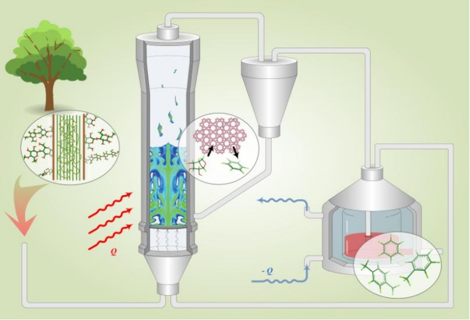
UMassAmherst



Anellotech

Renewable Petrochemicals from Biomass by Catalytic Fast Pyrolysis

Prof. George W. Huber
University of Massachusetts, Amherst
www.ecs.umass.edu/usfuels

Brazilian BioEnergy Science and Technology Conference
August 16, 2011

Pyrolysis is Cheapest Biomass Conversion Technology

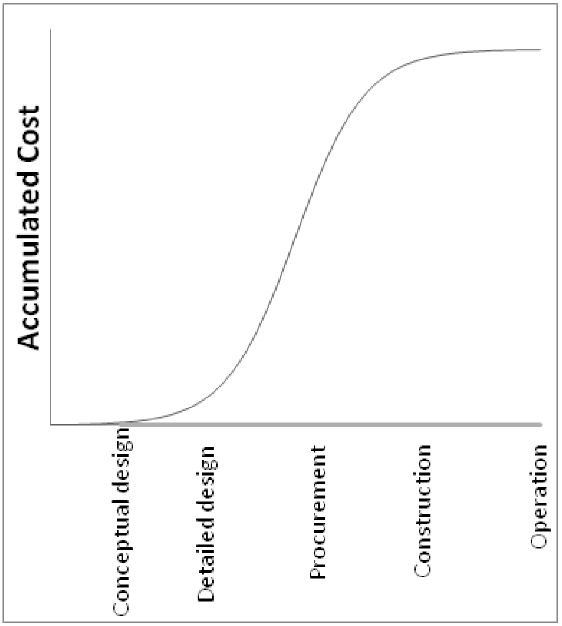
- Pyrolysis is the cheapest technology to convert biomass into a liquid fuel.
- Several companies are producing pyrolysis oils on commercial scale today.
- Iowa State (Robert Brown) and Conoco Phillips study concluded minimum cost of biofuel:
  - Hydrolysis $5-6/GGE > Gasification $4-5/GGE > Pyrolysis $2-3/GGE (GGE = gallons of gasoline energy equilvalence.)
  - (Study assumption: nth plant economics; 10% IRR; 2000 tons/day feedstock; Feedstock cost $75/ton; 100% equity financing.)
- Challenges with pyrolysis technology:
  - Controlling the chemistry
  - Low quality fuel
  - Upgrading of pyrolysis vapors
  - Catalysts and reaction engineering
  - Hydrogen requirements for upgrading (Hydrogen is more expensive than actual pyrolysis oil)

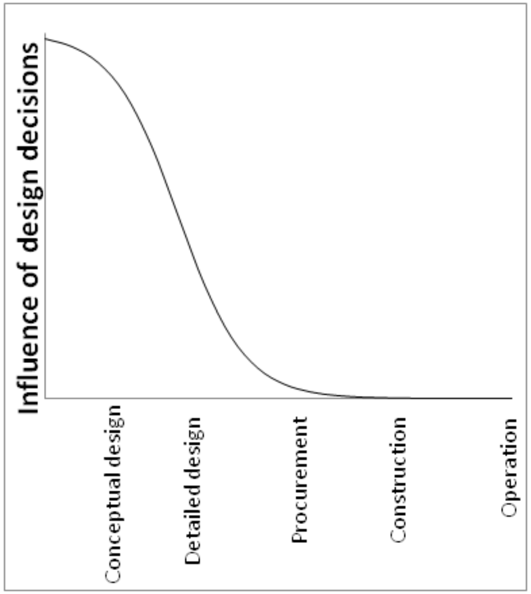
Pyrolysis Oils

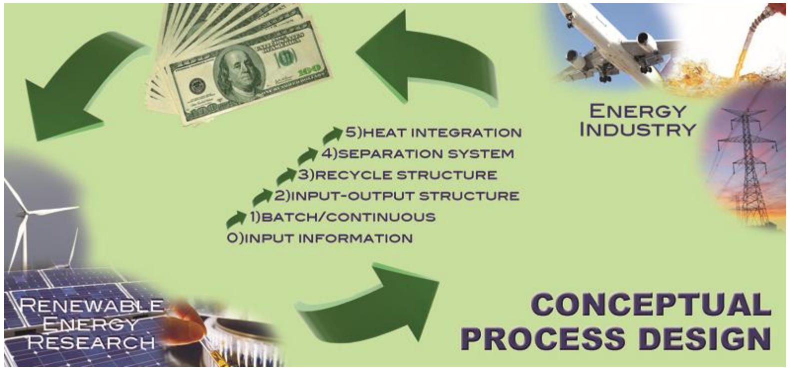
M. M. Wright, D. E. Daugaard, J. A. Satrio, R. C. Brown, Fuel 89 2010 S2-S10.
R.H. Venderbosch, W. Prins (2010) *Fast pyrolysis technology development.* In: Biofuels, Bioproducts and Biorefining (p 178-208).

Biomass Conversion Technologies are Capital Intensive

- Need to develop conversion technologies with low capital costs
- Decisions about cost are made very early in technology development in conceptual design stage
- Conceptual design should be used to guide R&D

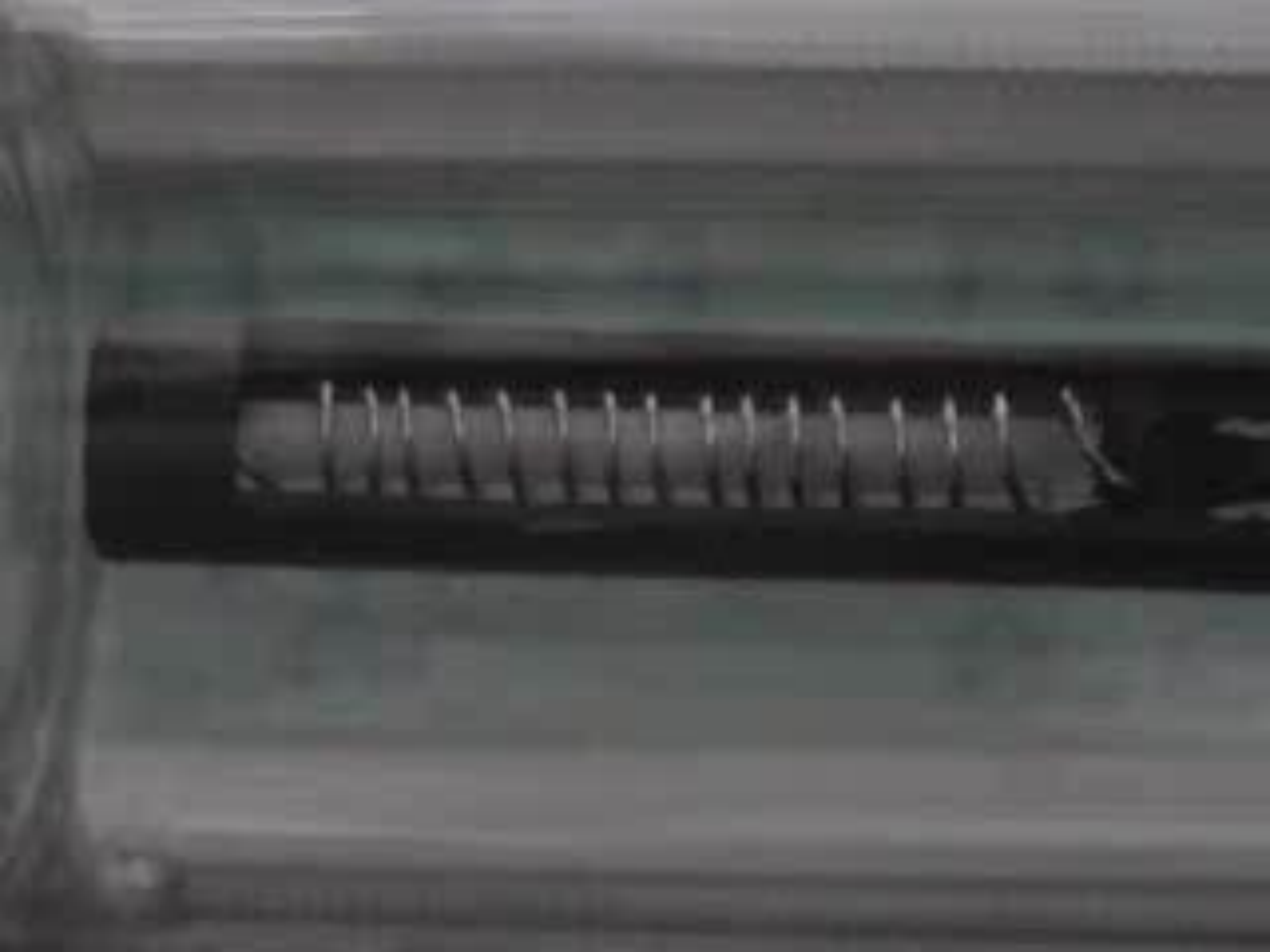




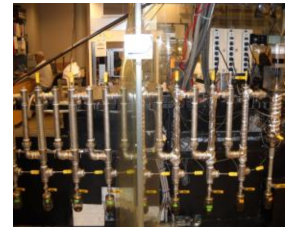


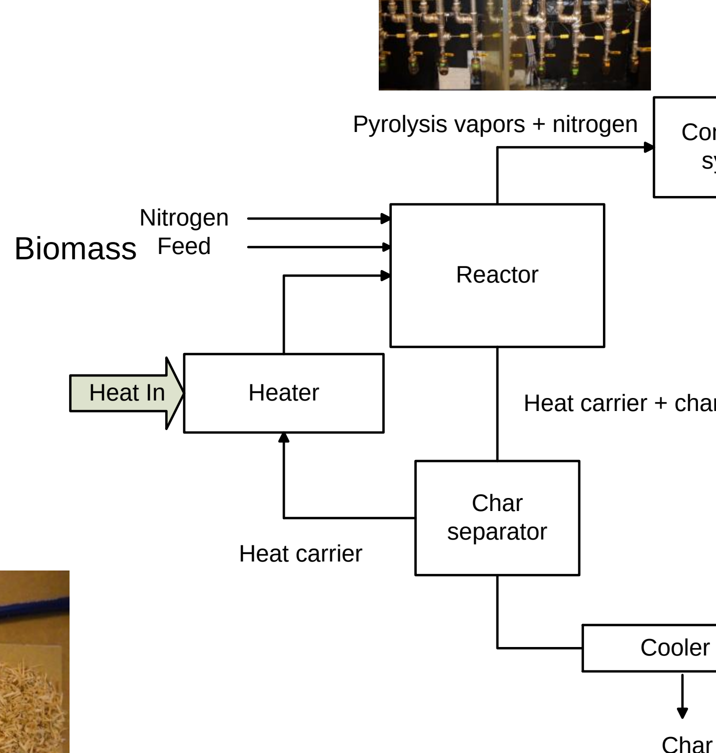
A. A. Upadhye, W. Qi, G. W. Huber. Conceptual Process Design: A Systematic Method to Evaluate and Develop Renewable Energy Technologies; AICHE Journal (cover story); (2011), 57 2292-2301.

