



**Project:**  
**Fractionation and Catalytic Upgrading of Bio-Oil**

**Program:**  
“Carbon, Hydrogen, and Separation Efficiencies in Bio-Oil  
Conversion Pathways (CHASE Bio-Oil Pathways)”

*U.S. Department of Energy  
Energy Efficiency and Renewable Energy*

**Speakers:**  
**D. E. Resasco, Steven P. Crossley, Vikas Khanna**  
*University of Oklahoma and University of Pittsburgh*

# Introduction



## Participating Institutions

- University of Oklahoma
- University of Wisconsin
- University of Pittsburgh
- Idaho National Laboratory

## Key personnel:



Daniel E. Resasco



Steven P. Crossley



Richard G. Mallinson



Lance L. Lobban



Christos T. Maravelias



Vikas Khanna

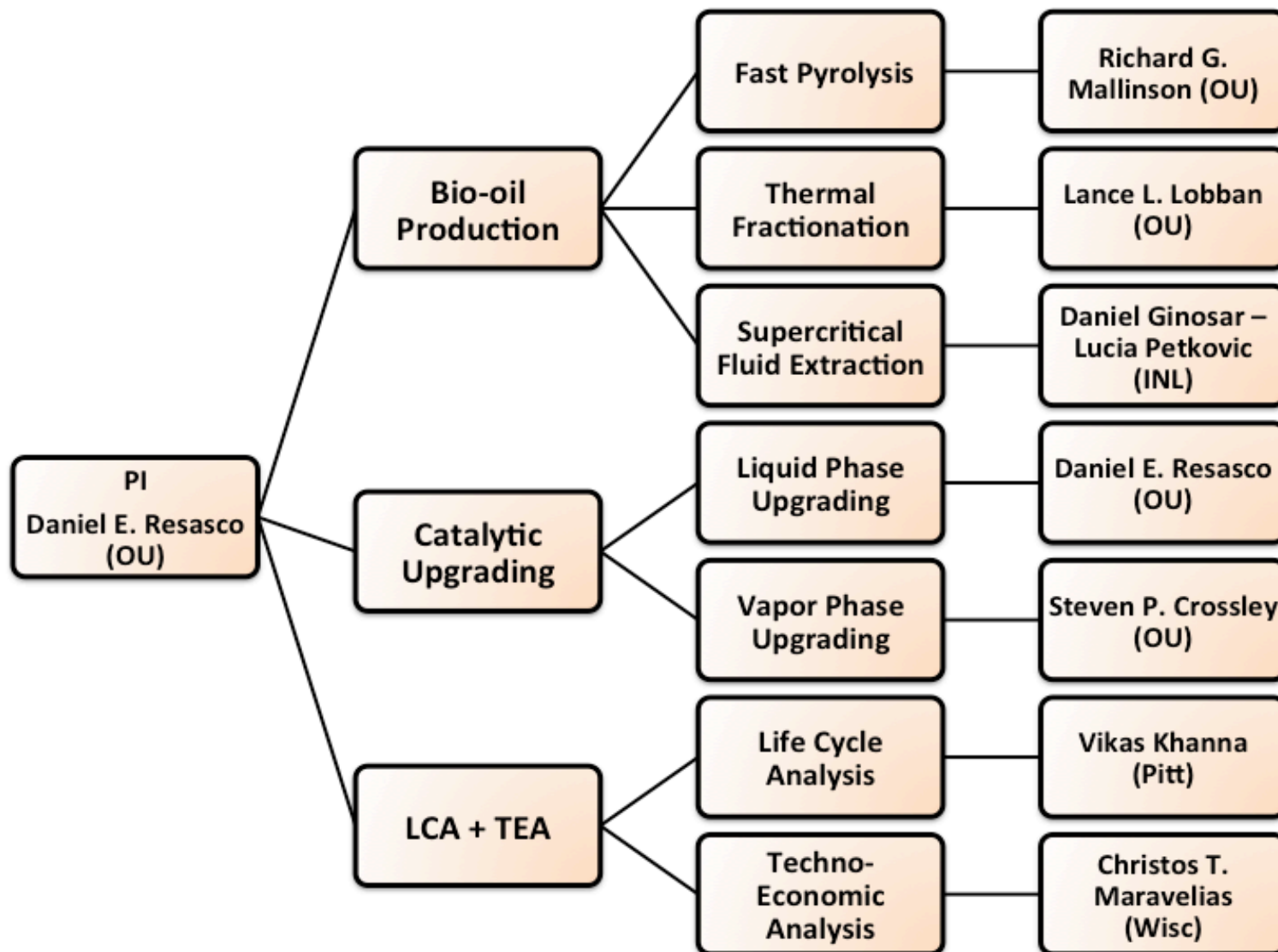


Dan Ginosar



Lucia Petkovic

# Introduction



Steven P. Crossley

Challenges and combined CHASE approach

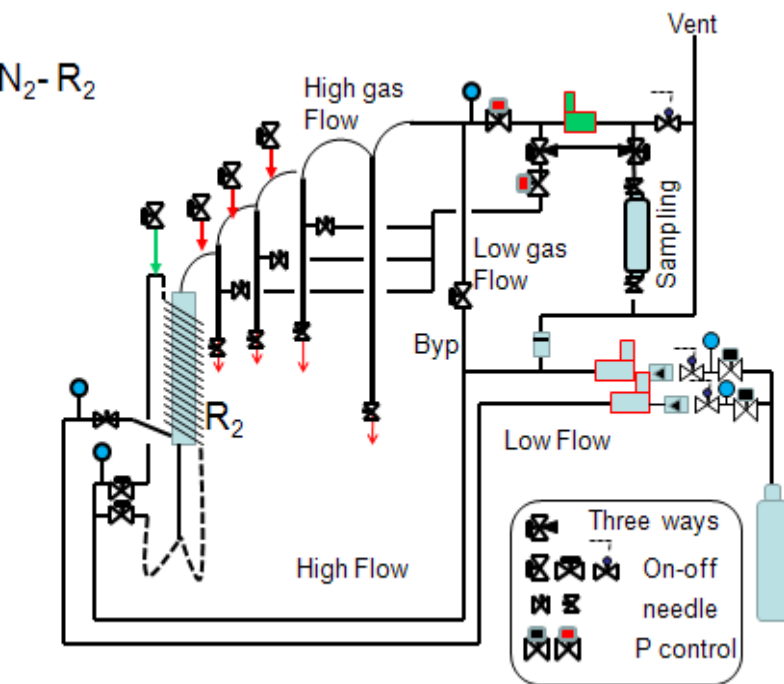
Daniel E. Resasco

Technical background, preliminary results, and Gantt chart for planned studies

Vikas Khanna

Life cycle analysis (VK)

# OU Pyrolysis Pilot Unit ( Kg-scale )



## Reactor operating conditions

biomass type: switchgrass  
 bed particle size: 425 -710  $\mu\text{m}$   
 Gas flow rate: 3.46 kg/hr  
 = 30L/min, 25 °C

