Catalyst Design and Reaction Strategies for the Optimization of Liquid Products from Biomass Pyrolysis

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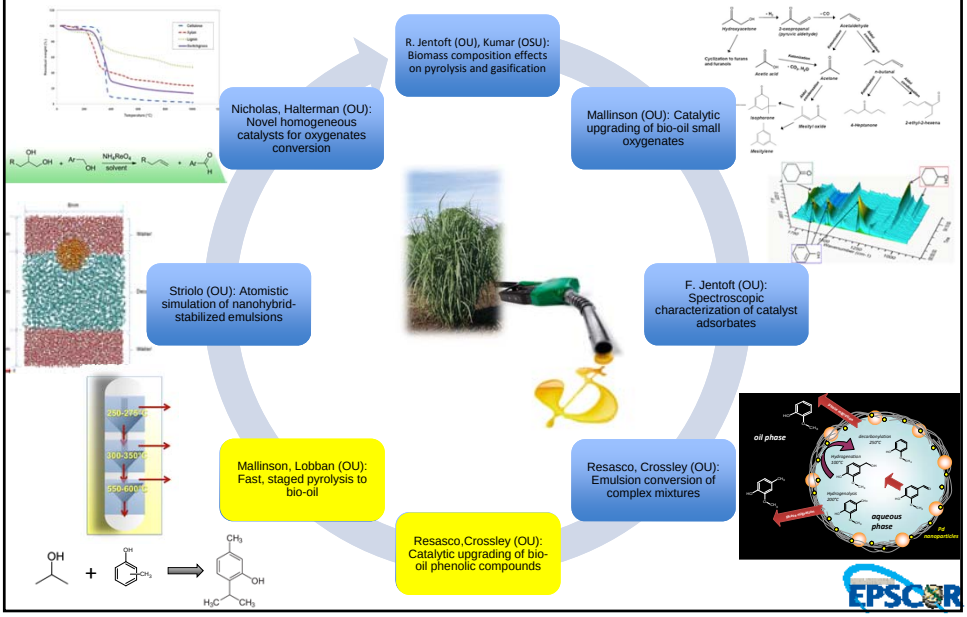
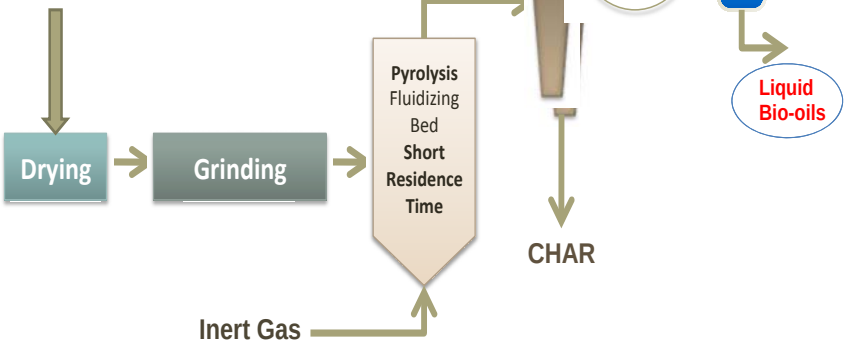
OK EPSCoR RESEARCH: OBJECTIVE 3

CATALYTIC/THERMOCHEMICAL CONVERSION PROCESSES

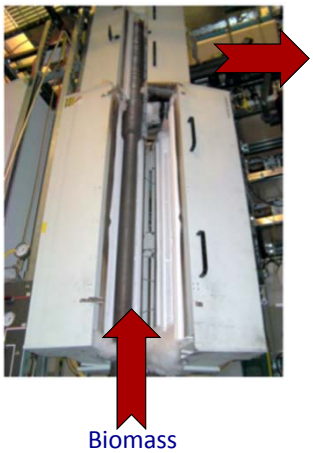


Ex-Situ Catalytic Fast Pyrolysis

BIOMASS
Switch grass
Sawdust, Pine
Torrefied-biomass

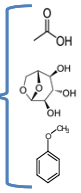


What should we ask from the catalysts ?