G. Towler, and R.K. Sinnott Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design, Butterworth-Heinemann .
J. M. Doulgas Conceptual Design of Chemical Processes, McGraw Hill.



PRODUCTION AND CHARACTERIZATION OF PYROLYSIS OILS





UMass Pyrolysis Pilot Plant 4.9 Gallons/day
Designed by: Phil Badger; Renewable Oil International

Bio-oil: Characterization

Oak Wood Bio-oil

C: 47.0%
H: 8.2%
O: 44.8%

Elemental Composition

Viscosity: ~150 cP

Viscometry

Non-Combustibles

Ash: 0.03 wt%

Solubility

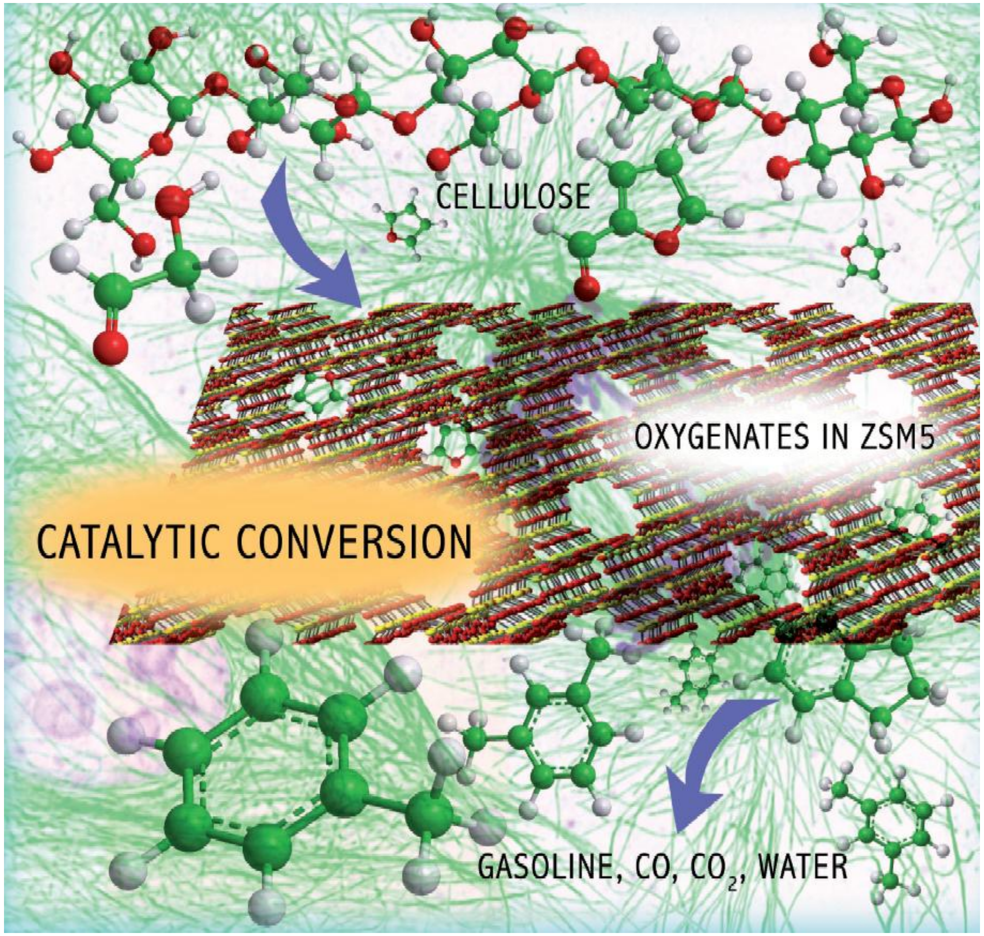
Water: 62%
Methanol: 98%
Toluene: 14%
Diesel Fuel: 4%

Acidity

pH: 2.75

S. Czernik, A. V. Bridgwater, Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **18,** 590-598 (2004).

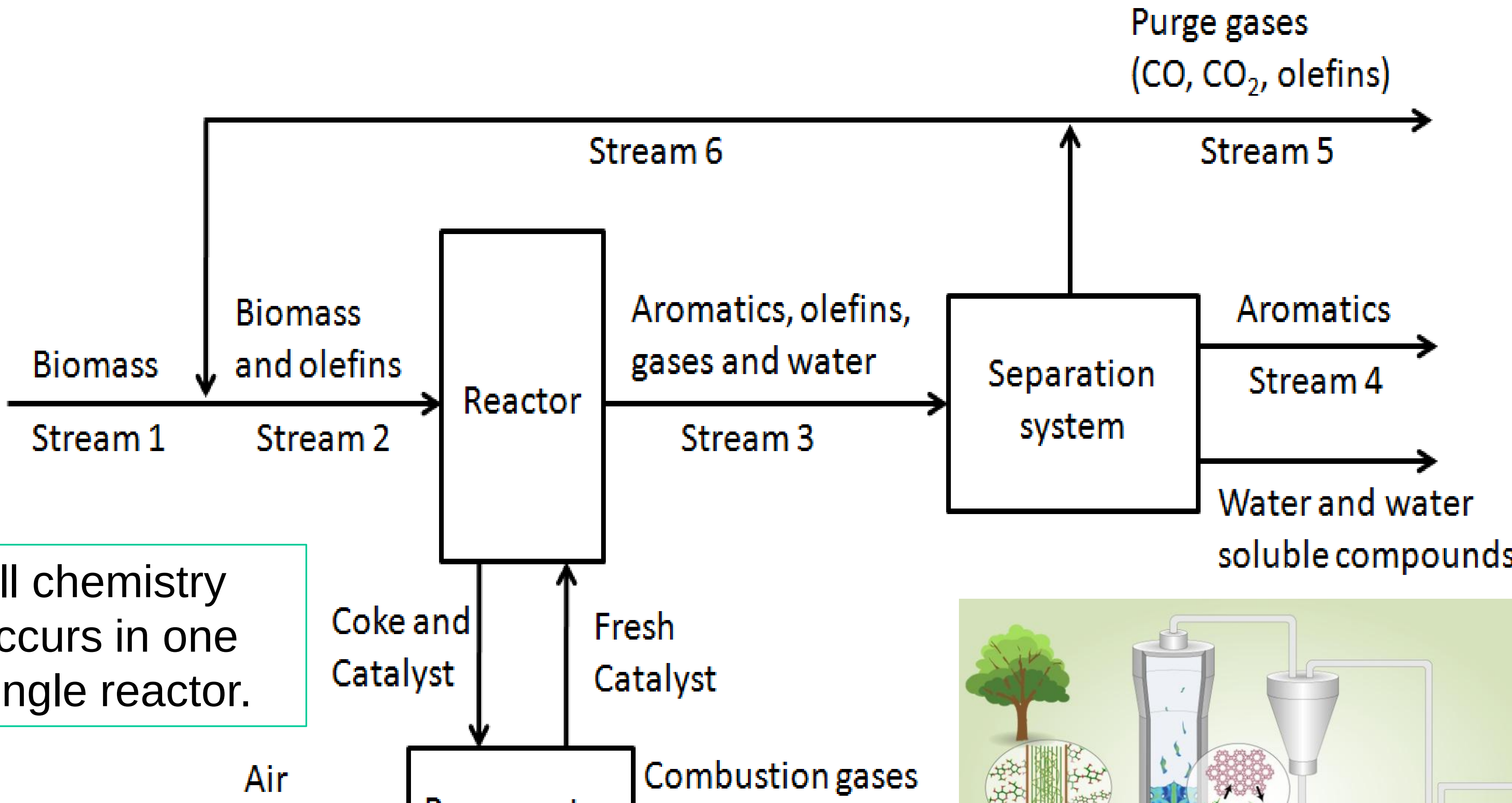
Catalytic Fast Pyrolysis Single Step Process to make Petrochemicals from Solid Biomass



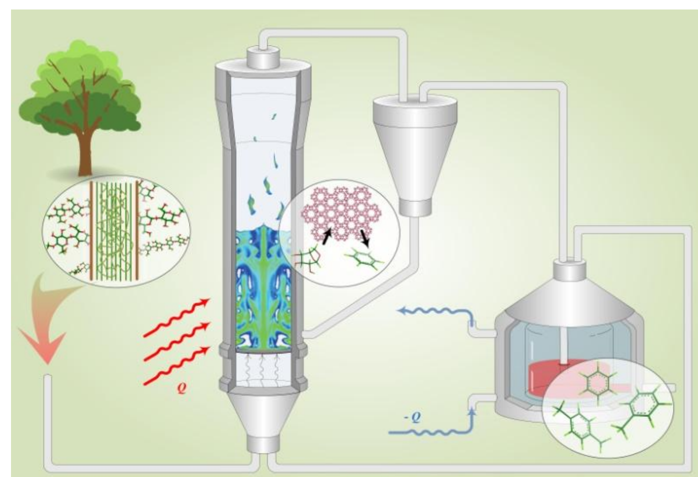
- Solid biomass converted into petrochemicals in a single reactor at short residence times:
  - Petrochemical that fits into existing infrastructure.
  - Inexpensive, recyclable zeolite catalysts.
  - Challenge is controlling chemistry.
  - Optimize reactor and catalytic chemistry to achieve high aromatic yields.