Fluidized bed material  
 Fluidizing gas  
 Reactor temperature  
 Biomass feed rate

ground glass  
 N<sub>2</sub>  
 500 °C  
 0.5 kg/hr



# Fast Pyrolysis Products

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**Biomass**

Switchgrass

Gases: CO<sub>2</sub>,  
CO, lights and  
water vapor

**10-15 %**



**Char  
+ Ash**

**15-20 %**



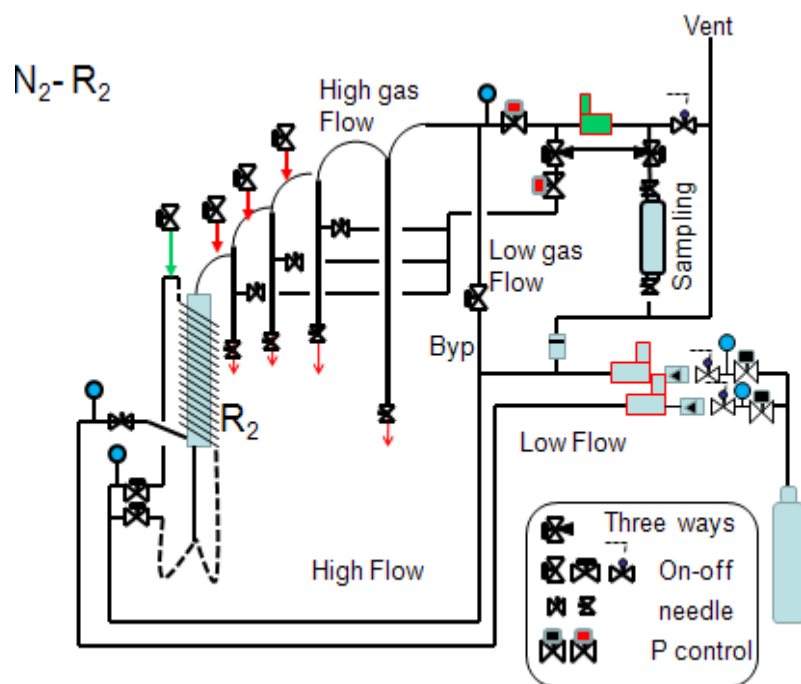
**Liquid**

**50-70 %**

**A challenge ...**

# The Challenge

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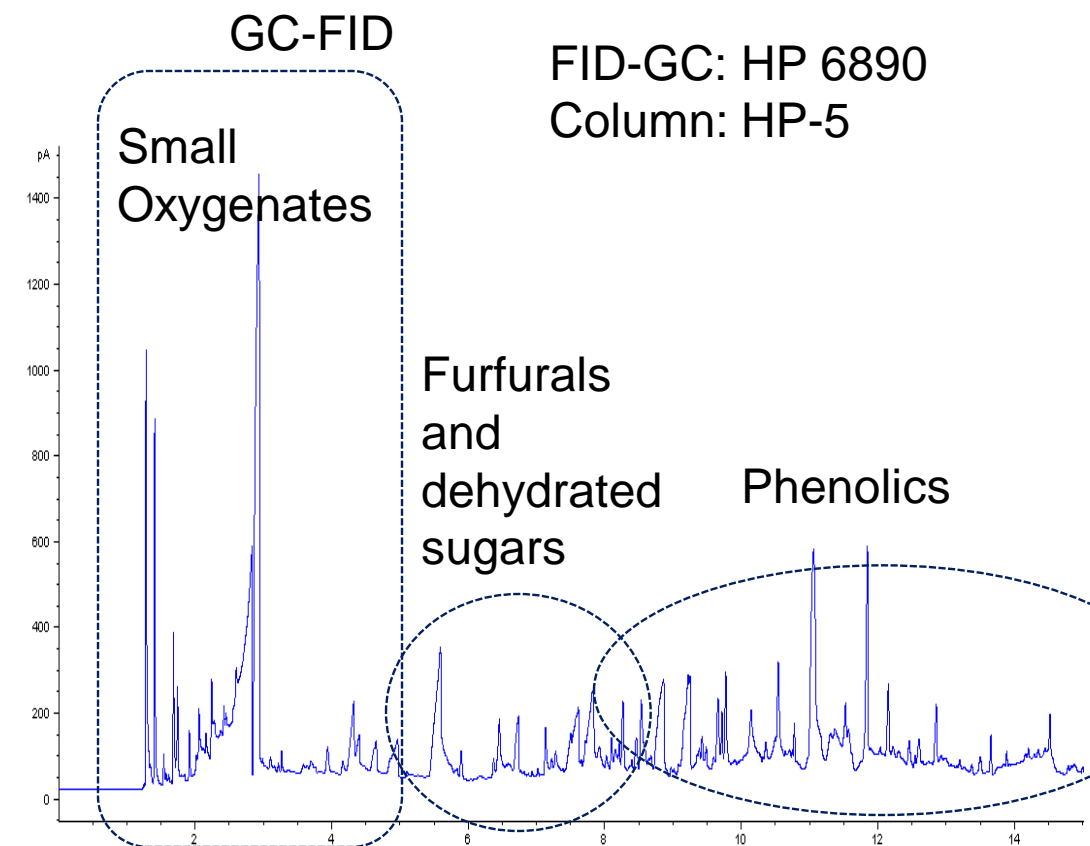


## Reactor operating conditions

biomass type: switchgrass / oak  
 bed particle size: 425 -710  $\mu\text{m}$   
 Gas flow rate: 3.46 kg/hr  
 = 30L/min, 25 °C

Fluidized bed material  
 Fluidizing gas  
 Reactor temperature  
 Biomass feed rate

