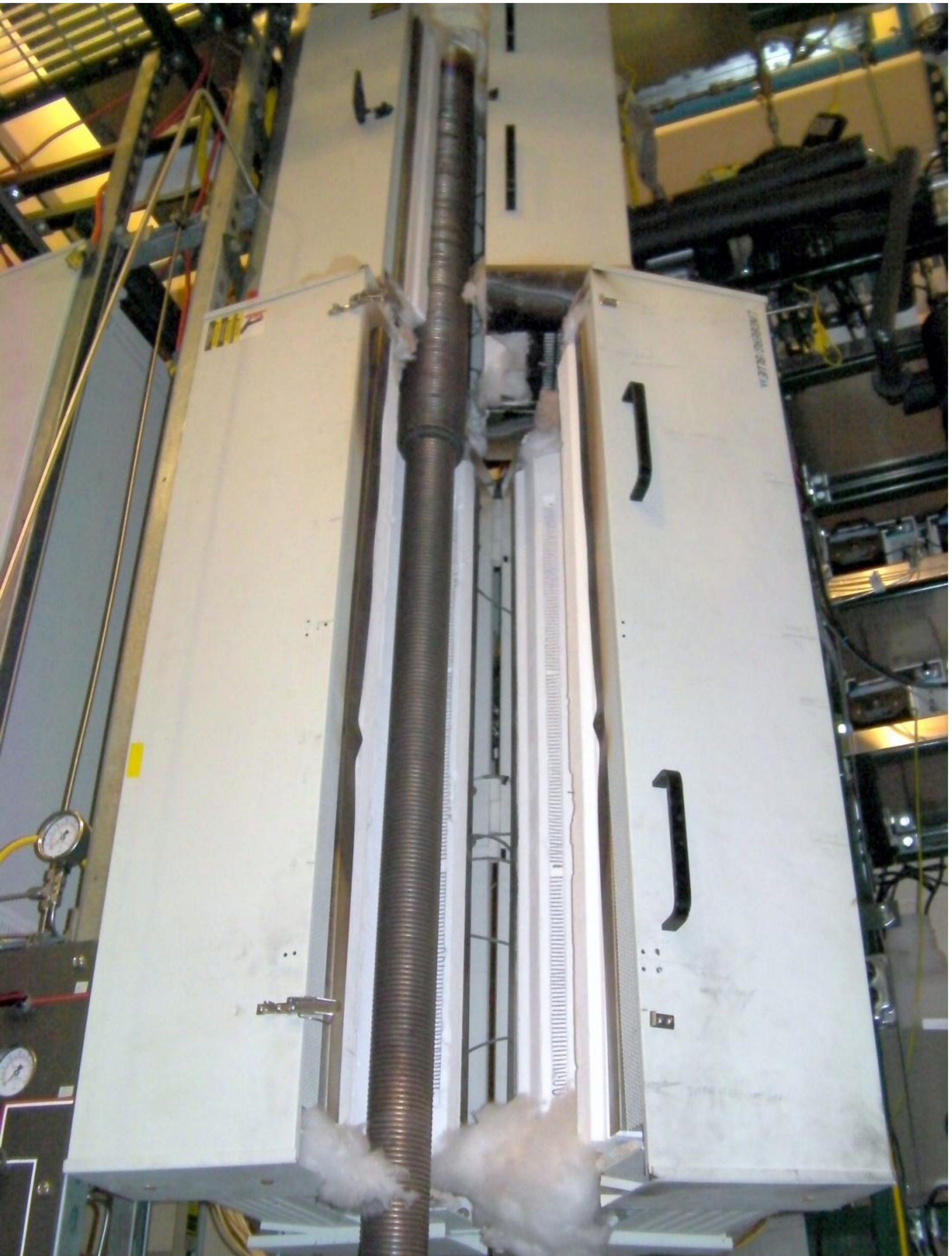
Source: "Techno-economic comparison of biomass to transportation fuels via pyrolysis, gasification and biochemical pathways,"Anex et al. (Iowa State University, ConocoPhillips, NREL), *Prep. Pap.-Am. Chem. Soc., Div. Fuel Chem.* ***2009,*** *54 (2), 704*

Fast Pyrolysis of Switchgrass



OU Biomass Pyrolysis Unit





Fluidized Bed Pyrolysis Reactor

- 0.5-2kg hr
- 400-600+ ^{o}C
  - multi-zone
- External preheat coil
- Variable residence time
- Pressurized feed system
- Sand disengagement zone
- Multi-stage quench/reaction