Carlson, T.R.; Vispute, T.P.; and Huber, G.W.; Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass-derived Compounds, ChemSusChem, **1**, 397-400 (2008).
J. Scahill and J. Diebold, *Research in Thermochemical Biomass Conversion, 1988,* ***40, 927-940.***

Block Flow Diagram for Catalytic Fast Pyrolysis

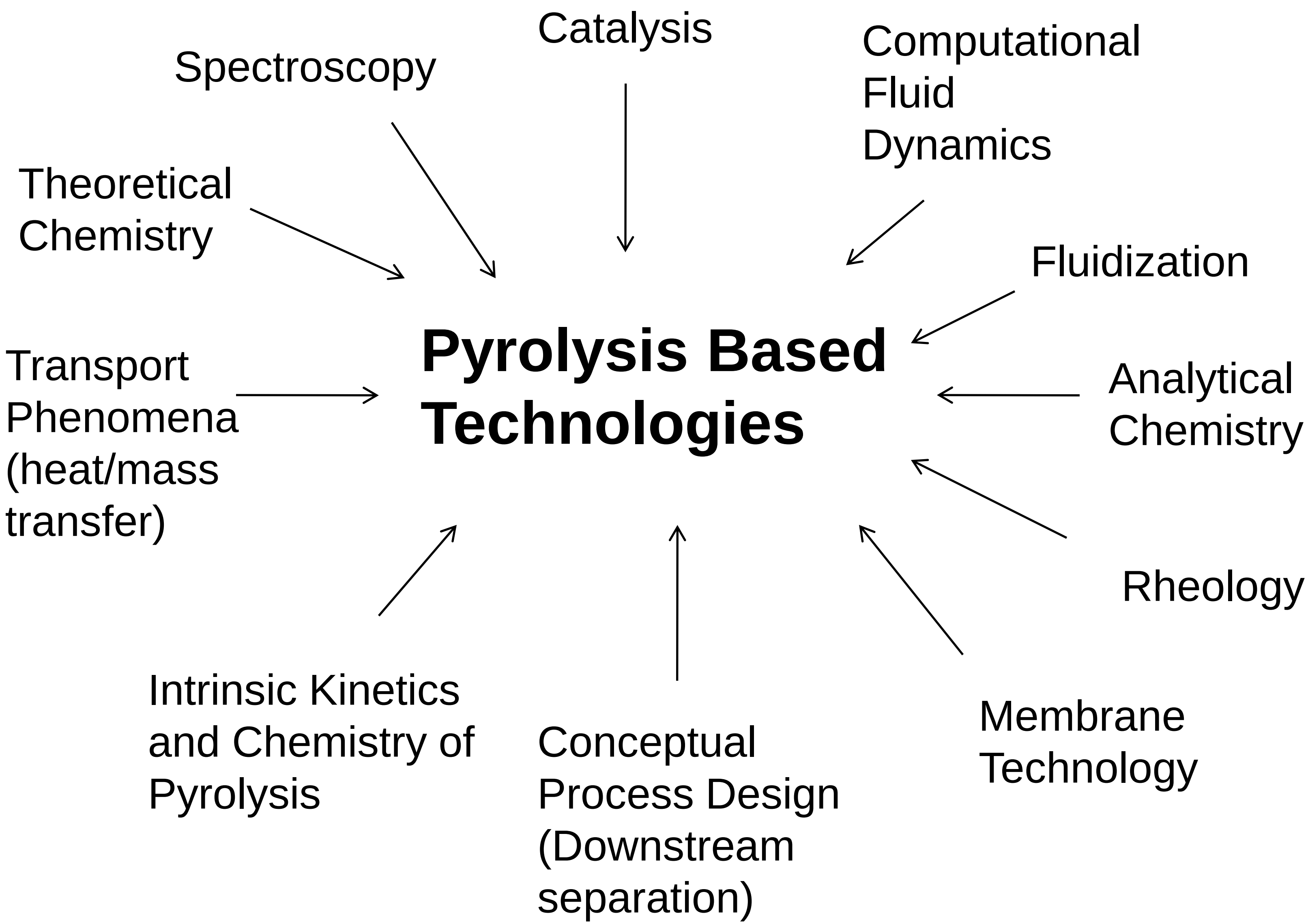


All chemistry occurs in one single reactor.

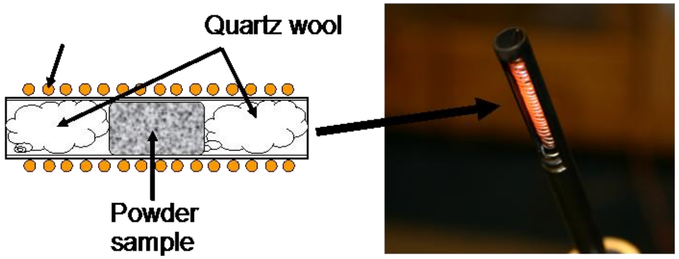


Torren R. Carlson, Yu-Ting Cheng, Jungho Jae and George W. Huber, Production of Green Aromatics and Olefins by Catalytic Fast Pyrolysis of Wood Sawdust, Energy and Environmental Science (2011) 4 145-161.

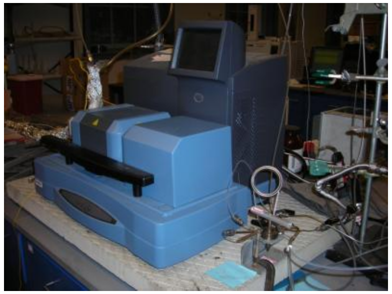
Variety of Scientific Tools to Optimize CFP



Wide Variety of Experimental Equipment used to Optimize CFP Technology



Pyroprobe (mg)
Fall 2006



TGA-MS
(mg)

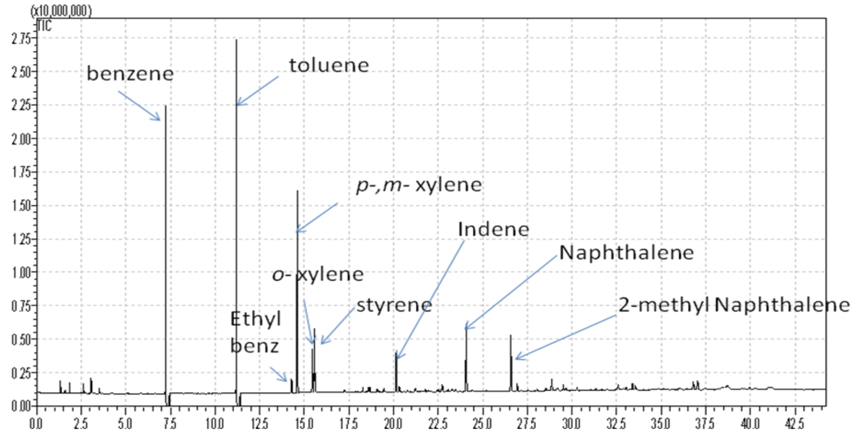
Fixed bed reactor (mg)
December 2008

1st generation
fluidized bed
December 2008

2nd generation
fluidized bed
March 2010

Process Development
Unit (PDU)
April 2011

Catalytic Fast Pyrolysis: Process Development Unit



GCMS of raw liquid only observe aromatics

Feed: Pine Wood Sawdust

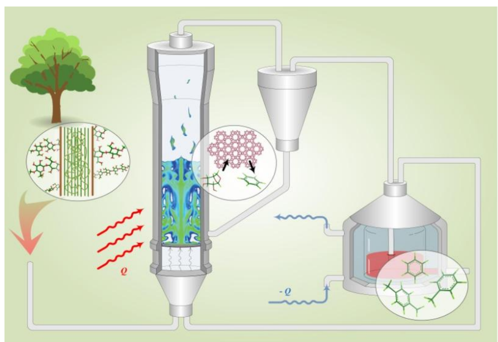
Process Development Unit (Continual flow of catalyst and biomass on stream since April 2011)

Raw Liquid Product (Contains aromatics and water)