ground glass  
 N<sub>2</sub>  
 500 °C  
 0.5 kg hr

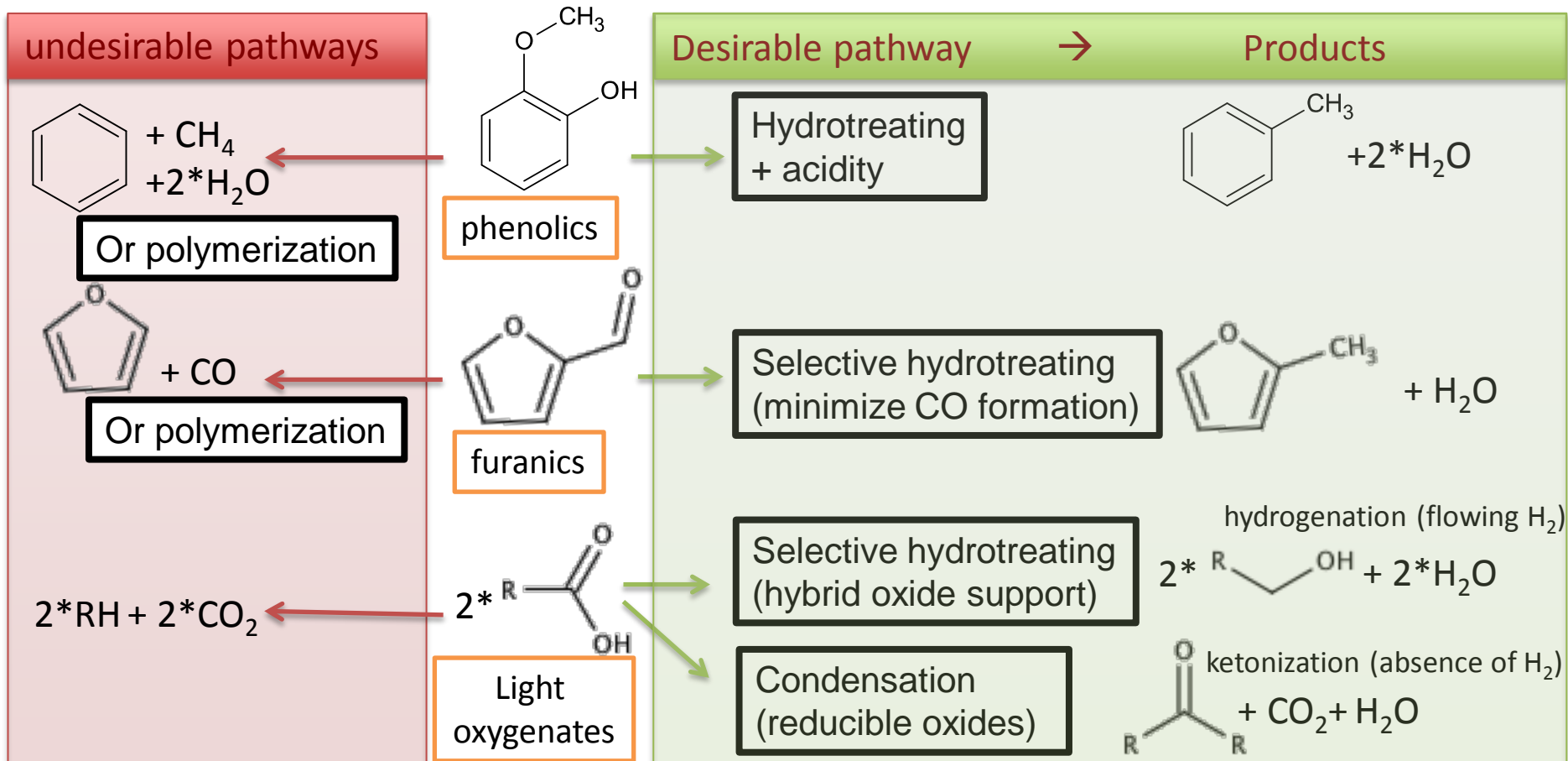


# The Challenge

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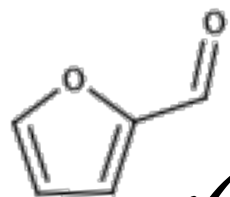
***Desirable outcome different for each family!***

*Any single upgrading step leads to significant waste*

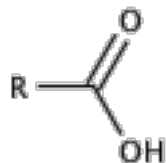




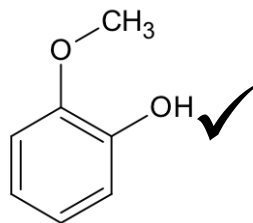
# The Challenge



✓ Furanics polymerize



✓ Acids catalyze polymerization



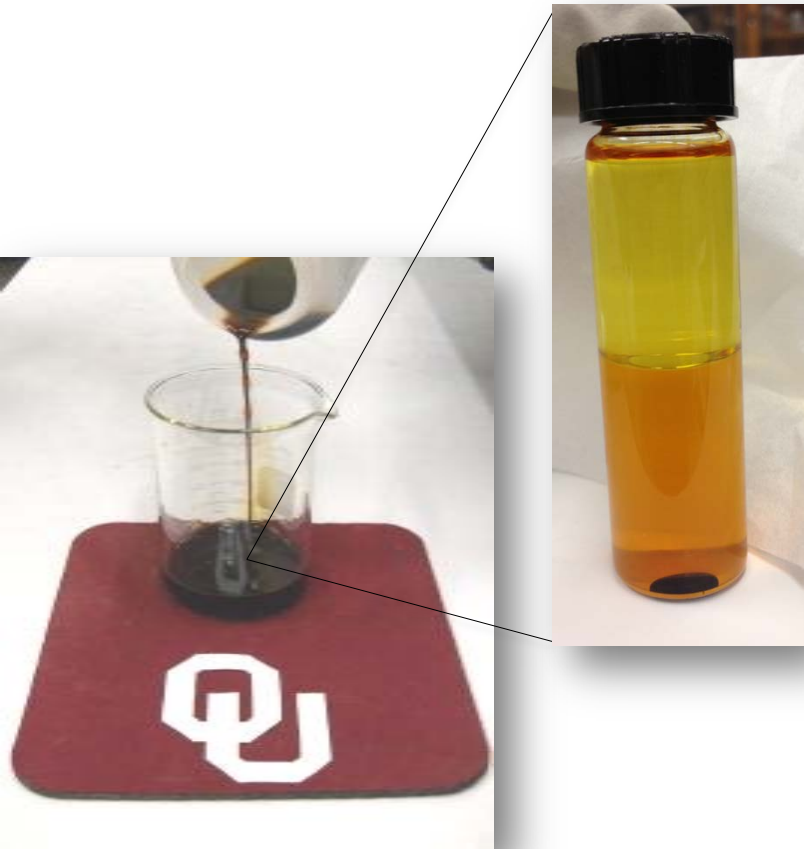
✓ Phenolics consume excess hydrogen

# Mix of aqueous, organic, and heavy tar all in one liquid

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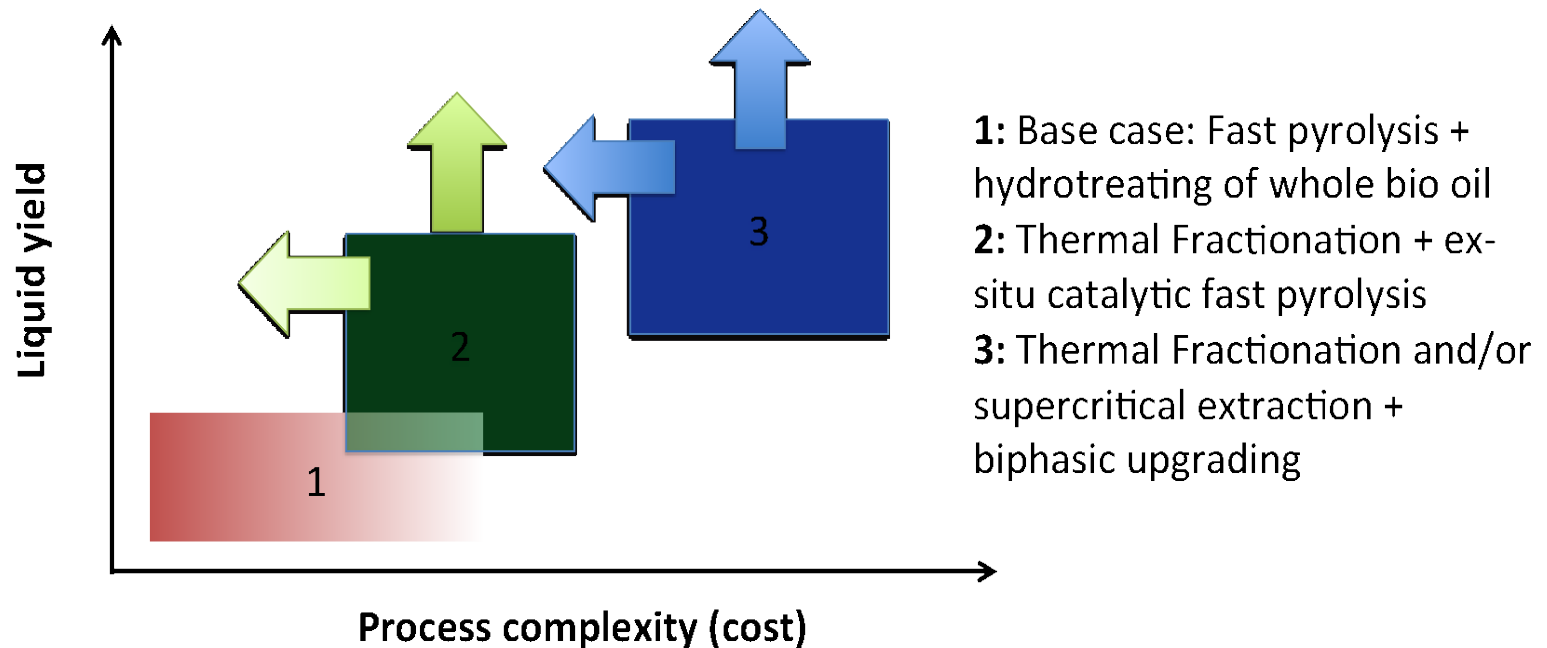
Separate into  
phases

heat all together → tar  
(distillation is not an option)