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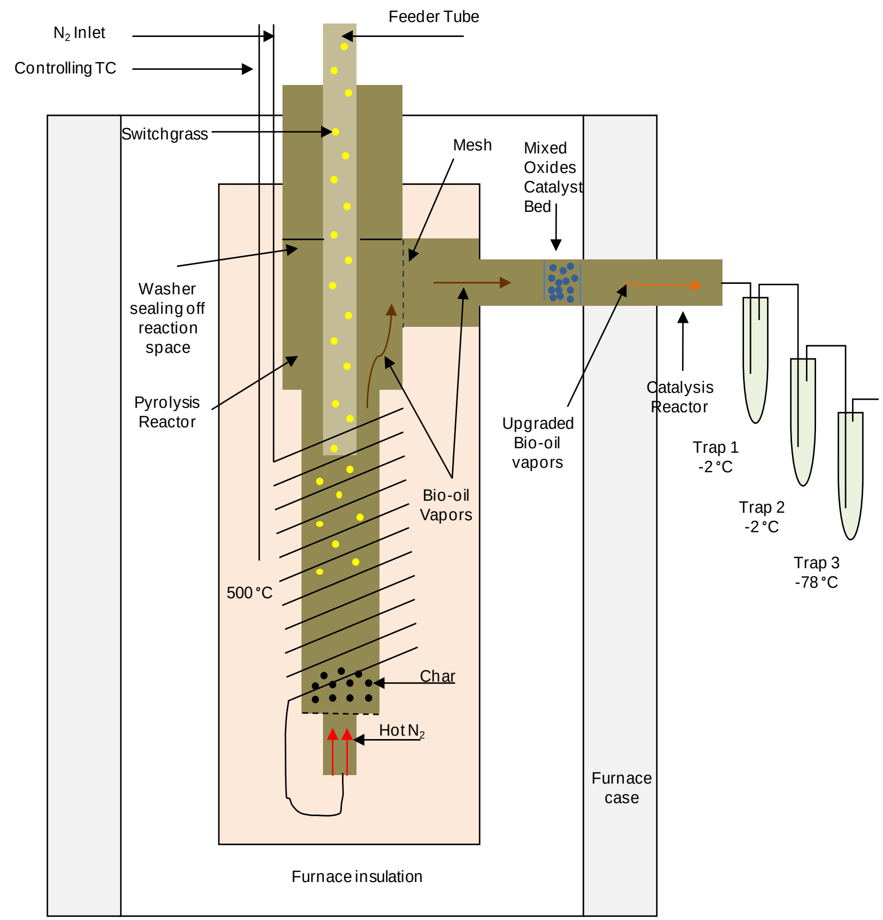
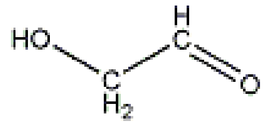
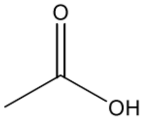
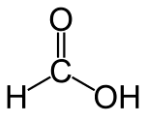
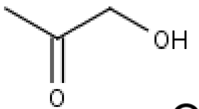
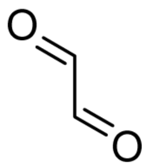
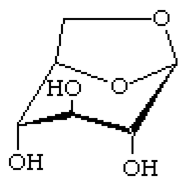
Micropyrolysis Unit



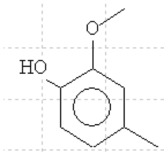
Characteristics: 1 inch OD, wide temperature capabilities; drop feed (auger)

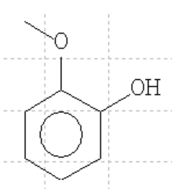
Studies: Fluidization dynamics, particle dynamics, quenching, sample generation for analytical development, switchgrass composition effects (with Noble Foundation)

Pyrolysis Oil (Bio-oil) Composition

Hydroxyacetaldehyde		5-12 %
Acetic Acid		3-9%
Formic acid		1-4%
Acetol		3-7%
Glyoxal		1-2%
Levoglucosan		2-10%
Lignin oligomers		15-30%
Water		15-30%
etc, etc (> 250 compounds)		15-30%