Biomass

- Cellulose
- Hemicellulose
- Lignin

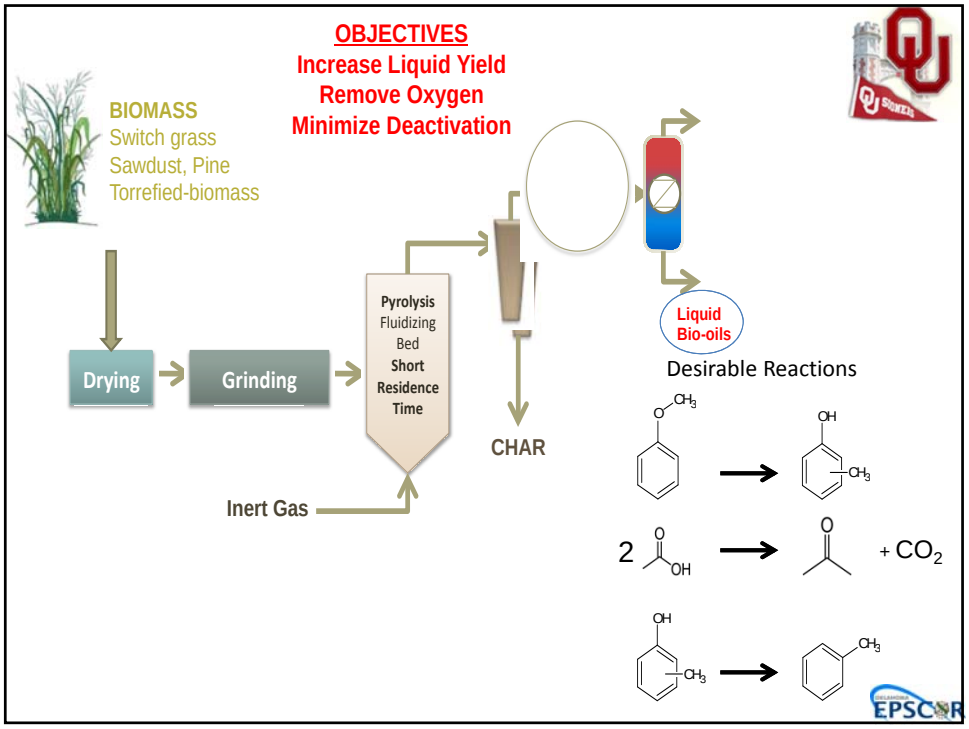


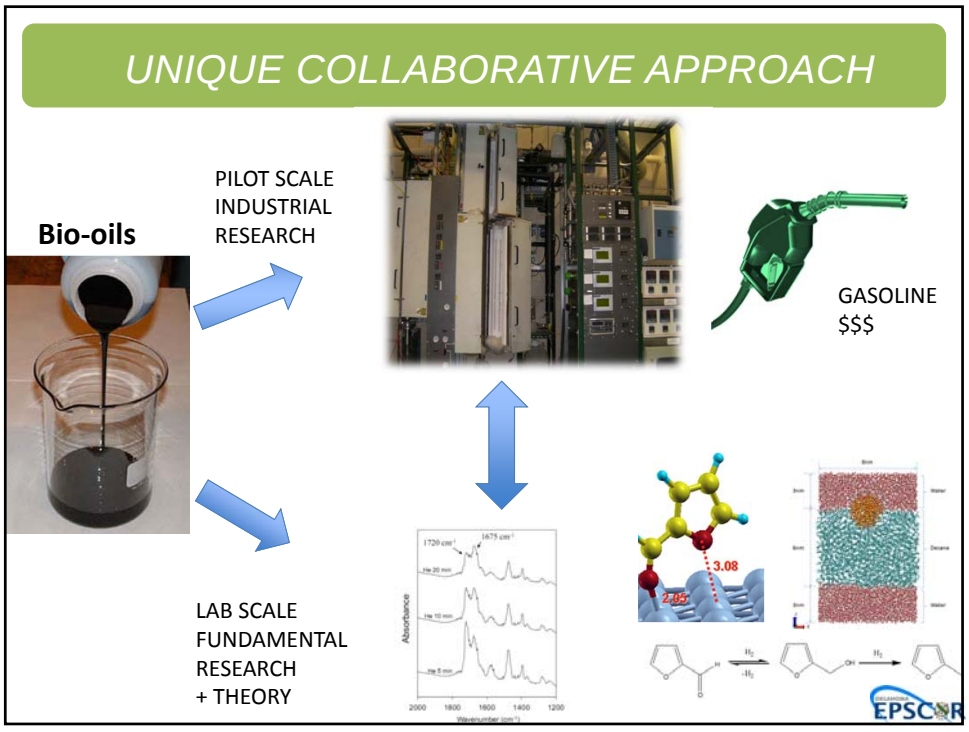
- **Small oxygenates**
  (aldehydes, alcohols, ketones, acids)
- **Sugar-derived compounds**
  (levoglucosan, furfurals)
- **Lignin-derived phenolics**
  (guaiacol, vanillin, anisole, etc.)