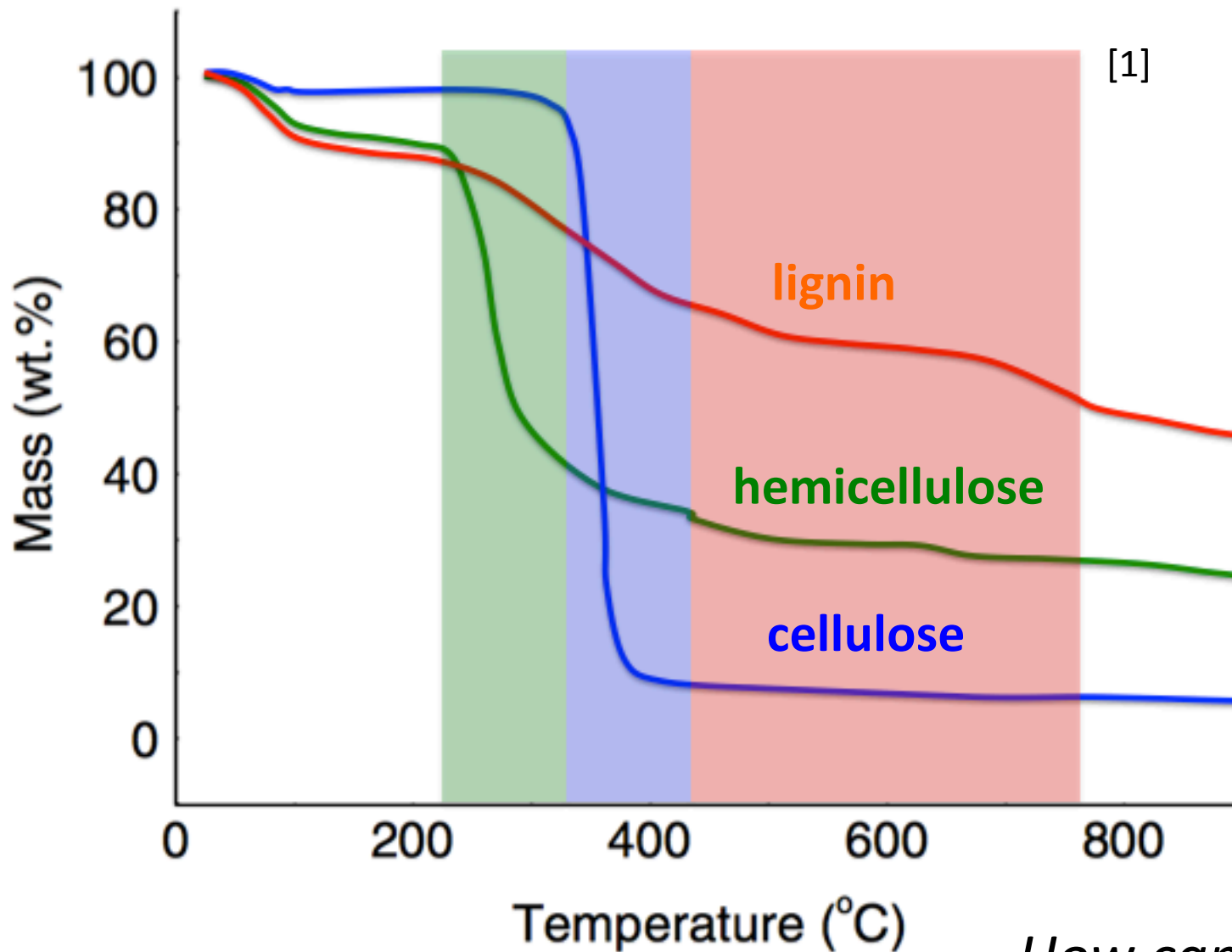
*What can we do to separate  
these incompatible compounds?*

## Include fractionation to increase total liquid



*How can we effectively achieve this separation?*

# Biomass components thermally convert at different Temps.



*How can we take advantage of this ?*

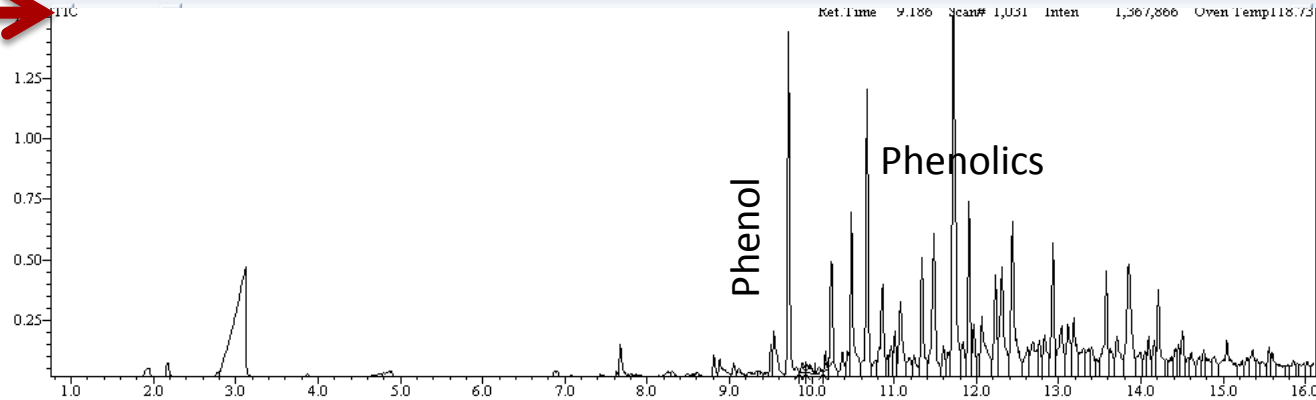
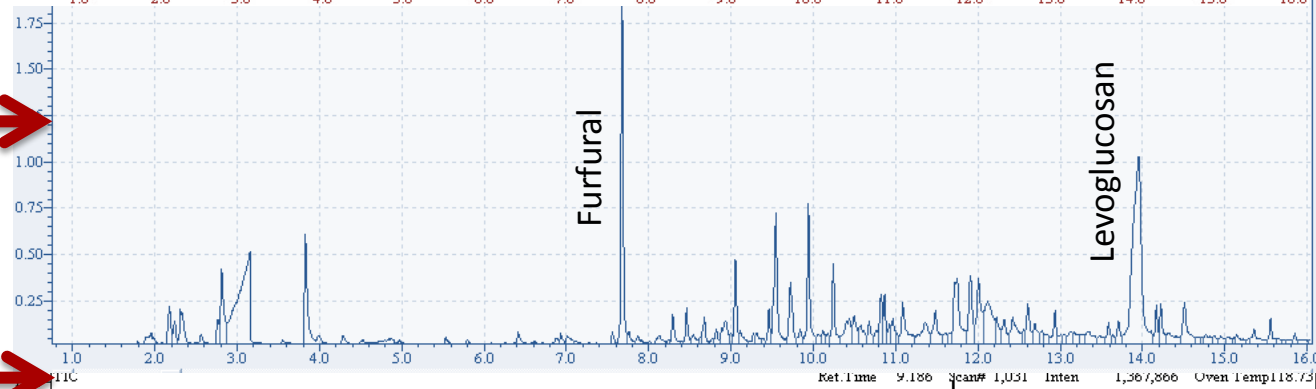
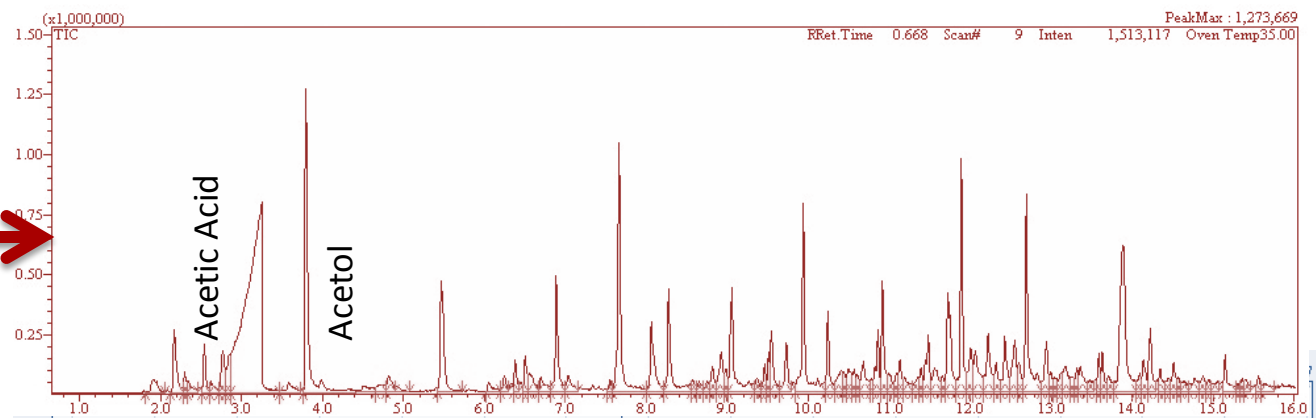
# Approach: Multi-stage pyrolysis → *separate families*