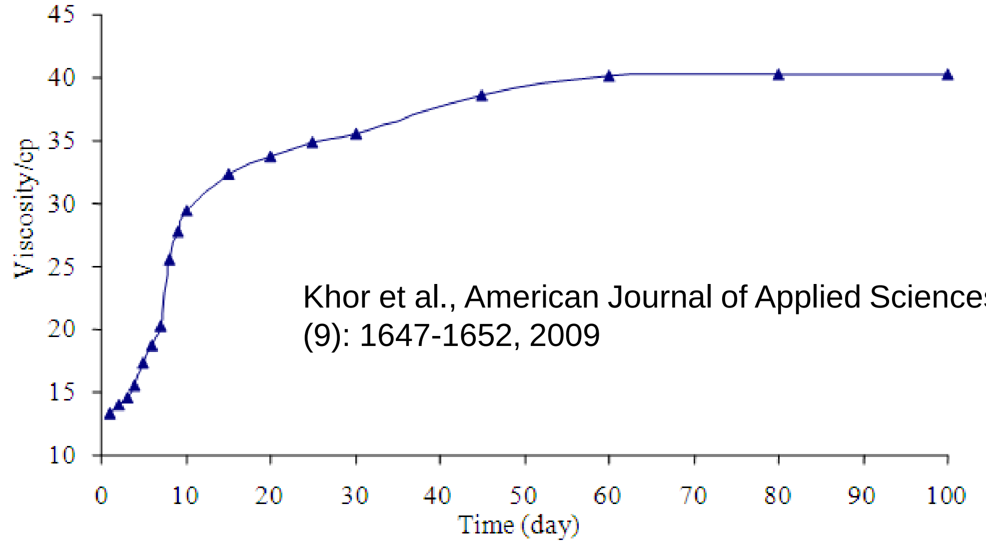
Guaiacols, phenols, vanillin, etc



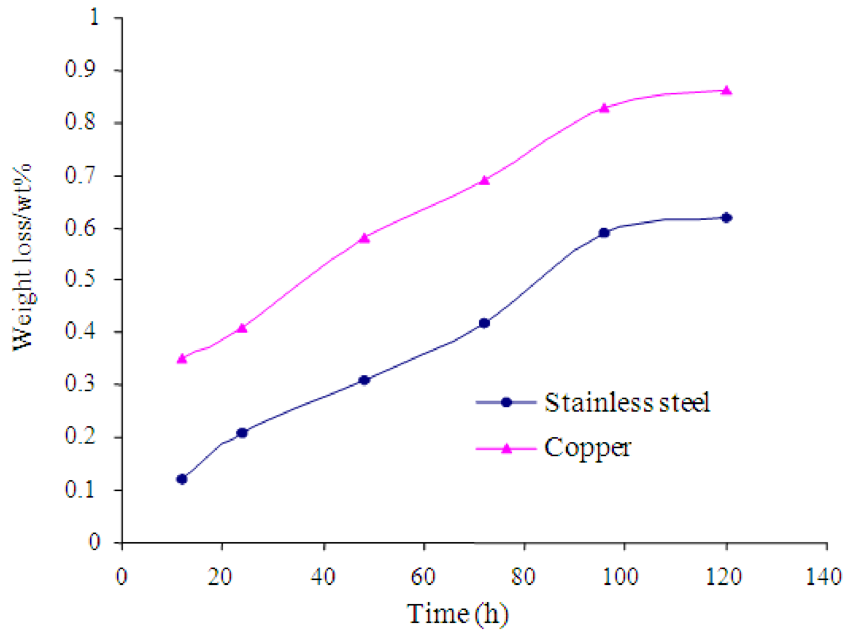


Bio-oil: Characteristics and Characterization

- Complex – hundreds of compounds, many different types of oxygen functionalities (GCMS, GC x GC)
- Unstable – viscosity increases with time due to polymerization, condensation reactions
- High water content
- Acidic (Total Acid Number)
- Nitrogen from proteins, high oxygen content (elemental analysis)



Khor et al., American Journal of Applied Sciences 6 (9): 1647-1652, 2009



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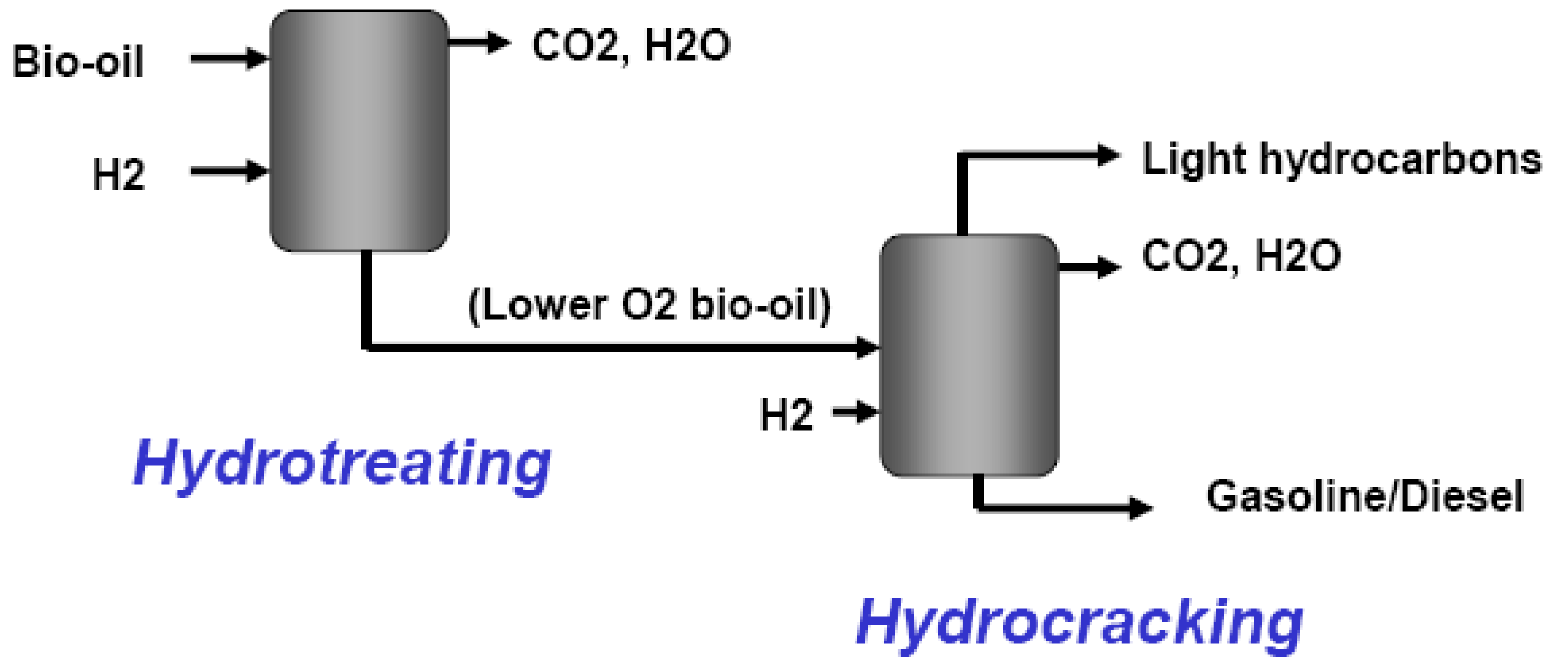
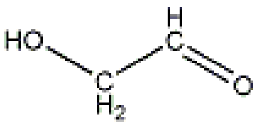
Bio-oil as Refinery Feedstock



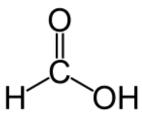
James Spaeth
DOE Golden Field Office

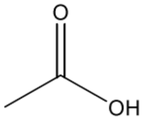
Bio-oil upgrading strategy

- Emphasize conversion in vapor phase before condensation of bio-oil

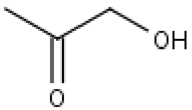


- Maximize carbon capture via condensation, ketonization, alkylation reactions

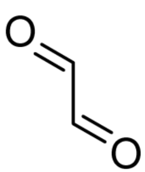


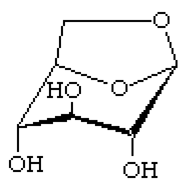


- Minimize hydrogen consumption by selective deoxygenation



- Target fungible fuel molecules





Biofuel Challenges: Fuel Properties

- octane number, cetane number
- sooting tendency
- vapor pressure, boiling temperature, heat of vaporization
- storage stability, thermal and chemical stability