Aromatic Products

Potential to Make Renewable Football Jersey

Biomass

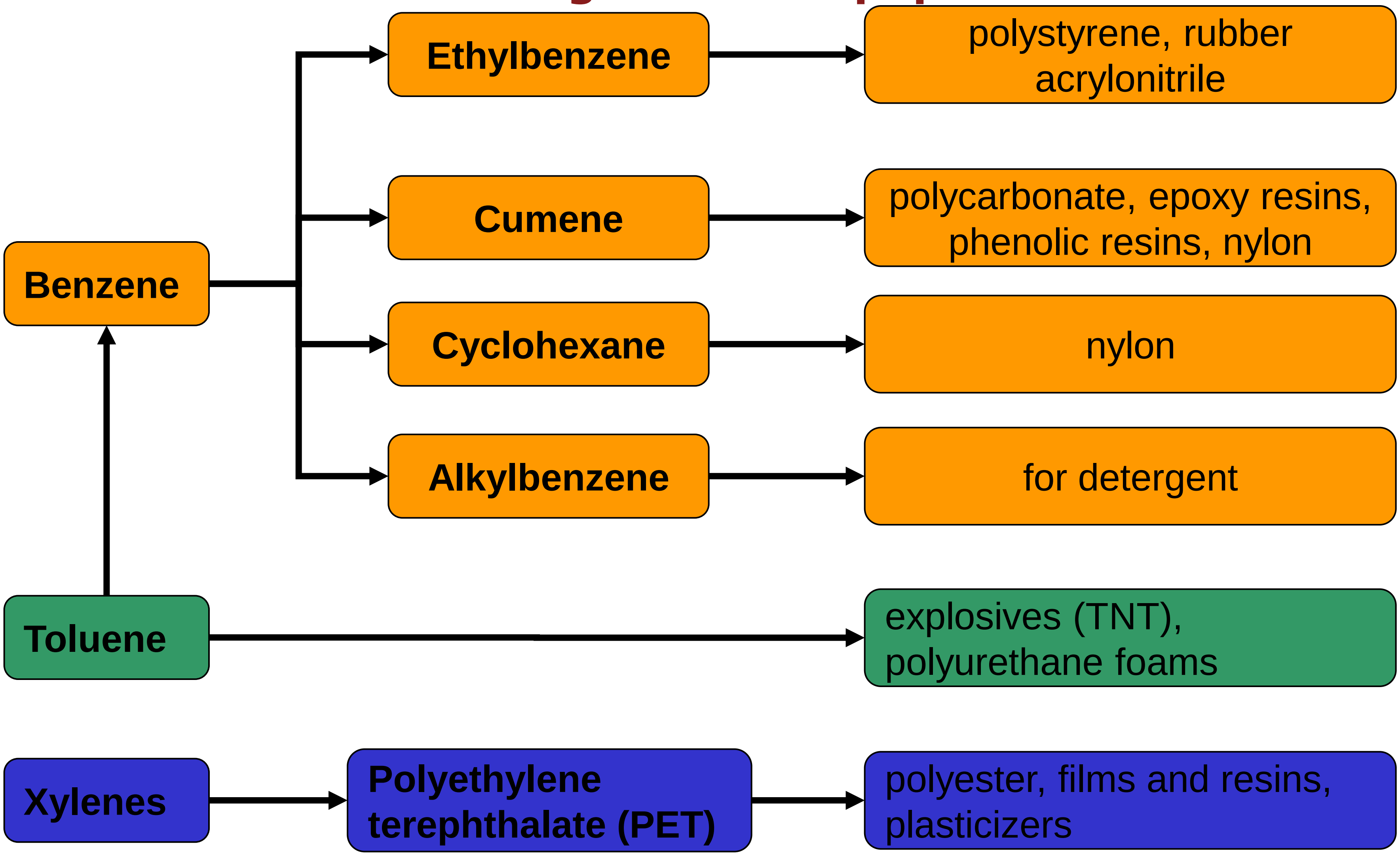


Catalytic Fast Pyrolysis

Aromatics

Aromatics can be added to conventional petrochemical infrastructure to make fungible products

Wide Range of Downstream Customers Can Use Green BTX in Existing Process Equipment



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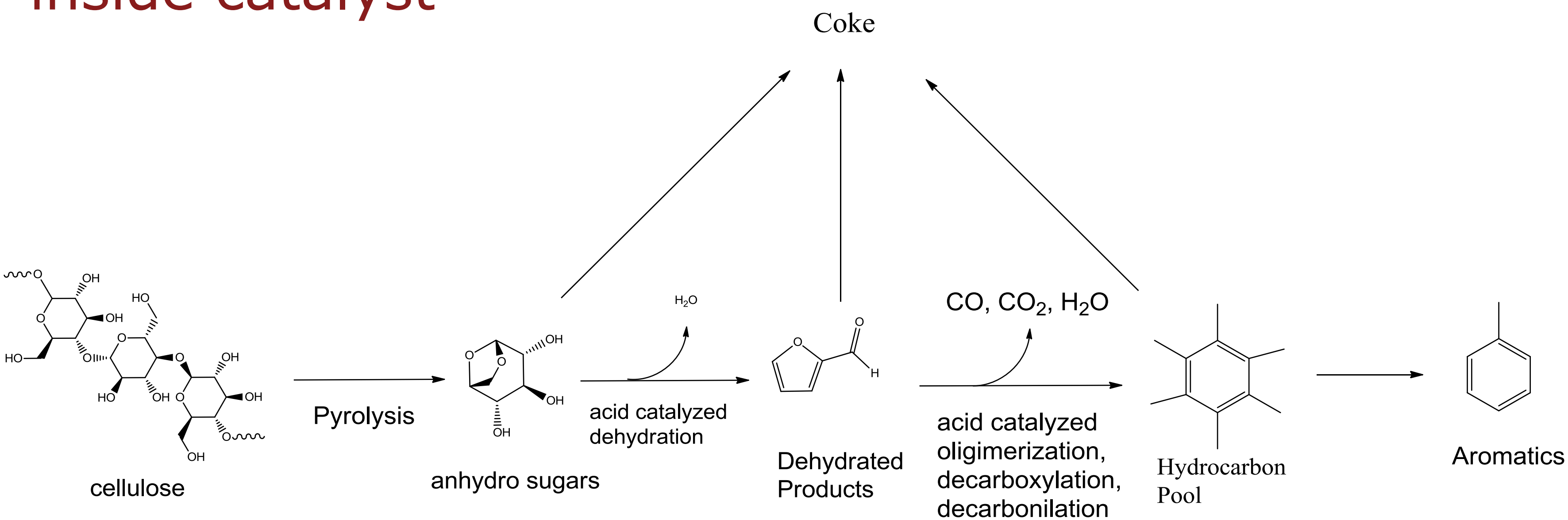
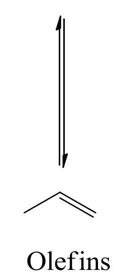
CFP involves reactions in solid biomass, gas phase and inside catalyst

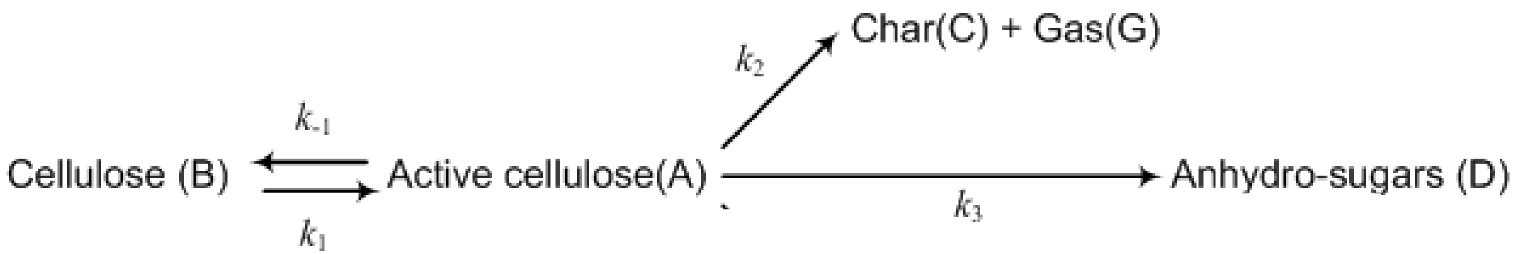




Desired Chemistry:
Pyrolysis (homogeneous)
Dehydration (heterogeneous & homogeneous)
Oligomerization & decarbonylation (heterogeneous)

Undesired Chemistry:
Homogeneous and Heterogeneous coke formation

Cellulose Pyrolysis Involves Series and Parallel Reactions



•At low temperatures (less than 300°C) cellulose forms coke.

•Coke formation is a low activation energy process and exothermic.

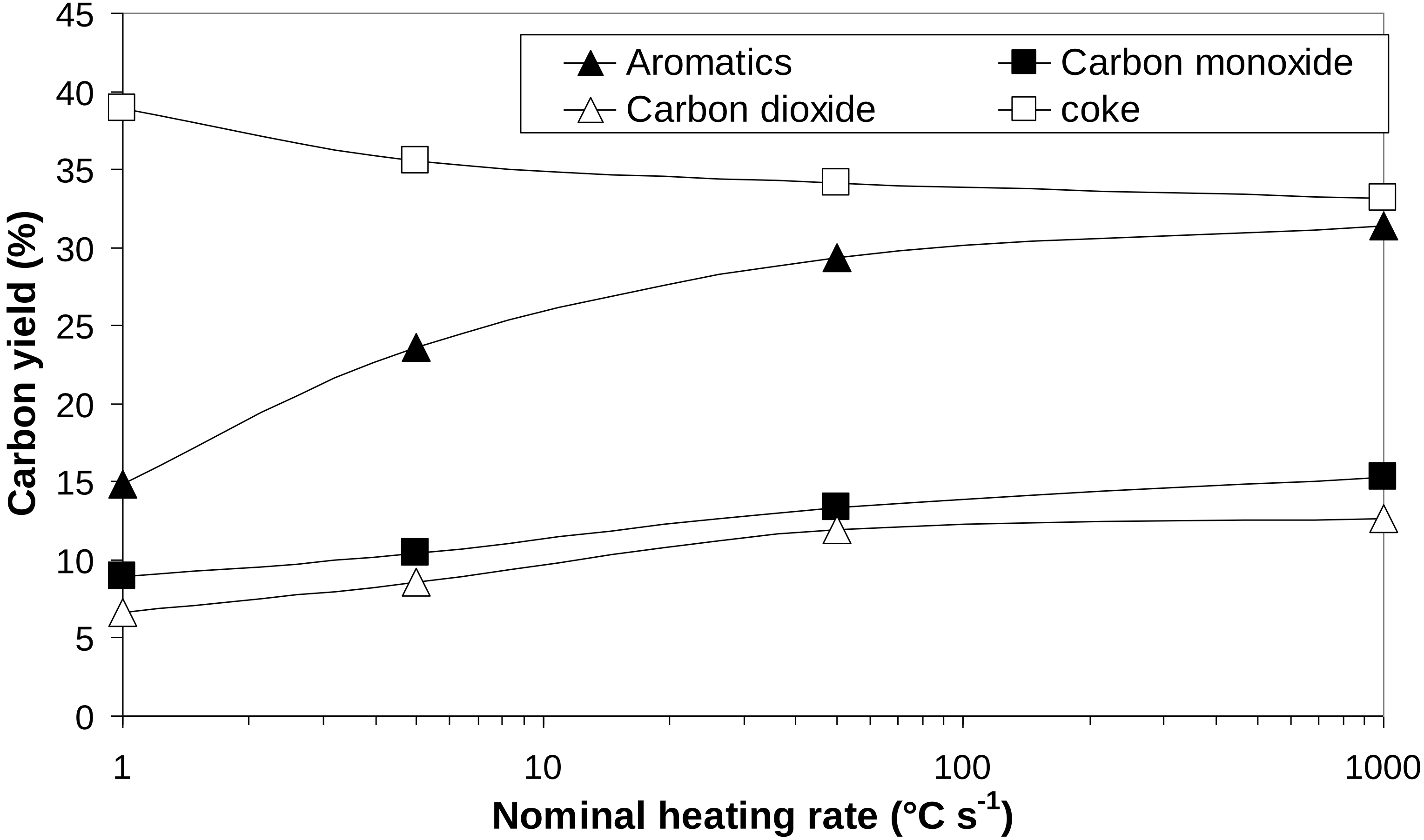
•Gases formed with coke include CO_2 and H_2O.