Challenges to catalysts:

- Remove O
- Maximize C capture
- Minimize H_2 consumption
- Minimize catalyst deactivation
- Tolerate hot liquid water

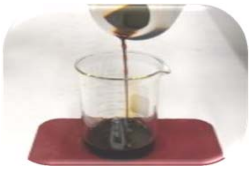
Resasco, **Journal of Physical chemistry Letters**, 2, 2294-2295, **2011**


OBJECTIVES
Increase Liquid Yield
Remove Oxygen
Minimize Deactivation
BIOMASS
Switch grass
Sawdust, Pine
Torrefied-biomass
Drying
Grinding
Pyrolysis
Fluidizing
Bed
Short
Residence
Time
Inert Gas
CHAR
Liquid
Bio-oils
Desirable Reactions
+ CO2
EPSCoR

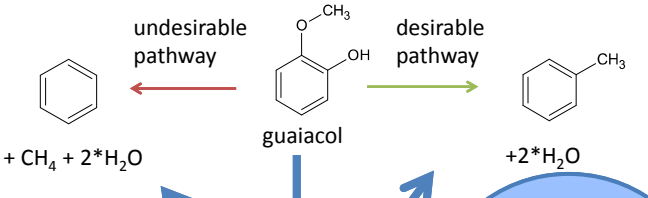

UNIQUE COLLABORATIVE APPROACH
Bio-oils
PILOT SCALE
INDUSTRIAL
RESEARCH
GASOLINE
$$$
LAB SCALE
FUNDAMENTAL
RESEARCH
+ THEORY
3.08
2.05
EPSCoR