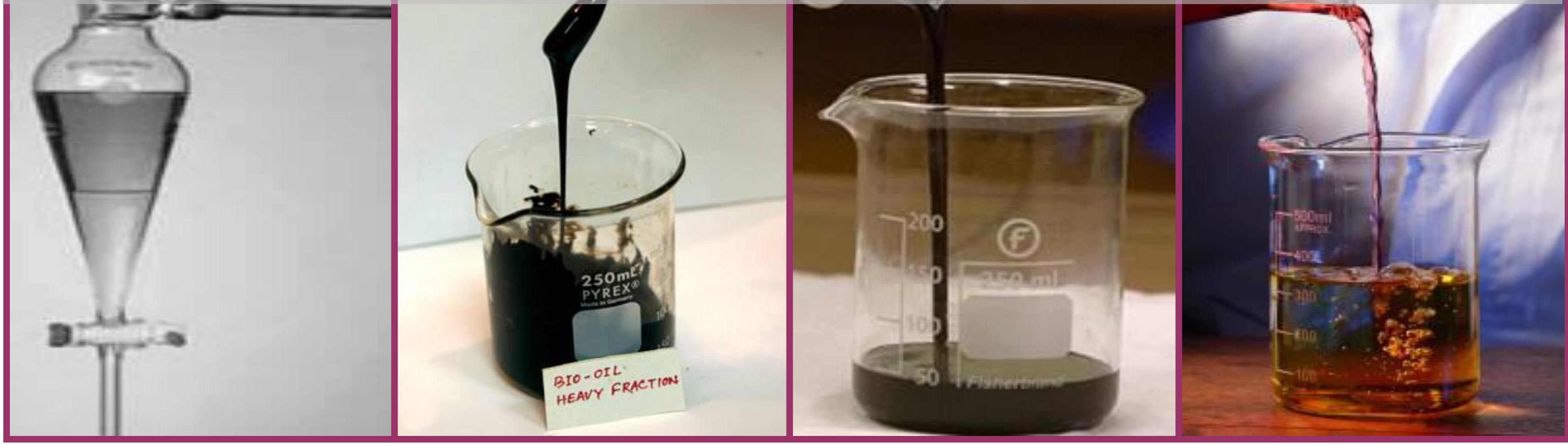
Many of these properties may be improved by

catalytic refining

eliminating oxygen functionalities and arranging molecular structure

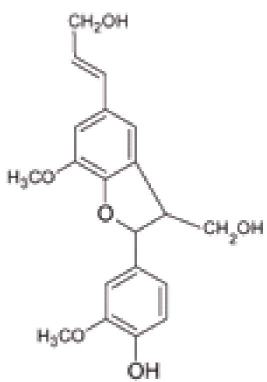
- transport in pipelines, water solubility, corrosion, toxicity,
- heating value, energy density, lubricity
- freezing point, viscosity, flash point, cloud point
- autoignition temperature, flammability limits
- sulfur content, aromatic content, density