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250-275°C

300-350°C

550-600°C



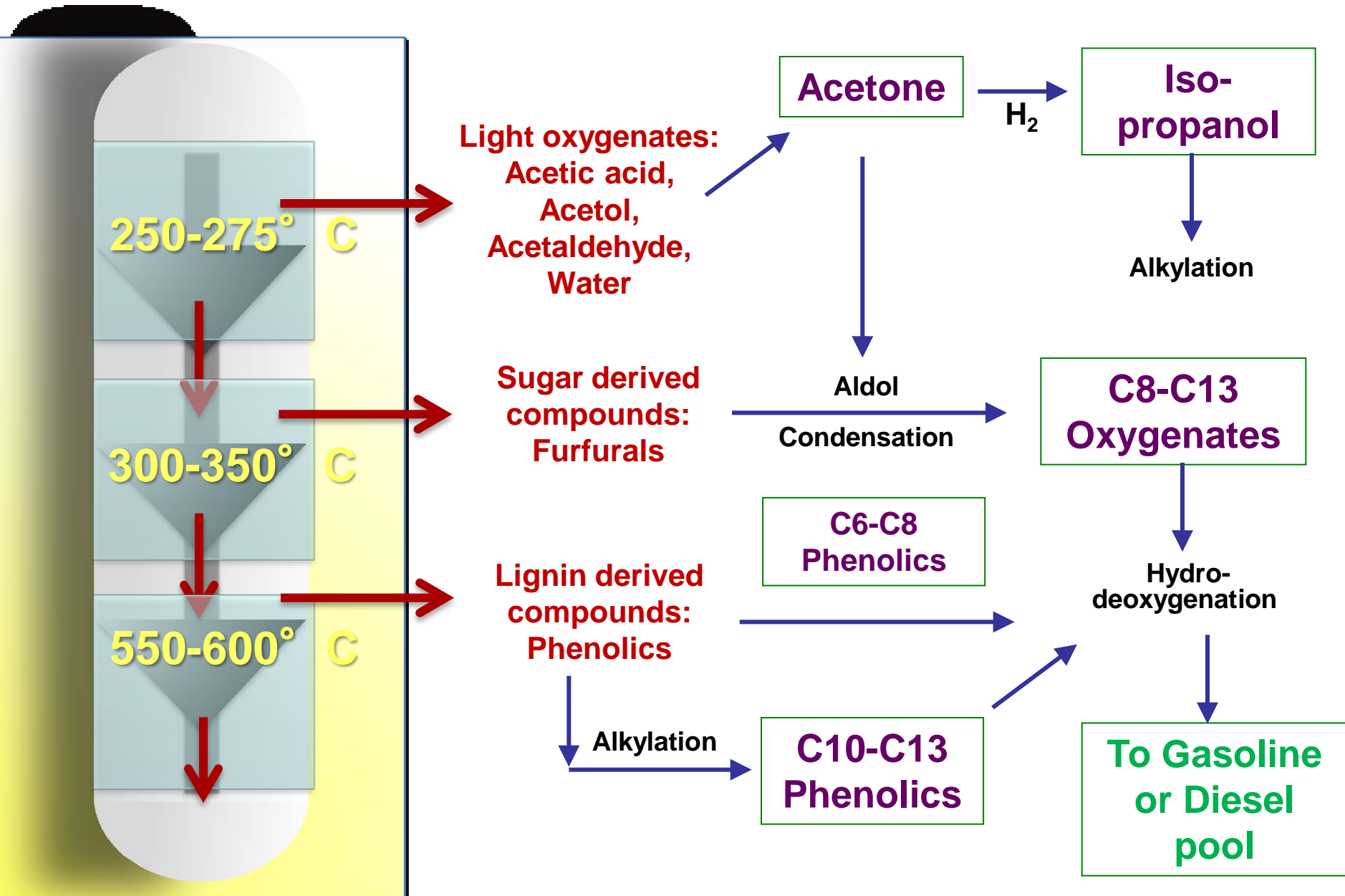
# Total yields from multi stage pyrolysis comparable to 1 step

<i>Temperature ( C)</i>	<b>240 °C</b>	<b>360 °C</b>	<b>500 °C</b>	<b>Cumulative yield / g of biomass</b>	<b>1-step full Pyrolysis</b>
<i>liquid yield (wt. %)</i>	9.4	41.3	18.0	50.0	51
<i>solid yield (wt. %)</i>	84.3	37.8	61.4	19.6	20
<i>gas yield (wt. %)</i>	6.1	9.6	7.9	17.2	18
<i>Total yield</i>				86.8	89