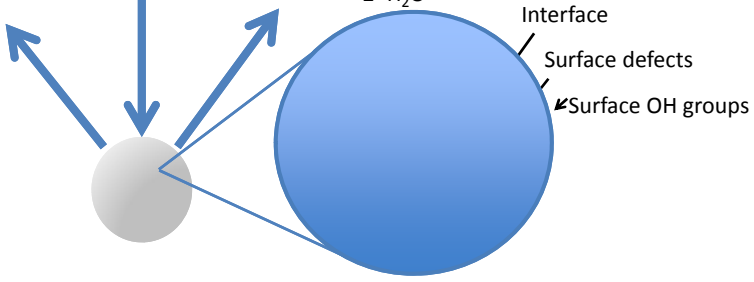
Approach

- Vapor phase
- Condensed phase
- Model compounds
- *Real bio-oil*



Model Compound Studies
lignin-derived phenolics

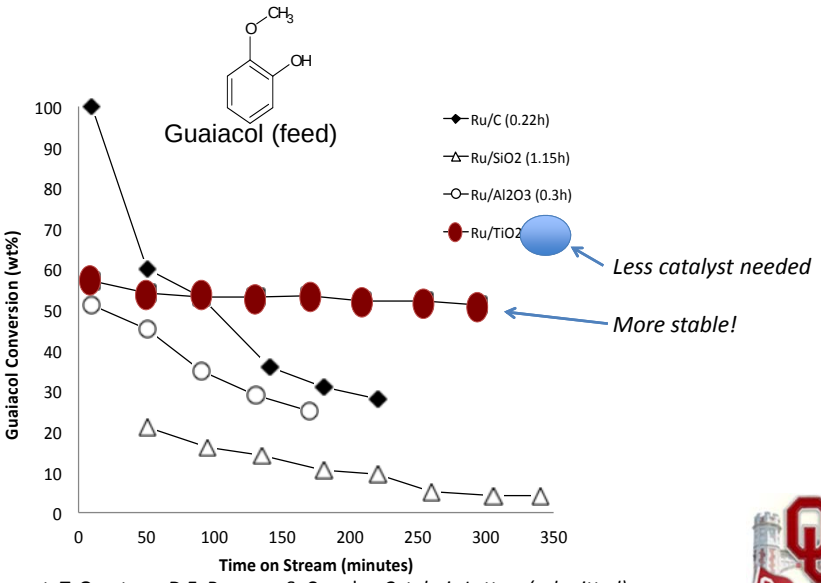




Vapor phase
T=400°C
P=1atm
H_2/Guaiacol molar ratio=60

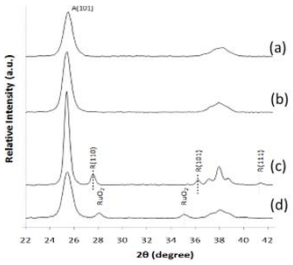
S. Boonyasuwat, T. Omotoso, D.E. Resasco, S. Crossley *Catalysis Letters (submitted)*

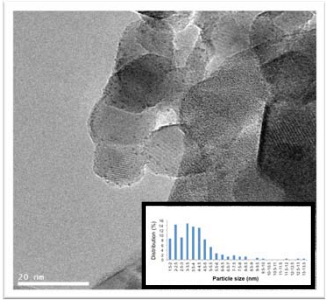
Influence of support on catalyst stability



S. Boonyasuwat, T. Omotoso, D.E. Resasco, S. Crossley *Catalysis Letters (submitted)*

Metal Particle Size

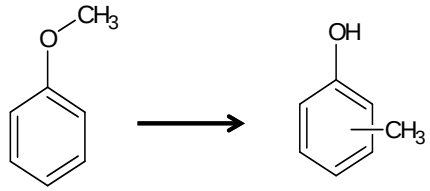


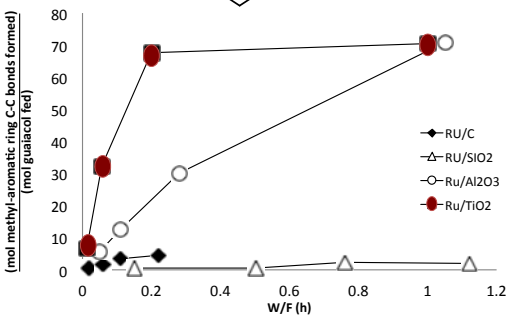


Metal particle diameter (nm)		
Catalyst	**d_{XRD}**	**d_{TEM}**
Ru/C	-	1.7
Ru/Al_2O_3	11.8	4.1
Ru/SiO_2	5.7	2.5
Ru/TiO_2	5.5	3.3