Bio Oil Fractions obtained by Liquid-Liquid extraction after the Pyrolysis

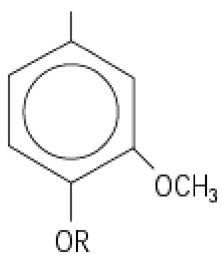


Each of these needs a different catalytic strategy

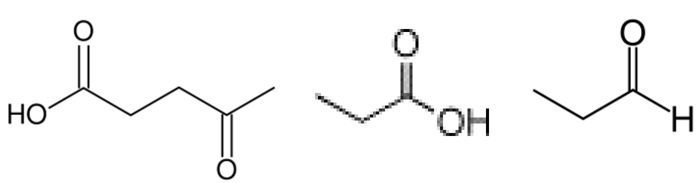
lignin oligomers



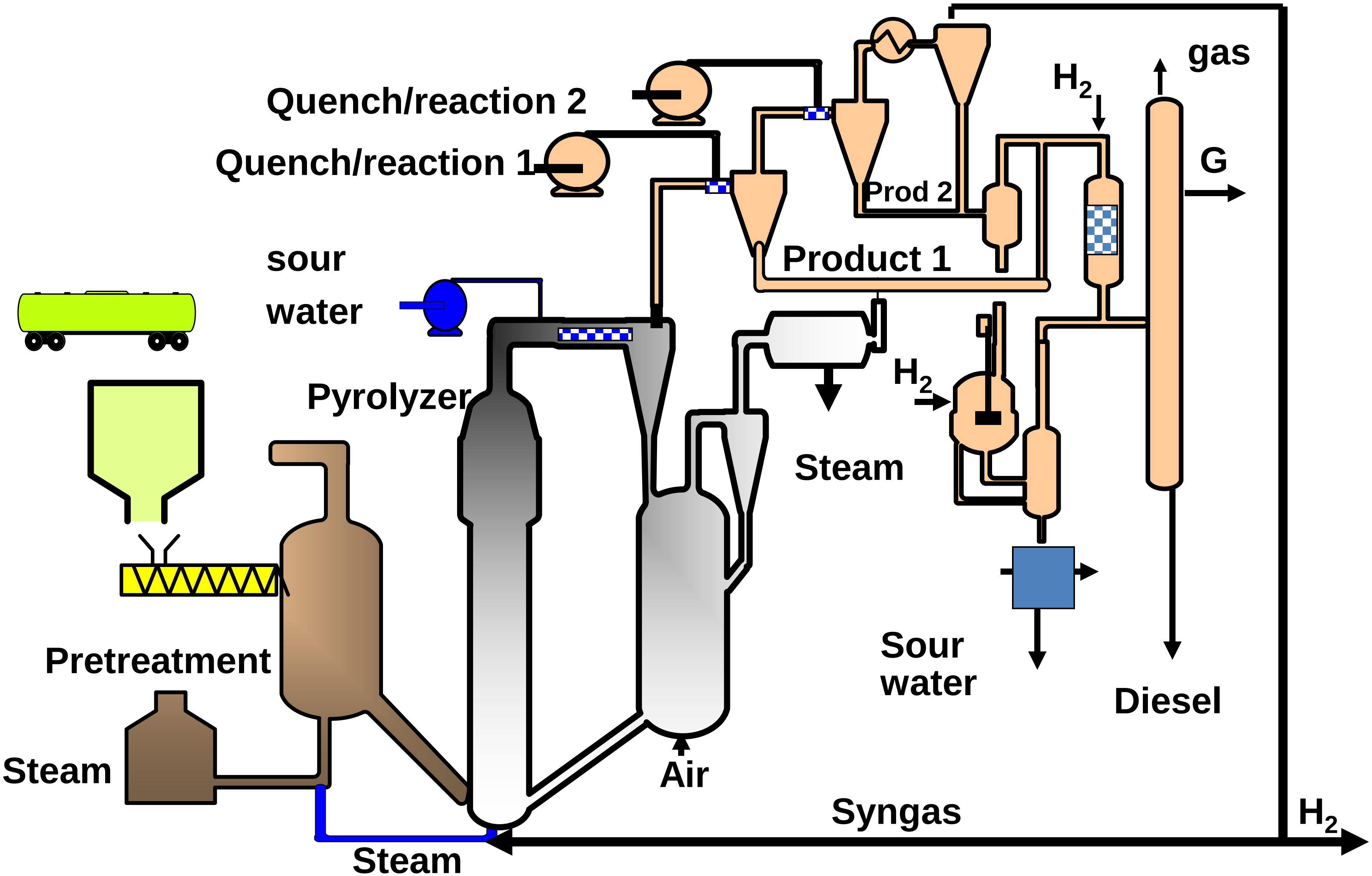
phenolics



Water soluble



OU Biomass Pyrolysis Unit

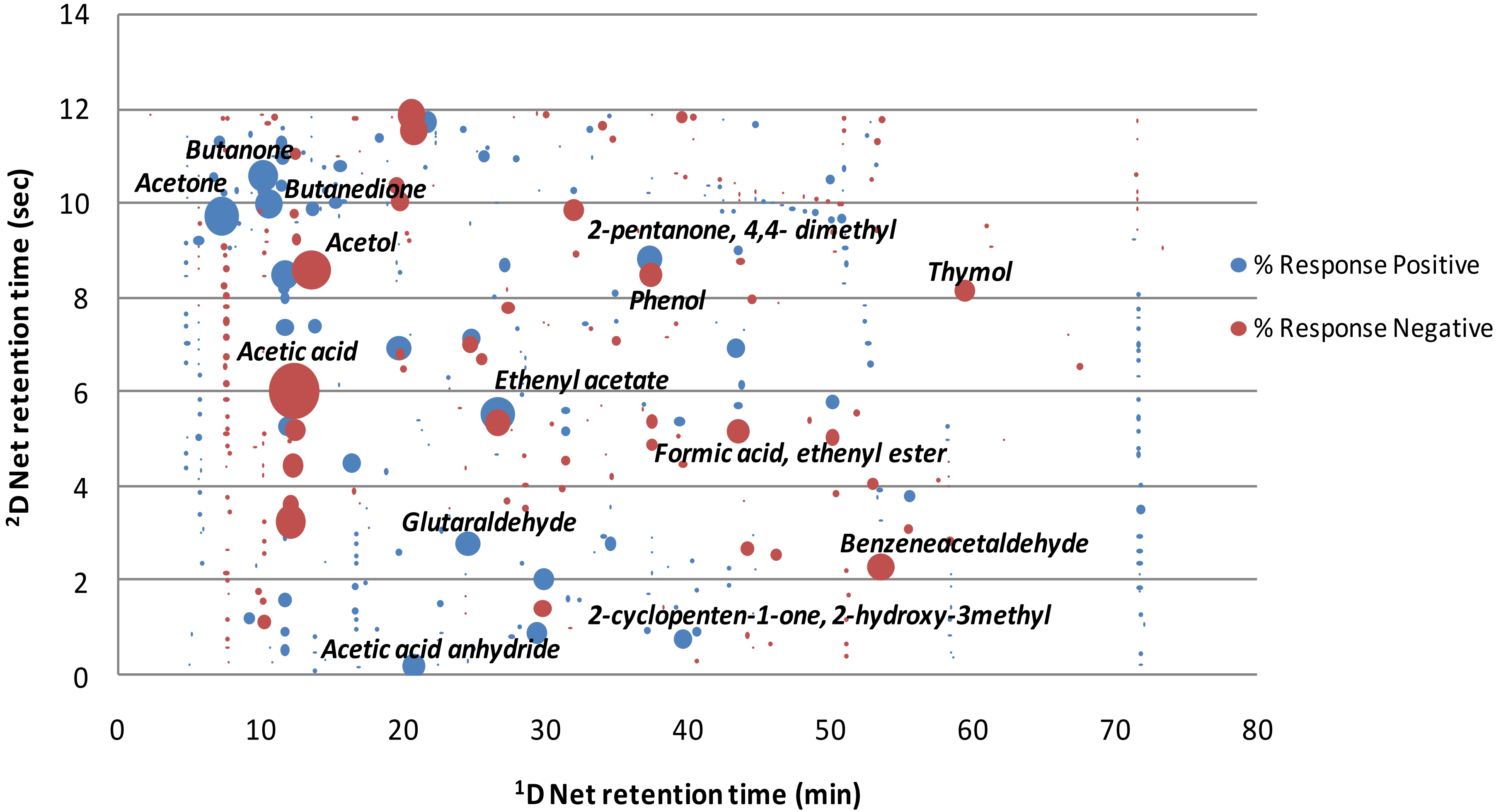


Catalytic Conversion Studies

1. Condensation of Small Oxygenates
   - 1.a. Aldol on basic/acids and deoxygenation on metals
   - 1.b. Aldol on basic/acids and etherification on metals
   - 1.c. Ketonization and deoxygenation