*Introducing more pyrolysis stages does not sacrifice yield*

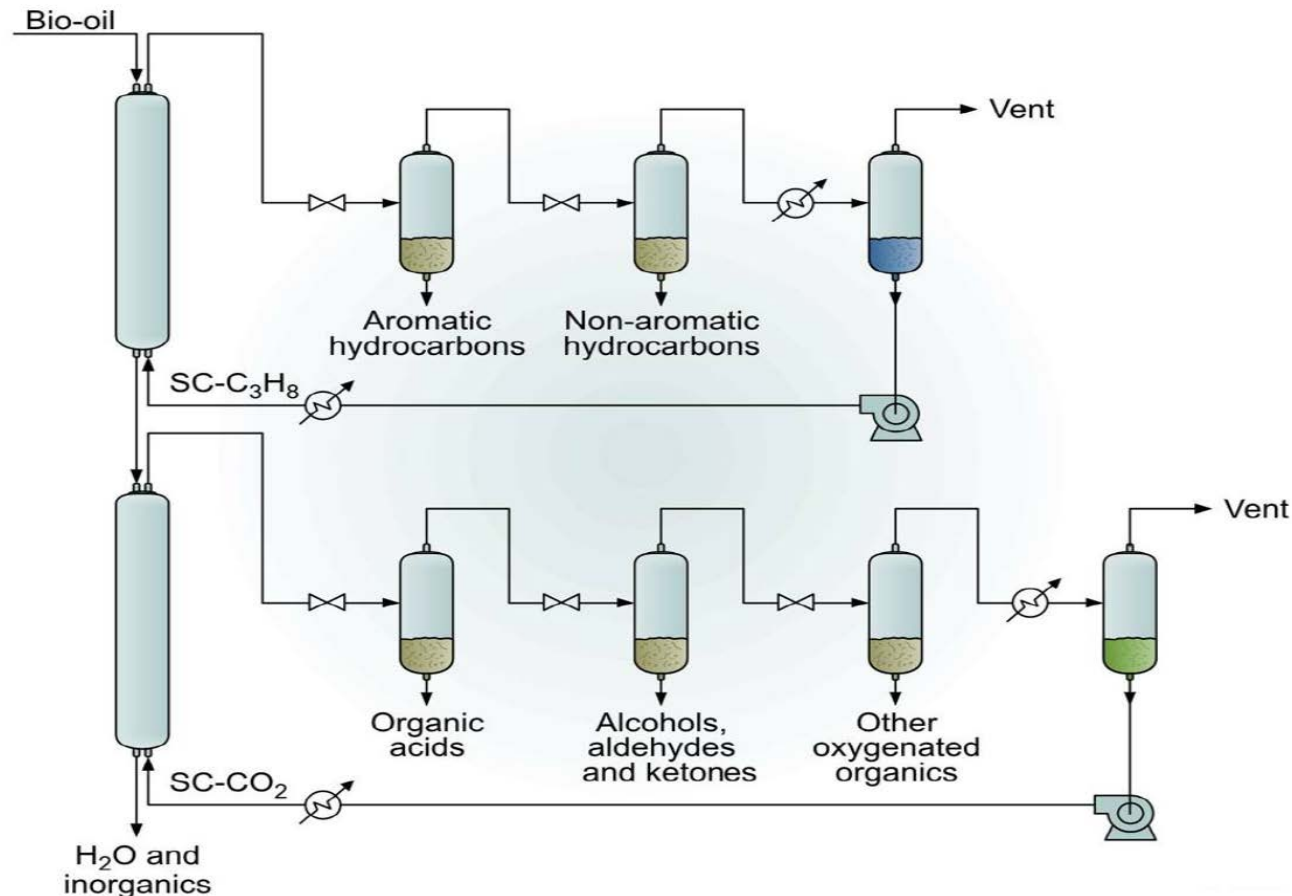


# multi-stage pyrolysis enables tailored upgrading



# Alternative strategy: supercritical separation

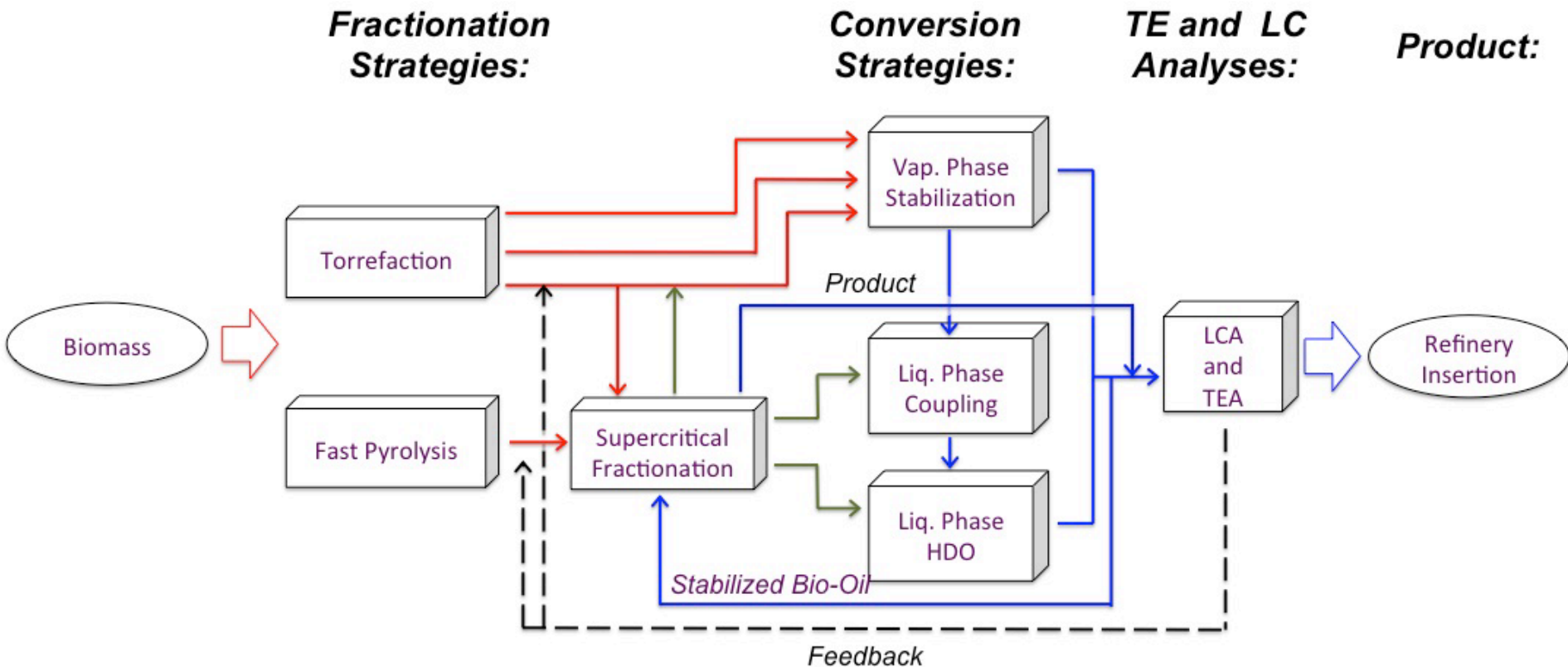
## *Separate oil into families*



***Purified streams enable improved upgrading strategies***

***How do we evaluate the effectiveness of our approach?***

# Approach: Feedback loop with TEA and LCA



*Enables constant evaluation and evolution of strategy*

# Differences with conventional oil refining

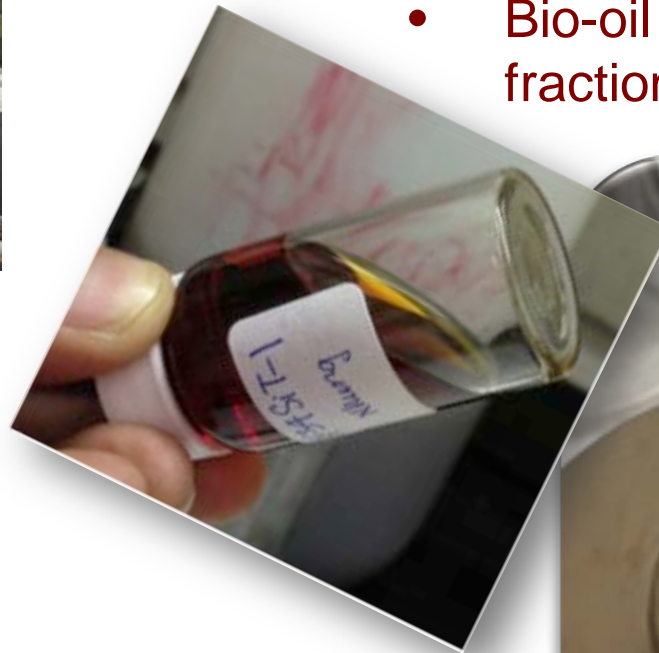


Crude oil distillation  
towers

- Conventional crude oil is thermally stable and can be easily fractionated by boiling point.
- Catalytic upgrading of different hydrocarbon cuts is possible ( cracking, HDS, reforming, etc.)