Metal particle size does not explain increase in activity and stability

Methyl Retention





70% of methyl groups conserved on ring

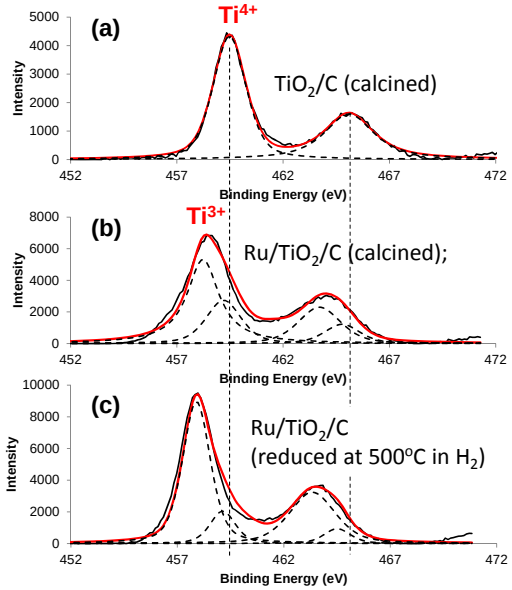
	W/F (h)	Conversion (mol %)
5 wt% Ru/Al_2O_3	0.29	45
Al_2O_3	0.29	18
5 wt% Ru/TiO_2*	0.33	100
TiO_2	0.33	7

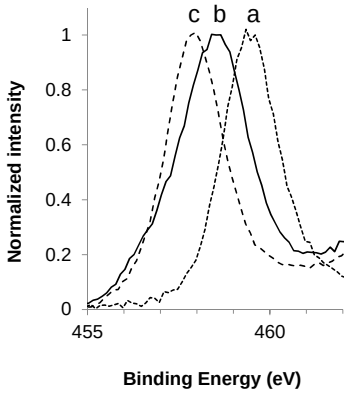
*note: 100% conversion was achieved at W/F of 0.2h

Strong synergy between reducible oxide and metal

S. Boonyasuwat, T. Omotoso, D.E. Resasco, S. Crossley *Catalysis Letters (submitted)*

Ru / TiO_2 / Carbon Catalyst - XPS

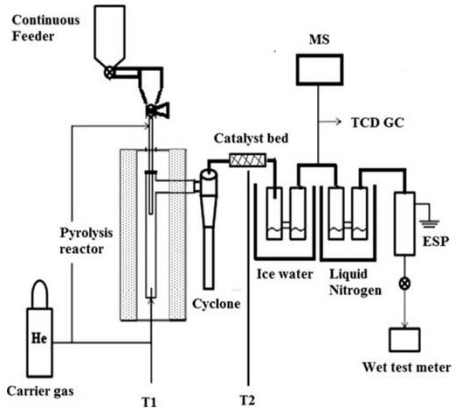




Resasco et al. (2012) Journal of Catalysis

Ru/TiO_2 interaction promotes the formation of oxygen vacancies
New active sites?

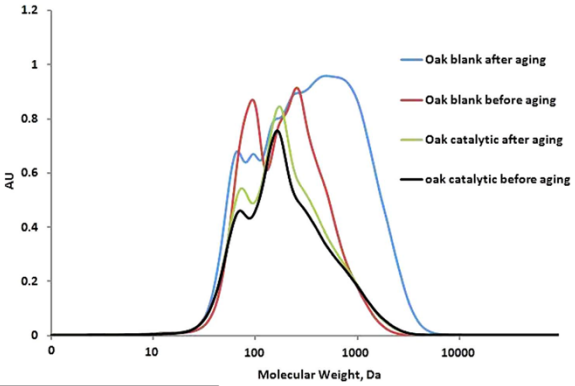
Ru/TiO_2 conversion of real bio oil vapors



Shaolong Wan, Trung Pham, Sarah Zhang, Lance Lobban, Daniel Resasco, and Richard Mallinson *AIChE Journal* (*in press*).