   - 1.d. Oxygenates to aromatics on zeolites
2. Deoxygenation of Aldehydes on Metals
   - Hydrogenation / Hydrogenolysis / Decarbonylation on Pd and Cu
3. Deoxygenation of Aromatic Oxygenates
   - 3.a. Decarbonylation on basic and Ga-modified zeolites
   - 3.b. Hydrogenolysis / decarbonylation on Pd
4. Mixtures, pyrolysis vapors

Vapor phase bio-oil catalytic upgrading

Insert GC x GC schematic



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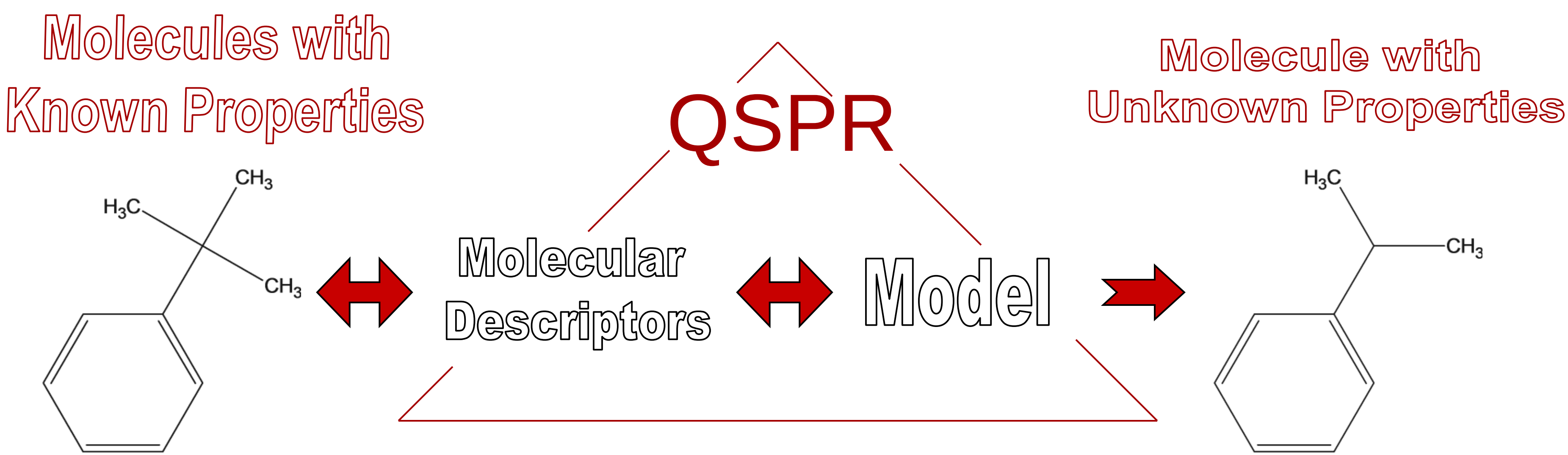
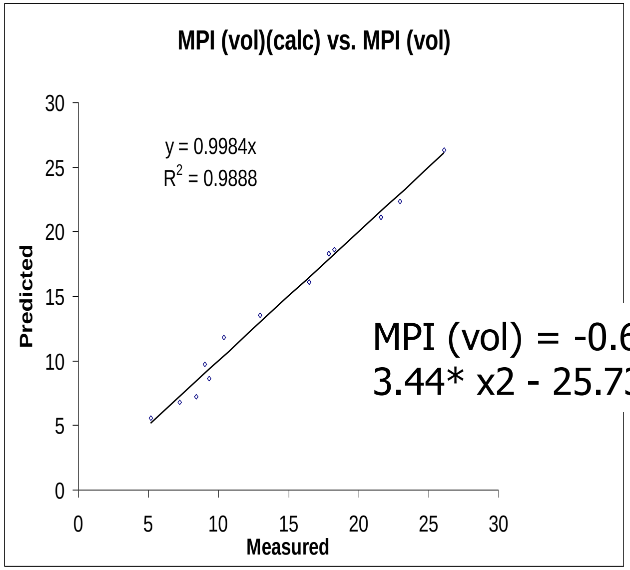
Property Prediction w/QSPR