•High rates of heat transfer are needed to avoid coke formation.

	log A (A in sec)	E_A (kJ/mol)	H_{rxn} (kJ/mol)
k_1	22	258	-1.5
k_2	5.7	103	-170
k_3	14.8	199	120

Joungmo Cho, Jeffrey M. Davis, and George W. Huber; The Intrinsic Kinetics and Heats of Reactions for Cellulose Pyrolysis and Char Formation, ChemSusChem (2010) 3 1162-1165.

Aromatic Yield Increases with Heating Rate



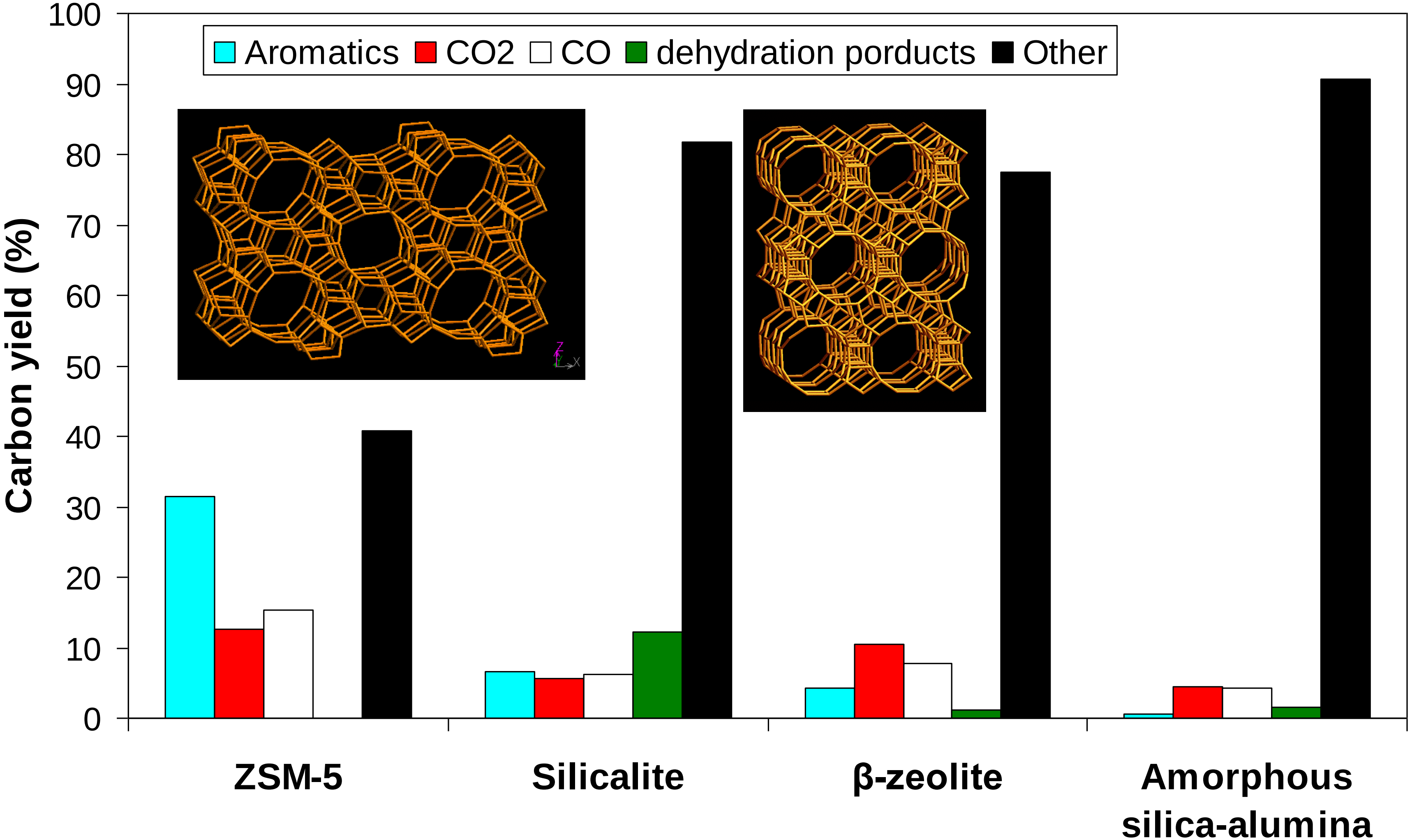
Reaction Conditions: Temperature 600°C; ZSM-5;

Feed: Glucose; Catalyst to Feed Ratio 19

$C_6O_6H_{12} \rightarrow$ 12/22 C_7H_8 (63 % Yield) + 48/22 CO (36 % Yield) + 84/22 H_2O

Carlson, T.R.; Vispute, T.P.; and Huber, G.W.; Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass-derived Compounds, ChemSusChem, **1**, 397-400 (2008).

Catalyst Design is Crucial to Achieve High Aromatic Yields



Carlson, T.R.; Vispute, T.P.; and Huber, G.W.; Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass-derived Compounds, ChemSusChem, **1**, 397-400 (2008).

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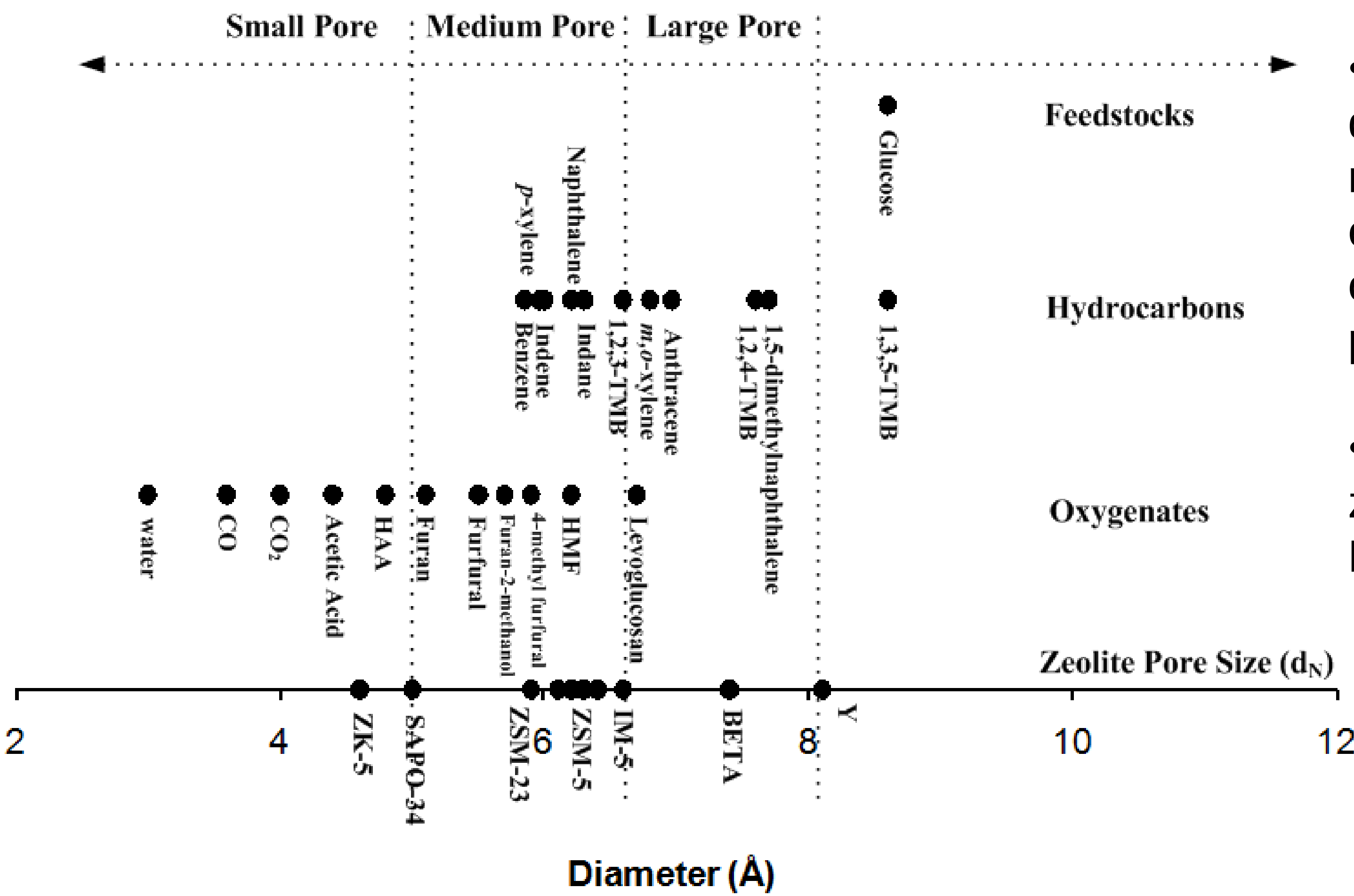
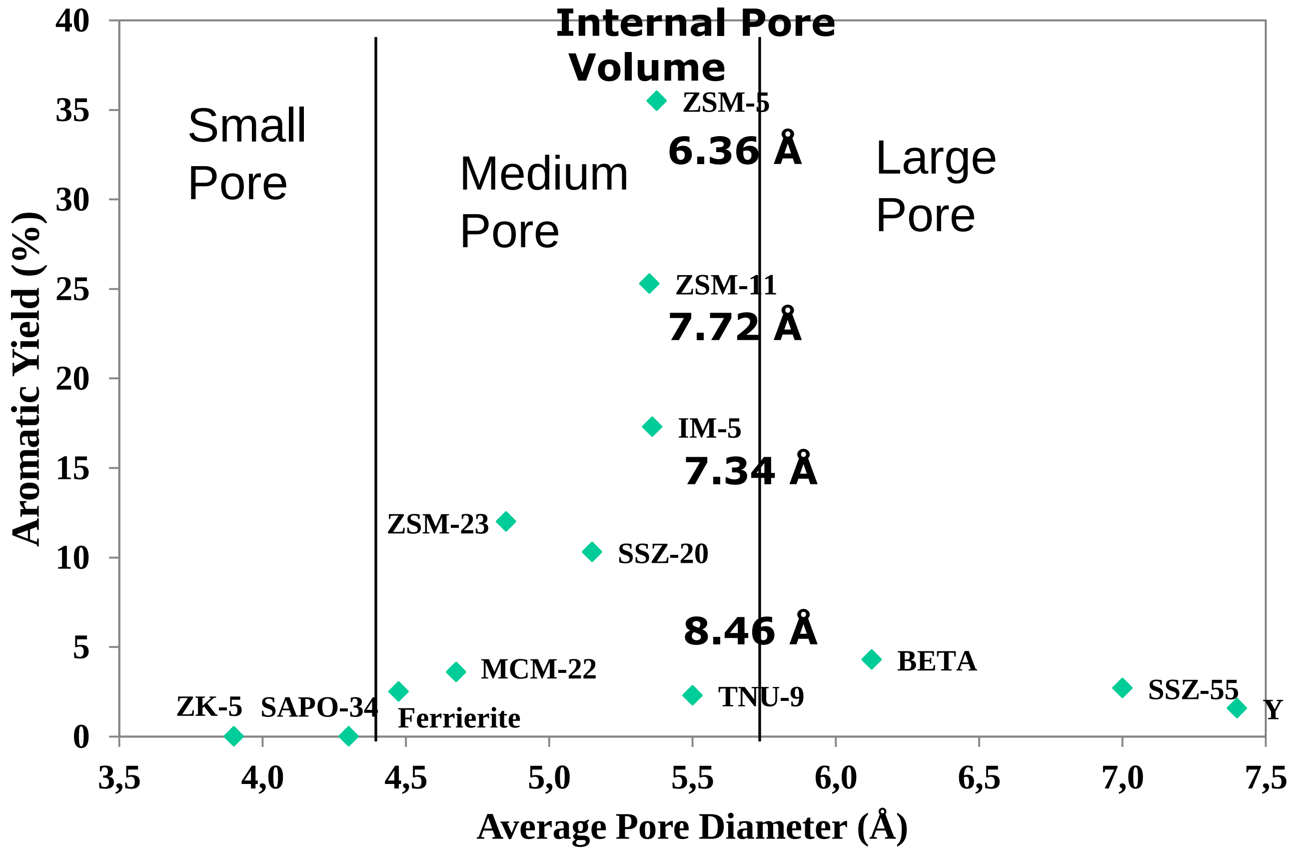
Pore size of feed, product and catalysts are critical for catalyst design