Real pyrolysis oil vapors

- 4g Ru/TiO_2
  - 400°C
  - 1Atm H2
- 30g oak/batch

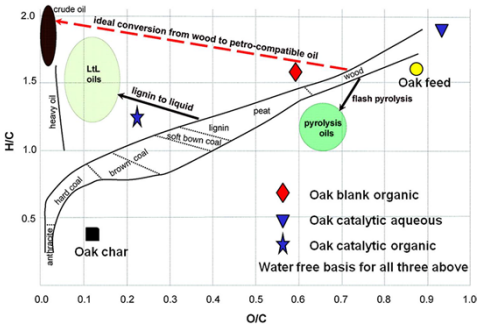


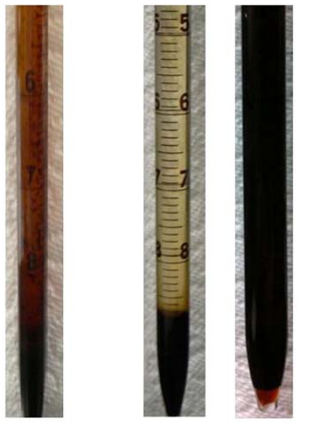
	Oak Blank	Ru-TiO_2 1st	Ru-TiO_2 3rd
Acetone	0.32 (0.09)*	1.62 (0.17)	0.74 (0.15)
Butanone		0.82 (0.12)	0.57 (0.10)
Acetic acid	6.26 (0.67)	0.84 (0.11)	2.42 (0.31)
Acetol	2.42 (0.29)		0.64 (0.14)
2-cyclopenten-1-one		1.51 (0.16)	1.44 (0.14)
Phenol	0.81 (0.15)	1.58 (0.17)	1.27 (0.16)
Levoglucosan	1.75 (0.19)	0.12 (0.04)	1.46 (0.21)

Less change in MW upon aging after Ru/TiO_2 treatment

Shaolong Wan, Trung Pham, Sarah Zhang, Lance Lobban, Daniel Resasco, and Richard Mallinson *AIChE Journal* (*in press*).