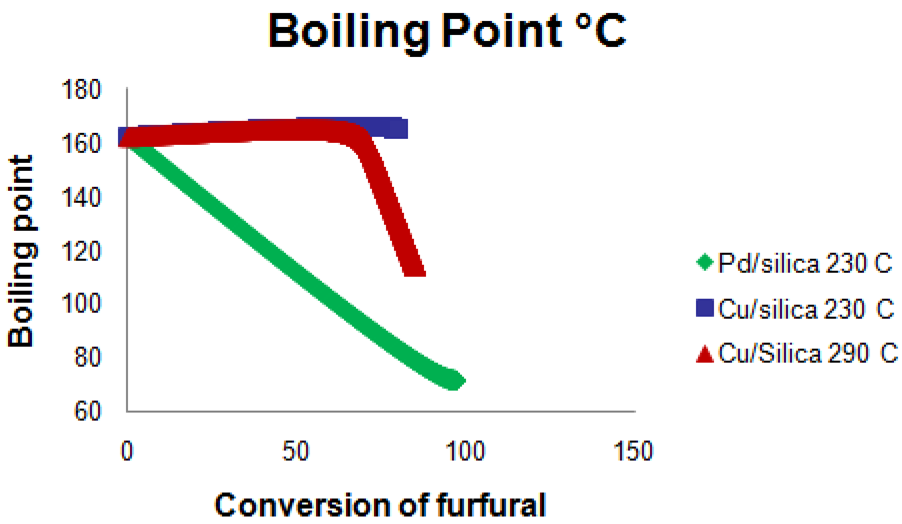
<u>Parameters</u>:

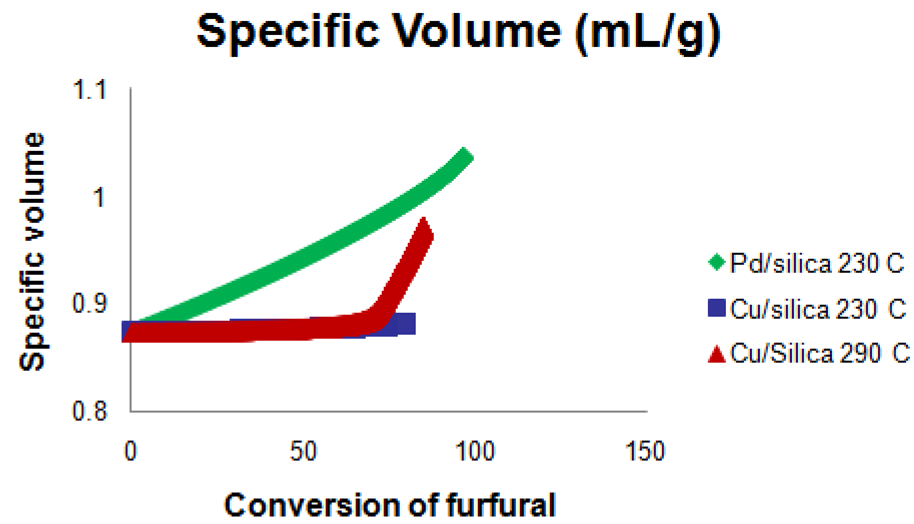
- maxhp (highest positive charge in H atom)
- Ovality (molecular surface area)$^{1/2}$/molecular volume)$^{1/3}$;
Gmin (min. E-state in)
- electron accessibility;
- Xpc4 (molecular connectivity)
- Chi index (branching)
SssCH2_acnt (number of–CH2–Groups)
- ka3 and phia (shape information)

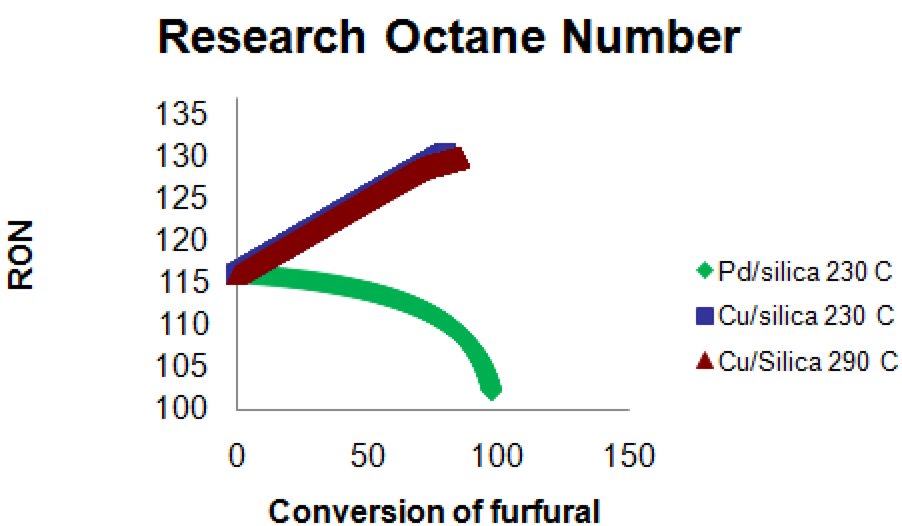


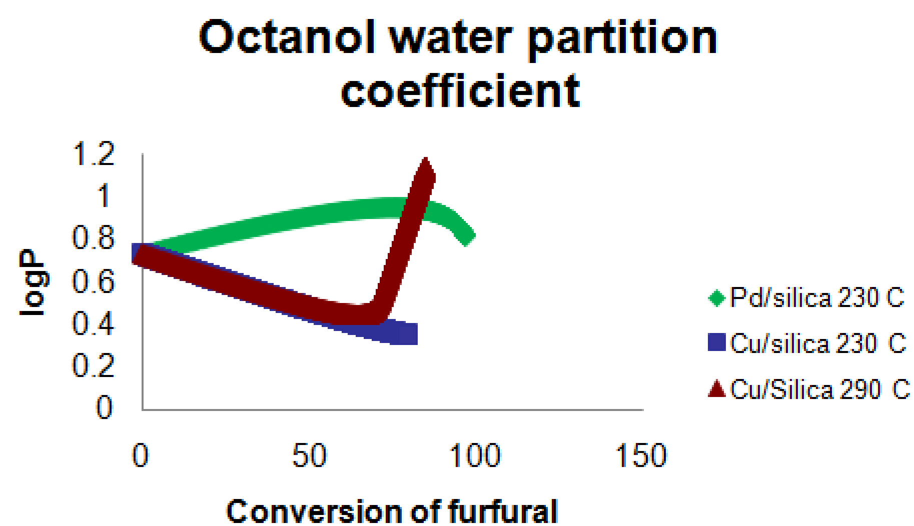
MPI (vol) = -0.6479 * ka3 + 7.139 * nrings + 3.44* x2 - 25.73 * xch6 + 3.1518