## BY CONTRAST ...

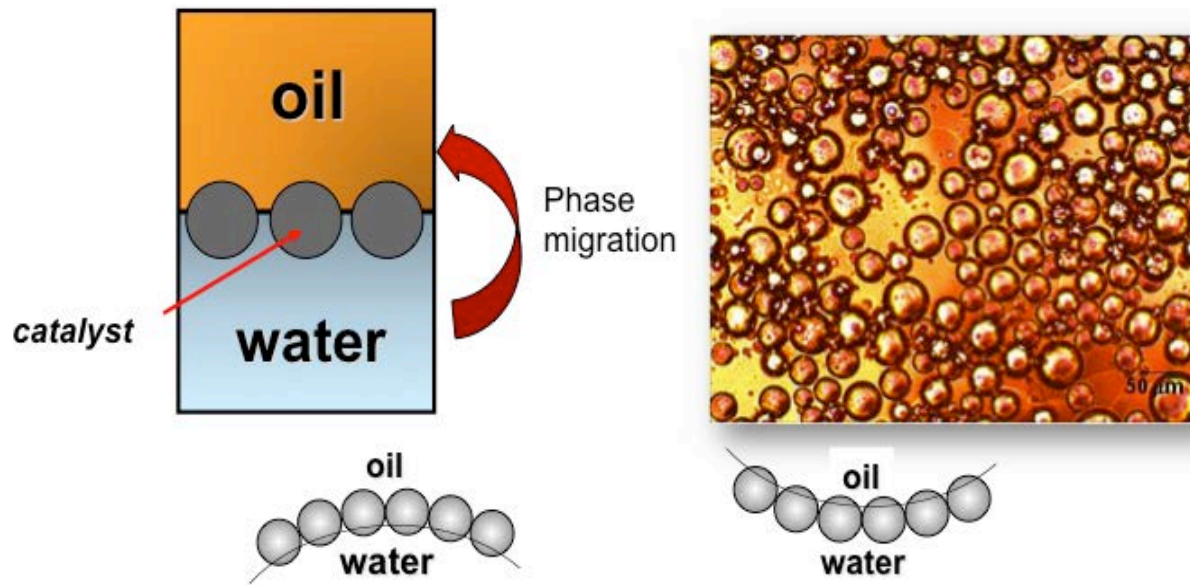
- Bio-oil cannot be thermally fractionated



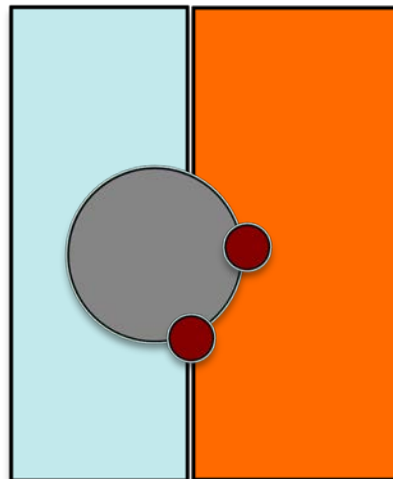
Highly diluted bio-oil;  
after heating at 200°C



# Emulsions with Nanohybrid Catalysts



- ❑ Hydrophobic / hydrophilic balance determines contact angle and type of emulsion.



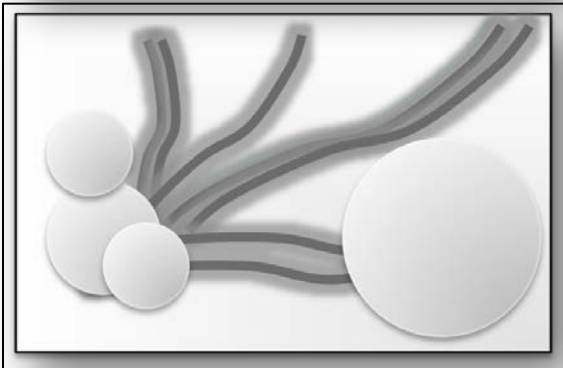
- ❑ By adding catalytic function one can impart the appropriate activity

Crossley S, Faria J, Shen M, Resasco DE, *Science*, **327**, 68-72 (2010).



# Pickering emulsions with Amphiphilic Nanohybrids

Single-Wall  
Carbon  
Nanotubes +  
Hydrophylic  
Silica  
Nanoparticles



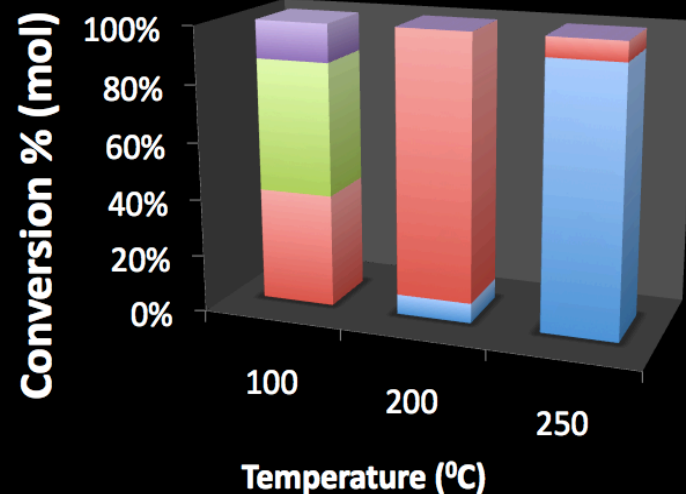
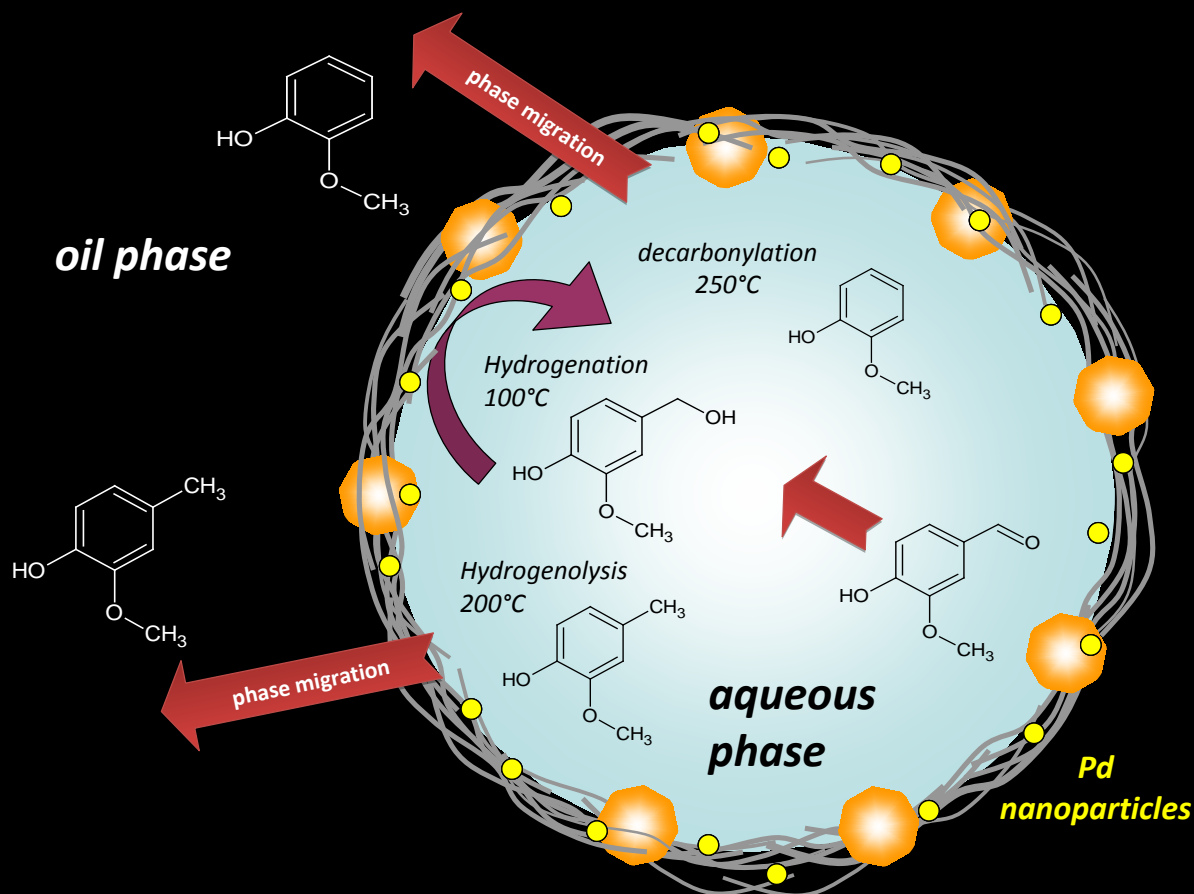
Shen and Resasco,  
*Langmuir* **25**, 10843 (2009).