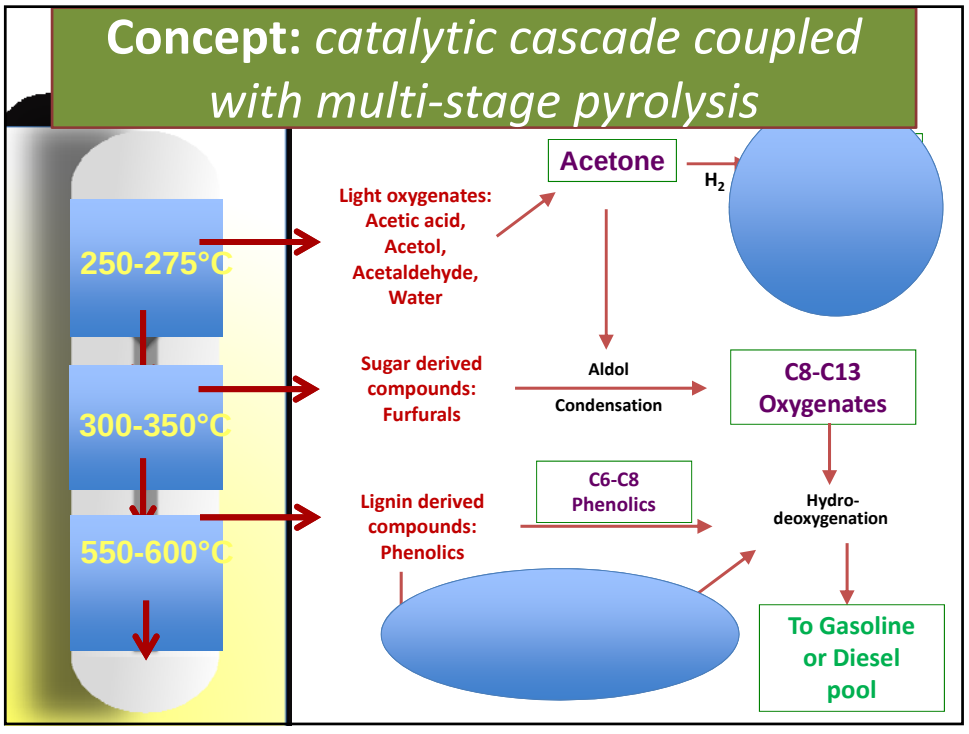
Real pyrolysis oil vapors



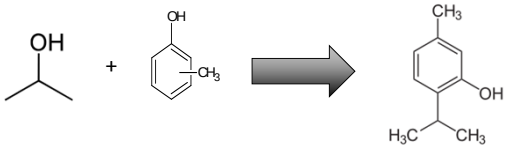


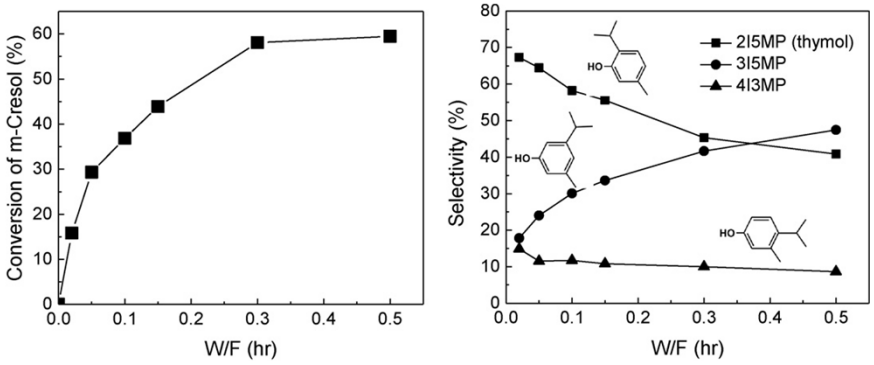
Ru/TiO_2 catalytic upgrading produces a stable intermediate product that has a high solubility in oil.

Shaolong Wan, Trung Pham, Sarah Zhang, Lance Lobban, Daniel Resasco, and Richard Mallinson *AIChE Journal* (*in press*).



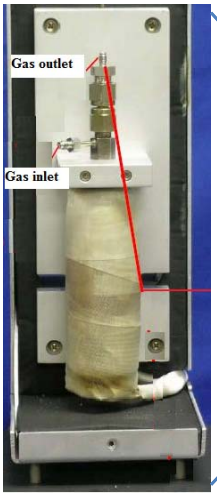
Alkylation of phenolics with light alcohols