Molecular Management example: conversion of furfural









Fast Pyrolysis Wrap-up

- Strong potential – feedstock flexibility, desirable product, good fit with Oklahoma capabilities
- Significant R&D challenges, much activity

CBR team

•Research Group

Faculty: Friederike Jentoft, Lance Lobban, Richard Mallinson, Daniel Resasco, Alberto Striolo

Researcher Associates: Roberto Galiasso, Rolf Jentoft, Tawan Sooknoi (visiting)

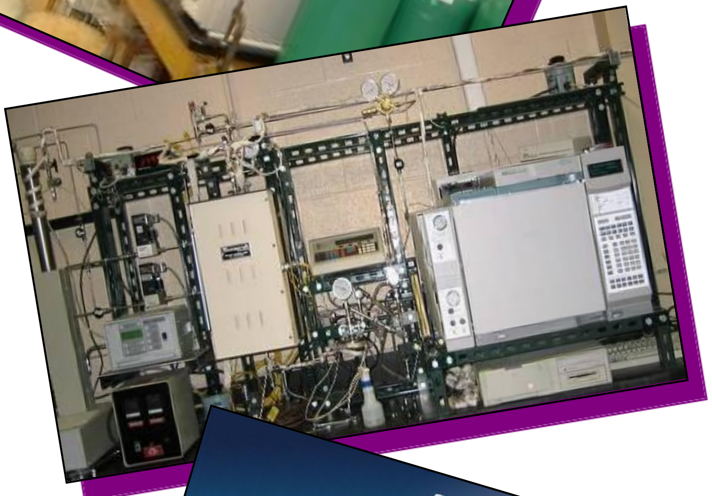
Students and post-docs: Xinli Zhu, Shaolong Wan, Trung Pham, Teerawit Prasomsrai, Phuong Do, Jimmy Faria, Surapas Sitthisa, Anh To The, Paula Zapata, Miguel Gonzalez Borja, Amalia Botero, Hernando Delgado Gamboa, Santiago Drexel, Kyle Elam, Anirudh Gangadharan, Sunya Boonyasuwat, Kassie Ngo, Matt Wulfers, Andrew D'Amico, Tu Pham, Lei Nie, Xiaohan Zhong, Rattiya Saetang, Christian Scherer, Michael Lang, Julien Bourgeois

• Funding

- NSF EPSCoR
- Oklahoma Secretary of Energy
- Oklahoma Bioenergy Center
- Procter & Gamble
- Department of Energy (DoE)

CBME reactor facilities

- 5 High-pressure flow reactors (up to 1,000 psi) with high precision liquid pumps.
- 5 Micro-catalytic flow reactors with gas chromatograph HP-GC 5890 series II (FID and TCD detectors) and HP-6890 (FID and TCD detectors).
- Micropyrolysis reactor and ~1 kg/hour fast pyrolysis unit
- Several Stirred High Pressure Reactors (Parr Series 4520)
- Transient kinetics, isotopic labeling, and temperature programmed techniques (TPD, TPO, TPR) (with MKS mass spec. quadrupole analysis)
- Cold plasma tubular reactor
- Microwave-assisted reactor (ASTEX 1500 W microwave power generator AX2115)
- Low pressure liquid phase stirred reactors



CBME catalyst characterization facilities

- BET area and pore size distribution (Micromeritics 2010) Volumetric Chemisorption System (Turbo V70 mini pumping station Varian)
- Microcalorimeter (Setaram DSC111)
- X-ray Photoelectron Spectrometer (PHI 5800 ESCA System)
- High Resolution Raman Microscope System for confocal Raman analysis, LabRam HR 800 (Yvon-Horiba)
- Diffuse Reflectance UV-VIS scanning spectrophotometer (Shimadzu, UV-2101PC)
- Diffuse Reflectance FTIR/NIR Spectrophotometer (Bruker Vertex 80)
- Thermal analysis equipment (being specified) – TGA, calorimeter

- X-ray absorption (EXAFS/XANES) at Brookhaven National Labs
- Wide angle X-ray diffraction (XRD Bruker)
- Small angle X-ray scattering (Rigaku)
- High-resolution Transmission electron microscopy (HRTEM) and Scanning Electron Microscopy (SEM)
- Scanning Tunneling Microscopy - Atomic Force Microscopy (STM/AFM- Veeco - NanoScope)

OU CBME Biofuels Research

1. Natural fats and oils conversion (Oklahoma Secretary of Energy, Procter & Gamble, Oklahoma Bioenergy Center, US Department of Energy)
2. Glycerol and small oxygenates conversion (Oklahoma SoE, OBC, US DoE, National Science Foundation EPSCoR)
3. Fast pyrolysis and conversion/upgrading of bio-oil (OBC, DoE, NSF EPSCoR, NSF Major Research Instrumentation
4. Biomass and bio-oil characterization (NSF EPSCoR, NSF Major Research Instrumentation)