- Kinetic diameter of molecules estimated based on critical properties.
- Pore size of zeolite based on Norman radii

Jungho Jae, Geoffrey A. Tompsett, Andrew J. Foster, Karl D. Hammond , Scott M. Auerbach, W. Curtis Conner, Raul F. Lobo, and George W. Huber, The Shape Selectivity of Zeolite Catalysts for Biomass Conversion, (in press).

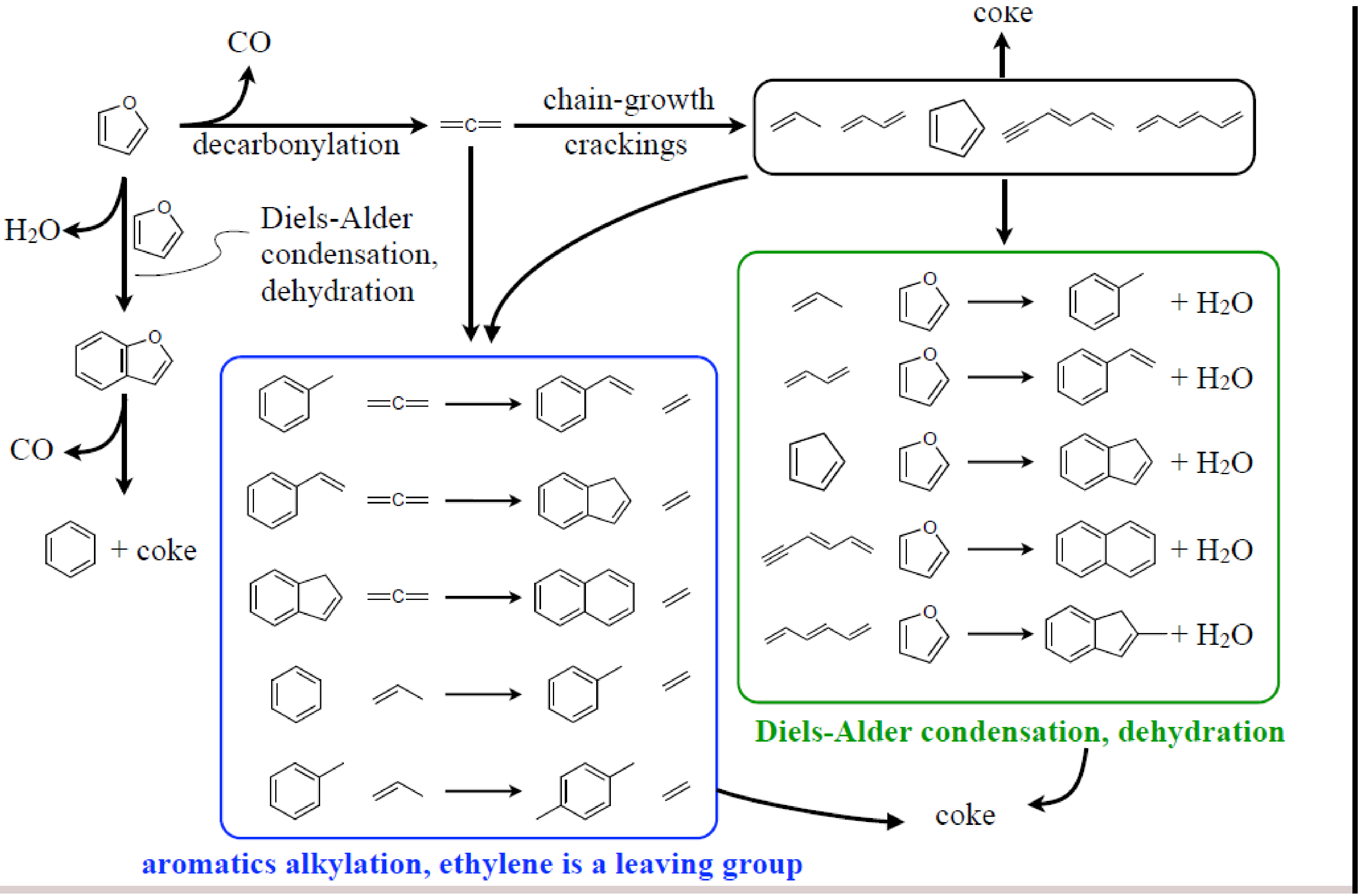
Aromatic Yield is a Function of Zeolite Pore Size and Internal Pore Volume



CFP of glucose at 600°C.
Yield is a function of zeolite pore size.

Jungho Jae, Geoffrey A. Tompsett, Andrew J. Foster, Karl D. Hammond , Scott M. Auerbach, W. Curtis Conner, Raul F. Lobo, and George W. Huber, The Shape Selectivity of Zeolite Catalysts for Biomass Conversion, J. Catalysis (in-press).

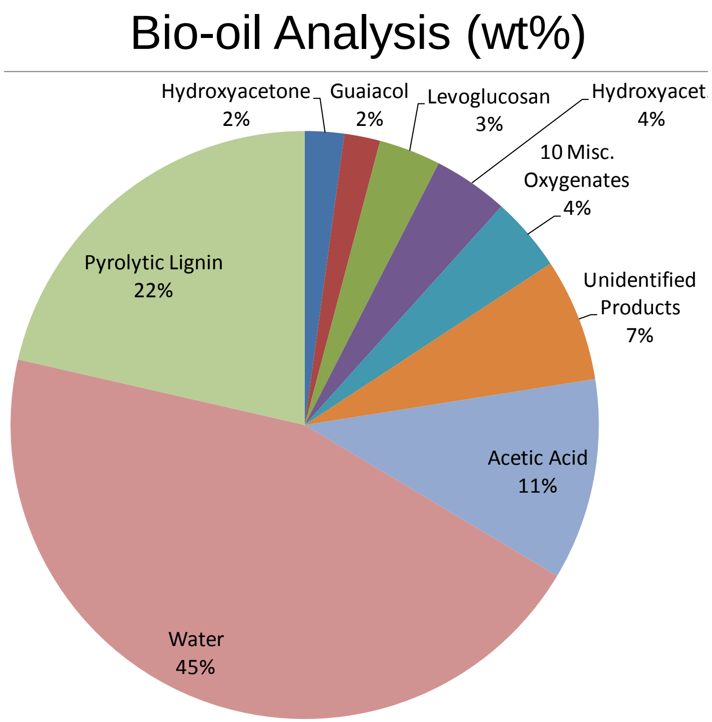
Model Compounds Help Understand the Zeolite Chemistry



Y. Cheng and G.W. Huber, Chemistry of Furan Conversion into Aromatics and Olefins over HZSM-5: A Model Biomass Conversion Reaction; *ACS Catalysis* (2011), in-press.