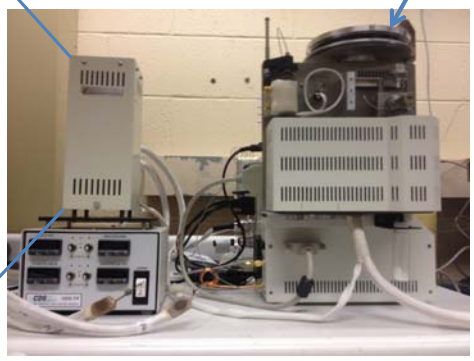




L. Nei, D. Resasco, Applied Catalysis A: General 447– 448 (2012) 14– 21

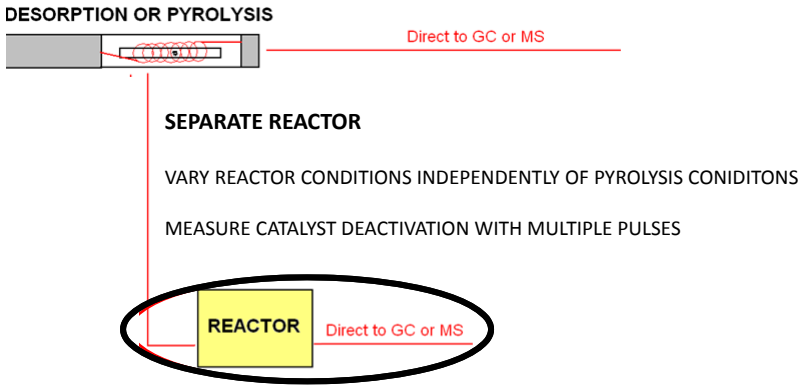
Pyroprobe for rapid catalyst evaluation



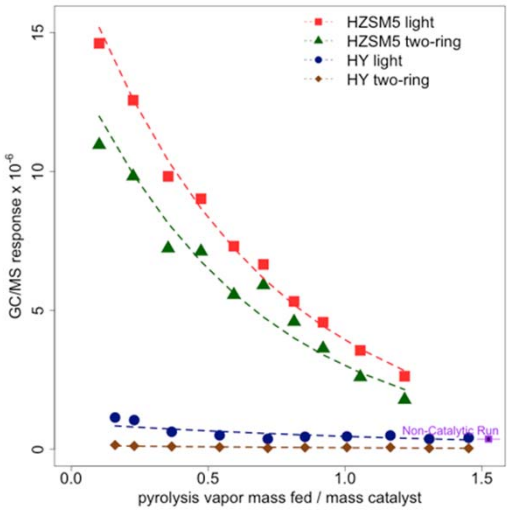


SEPARATE CATALYTIC REACTOR

Pyroprobe 5250



Results: HZSM-5 vs. HY Aromatics



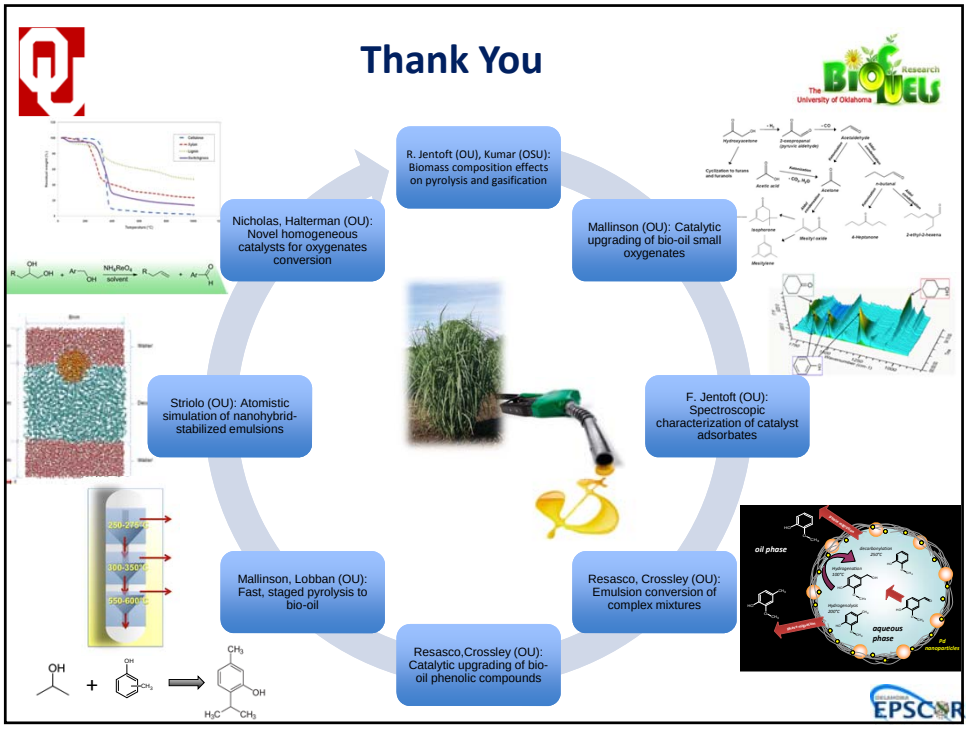
Conditions

Catalyst Bed Temperature:
- 400°C

Pyrolysis Temperature:
- 500°C

Weight of Catalyst:
- HY→5mg
- HZSM-5→5mg

Si/Al:
- HY→40
- HZSM-5→45


Thank You
R. Jentoft (OU), Kumar (OSU): Biomass composition effects on pyrolysis and gasification
Mallinson (OU): Catalytic upgrading of bio-oil small oxygenates
F. Jentoft (OU): Spectroscopic characterization of catalyst adsorbates
Resasco, Crossley (OU): Emulsion conversion of complex mixtures
Resasco,Crossley (OU): Catalytic upgrading of bio-oil phenolic compounds
Mallinson, Lobban (OU): Fast, staged pyrolysis to bio-oil
Striolo (OU): Atomistic simulation of nanohybrid-stabilized emulsions
Nicholas, Halterman (OU): Novel homogeneous catalysts for oxygenates conversion
oil phase
aqueous phase
250-275°C
300-350°C
550-600°C