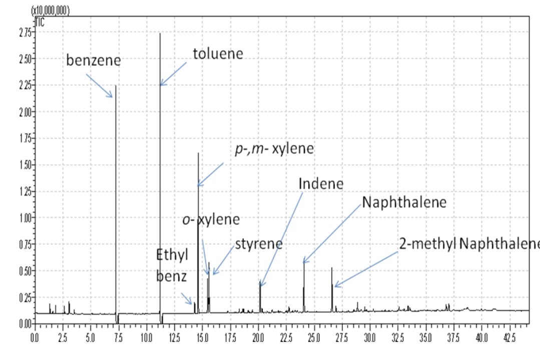
Bio-oils Produced by Fast Pyrolysis of Mixed Hard Woods

Bio-oil mixture of oxygenated products analyzed by GCMS, GPC, HPLC, Karl Fisher

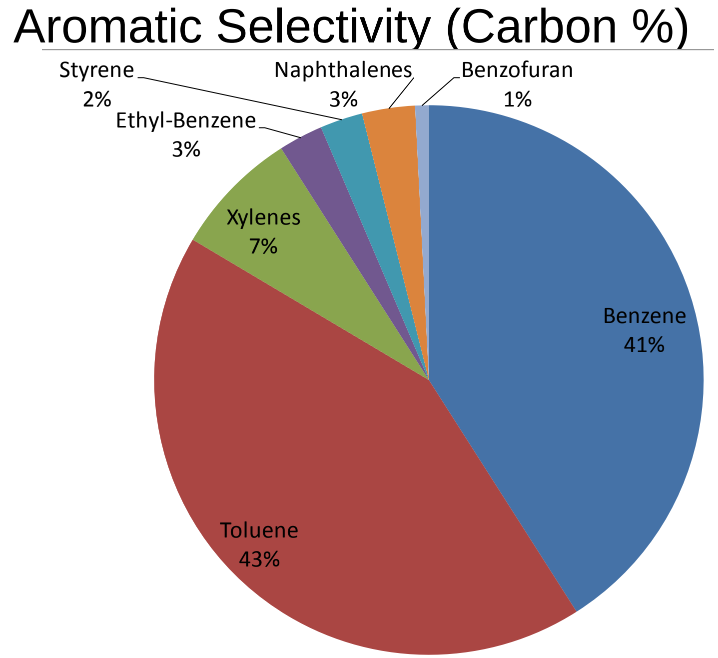


Commercial Yields: 70 wt% Bio-oils

Aromatics Produced by CFP of Pine Wood in PDU

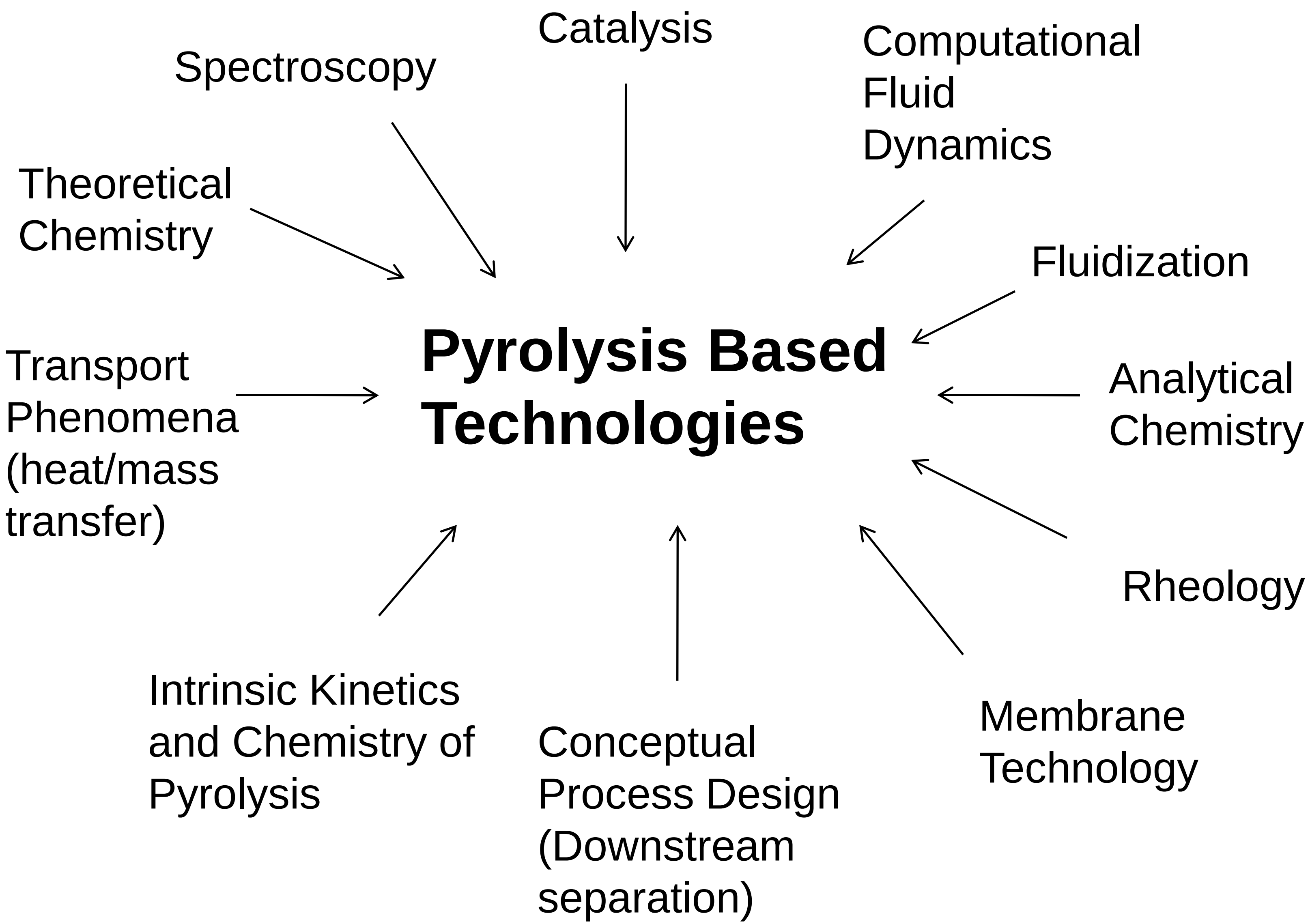


GCMS of Aromatic Products

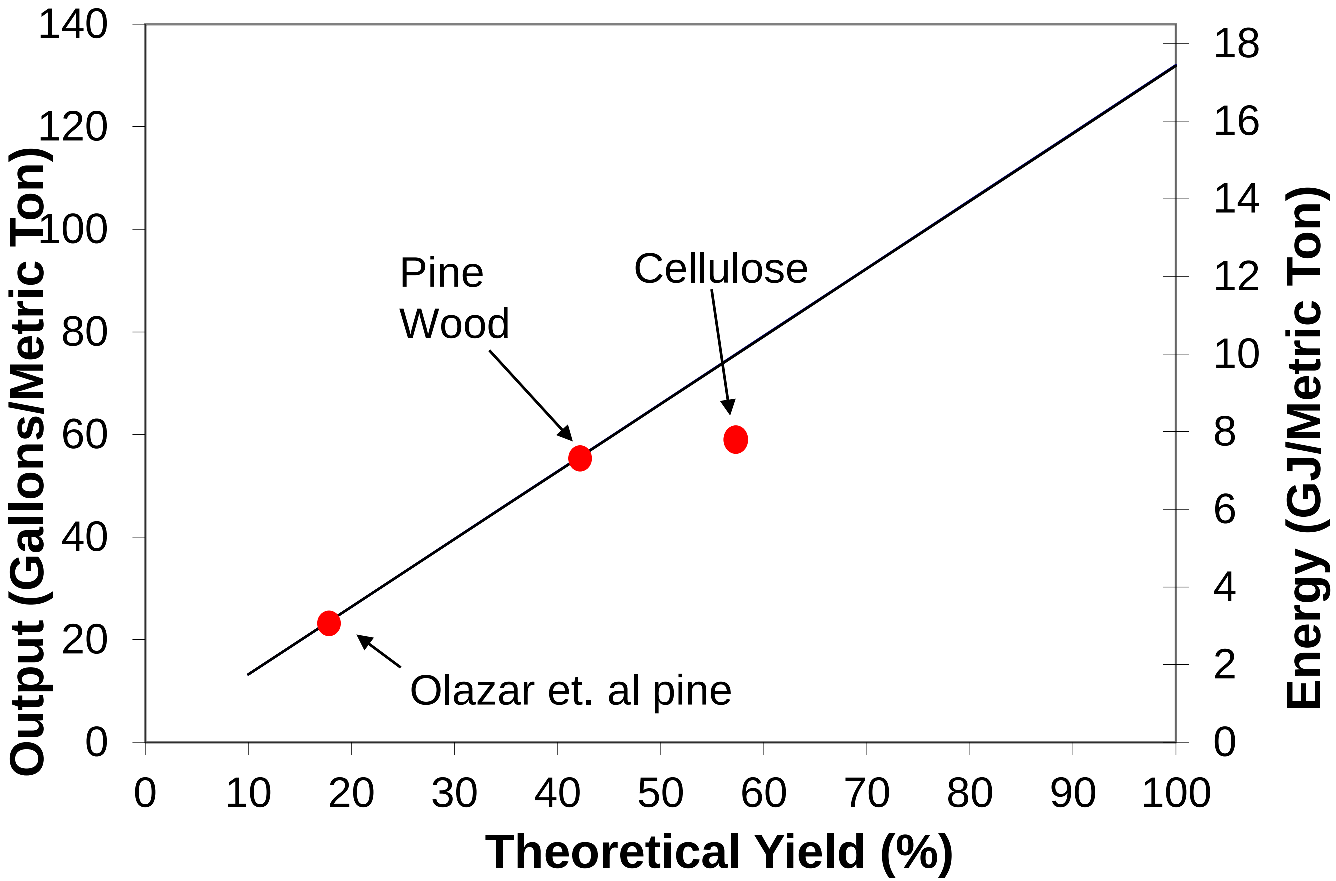


Current Yields: 17 wt% Aromatics

Tools: Optimization of Pyrolysis Technologies



Yields from Catalytic Fast Pyrolysis



Maximum Yields:

10 $C_{42}O_{26}H_{60}$ (wood)$\rightarrow$ 46 C_7H_8 (77% carbon yield) + 48 CO + 48 CO_2 + 115 H_2O

M. Olazar, R. Aguado, J. Bilbao, A. Barona, AIChE Journal 46 (2000) 1025.

Conclusions

- All products made from petroleum today can be made from biomass
- Clear need to develop new processes for sustainable production of liquid fuels and chemicals
- Catalytic fast pyrolysis allows the direct production of aromatics and olefins from solid biomass in a single catalytic step
- High yields of petrochemicals are possible in a single catalytic reactor
- Adjust aromatic yields by tuning catalytic properties, adjusting the pyrolysis chemistry and reactor design
- Focusing on understanding the basic chemistry and catalysis can help us design improved processes for biomass conversion

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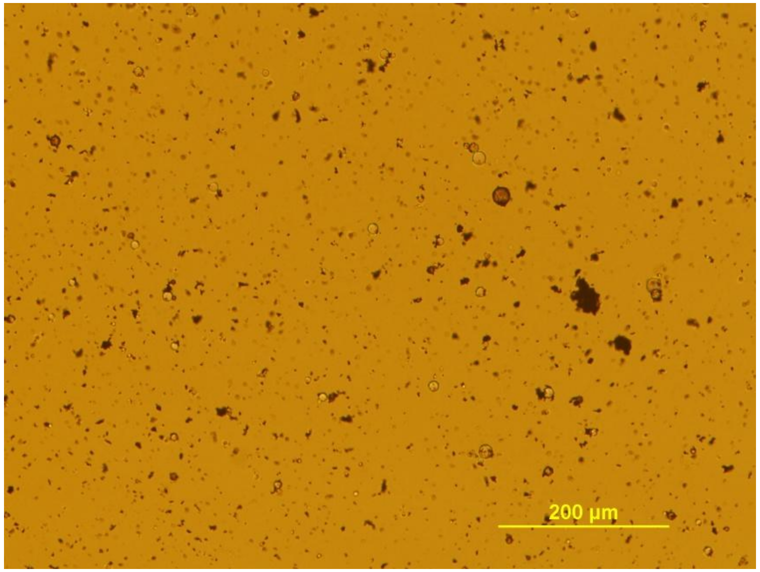
•**Collaborators:**
UMass: S. Auerbach (first principle modeling); S. de Bruyn Kops (CFD); Prof. W. Curt Conner (Catalyst); Prof. P. Dauenhauer (Pyrolysis); Prof. Wei Fan (Zeolite Synthesis); Prof. T. J. Mountzarias (Fluidization).

Anellotech: Dr. Anne Gaffney, Dr. Cawas Cooper; Jeff Whiting; Dr. Fred Pesa

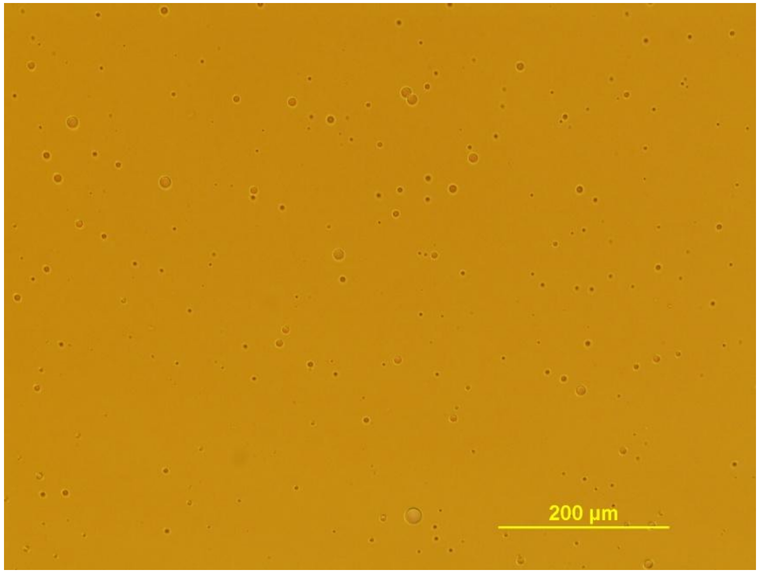
Disclosure: I have financial interest in Anellotech (www.anellotech.com).

Huber Team:
Former CFP Team: Dr. Y. Lin; **Dr. T. Carlson**; **Dr. K. Routray ; H. Zhang**
Staff: **Dr. G. Tompsett**; **J. Polin.**
Post-doc: Dr. J. Cho; Dr. W. Shen; Dr. R. Xing.
Graduate Students: H. Olcay; **T. Vispute; V. Agarwal;** R. Weingarten; **J. Jae; Y. Cheng; R. Coolman**; S. Green; A. Upadhye; **J. Shi;** C. Gilbert; A. Nikolopoulou.

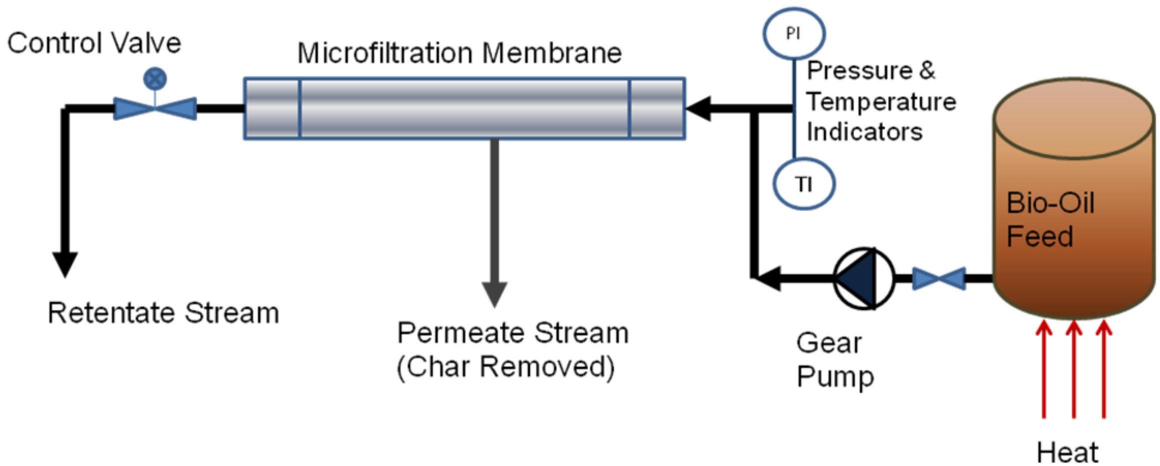
Bio-oil is an emulsion



Bio-oil before filtration

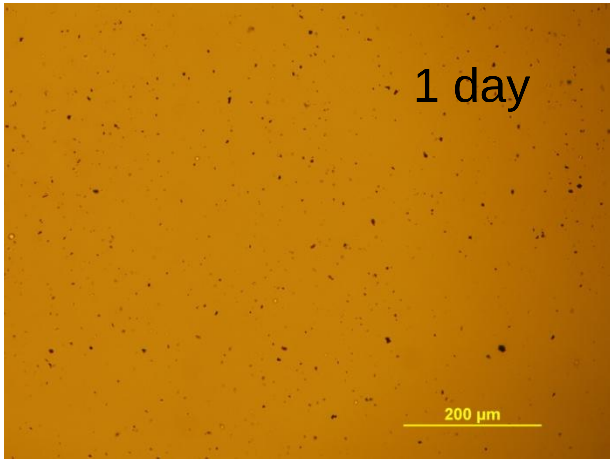


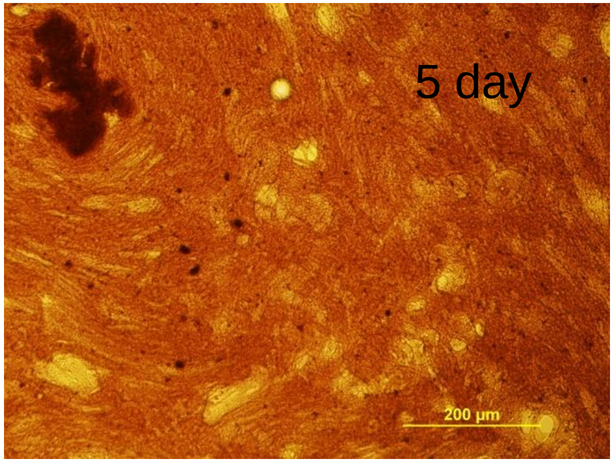
Bio-oil after microfiltration

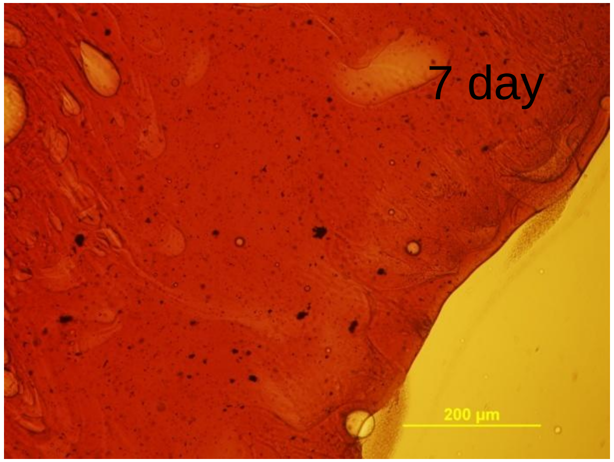


A. Javaid, T. Ryan, G. Berg, X. Pan, T. Vispute, S. Bhatia, G. W. Huber, and D. M. Ford; Removal of Char Particles from Bio-oils by Microfiltration, Journal of Membrane Science (2010), 363(1-2), 120-127.

Bio-oil undergoes phase separation when heated







- Bio-oil phase separates on accelerated aging (heated to 90^{o}C)
- A thick tarry phase is formed at the bottom and a less viscous top phase

Pyrolysis Conclusions

- Pyrolysis oil is cheapest liquid fuel made from biomass
- Pyrolysis oils is a mixture of products including: water, organic acids, hydroxyacetone, carbohydrates, and pyrolytic lignin
- Bio-oil phase separates with time
- Needs to be upgraded which requires large amounts of hydrogen (expensive)