Crossley S, Faria J, Shen M,  
Resasco DE, *Science*, **327**, 68-72  
(2010).



## Phase migration of the different products during the HDO of vanillin

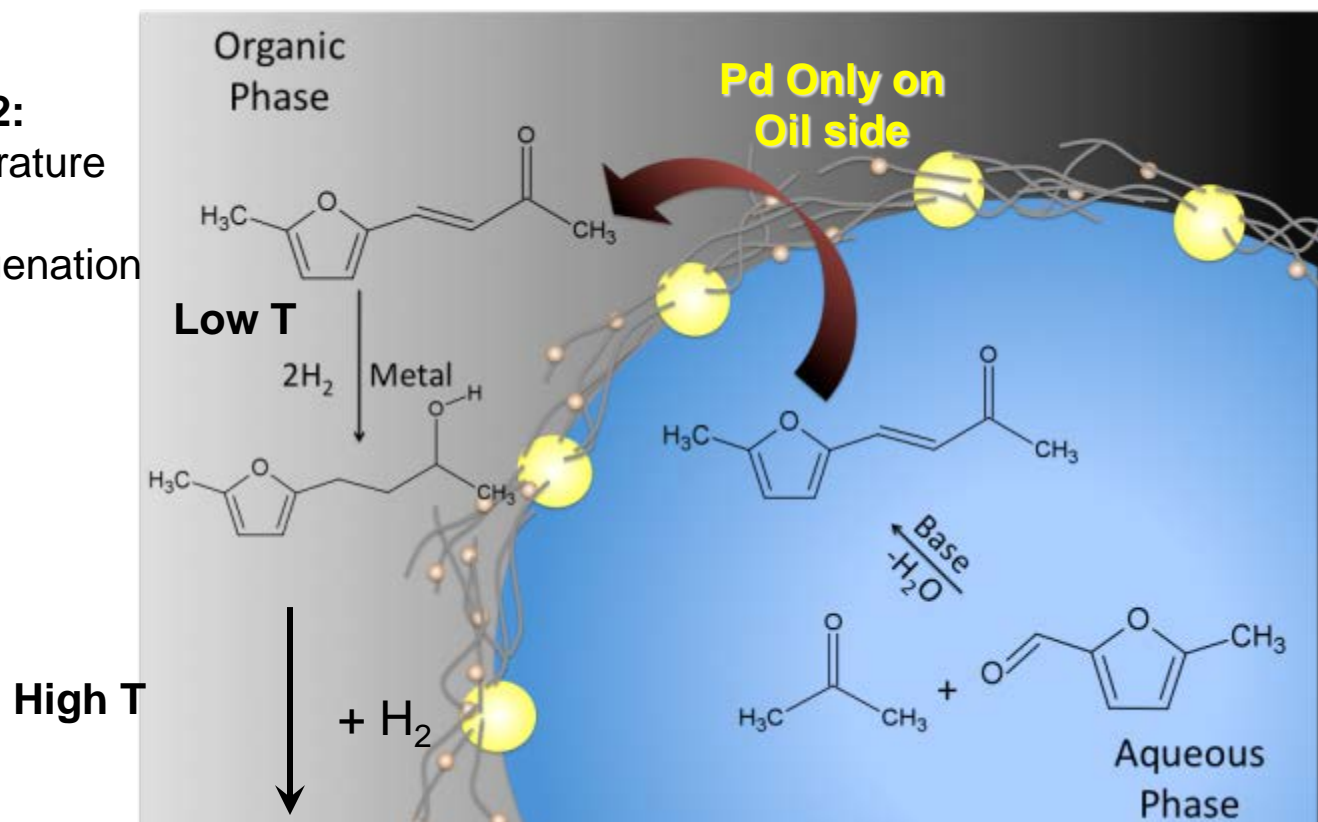


Product distribution for the HDO of vanillin at different reaction temperatures.

# Tandem Condensation / HDO in Emulsion

## STEP 2:

Temperature  
Staged  
Hydrogenation



## STEP 1:

Based-catalyzed  
aldol  
condensation:

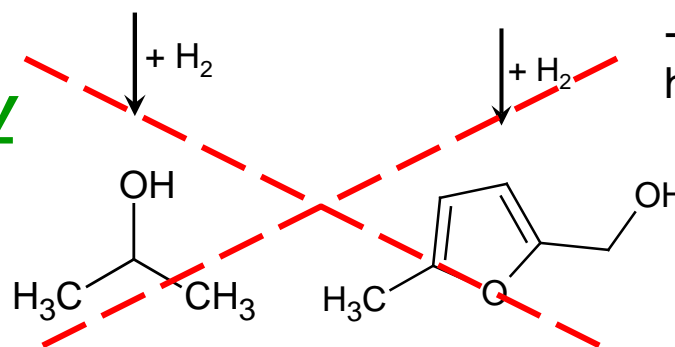
- MgO nanoparticles

- Na(OH)  
homogeneous

Need to  
hydrogenate  
in oil phase  
ONLY

Importance of Phase Selectivity  
To Maximize Yield


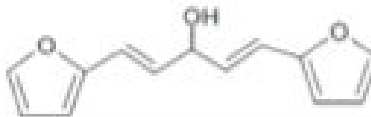



Crossley, Sen, Faria, Resasco  
*SCIENCE*, **327**, 68-72 (2010)

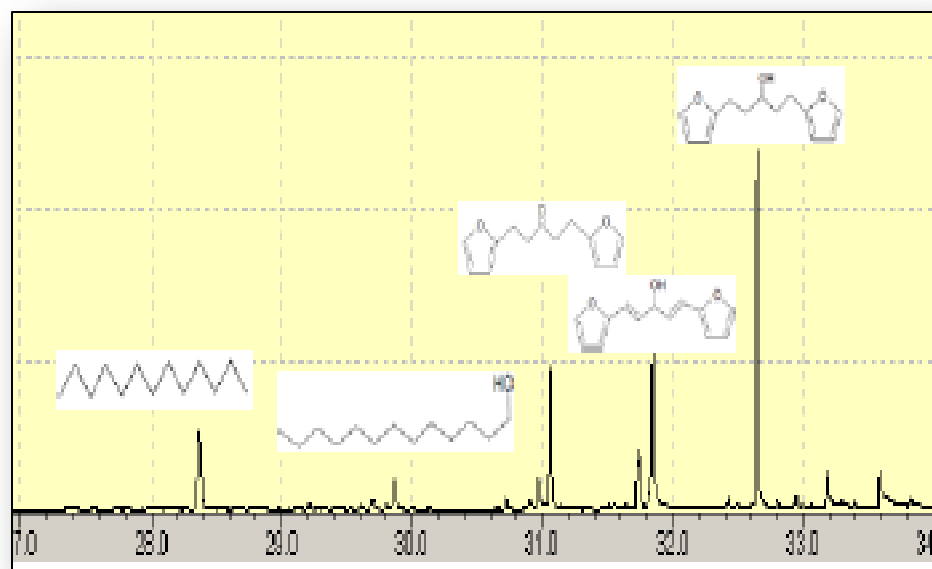


# Tandem Condensation / HDO in Emulsion

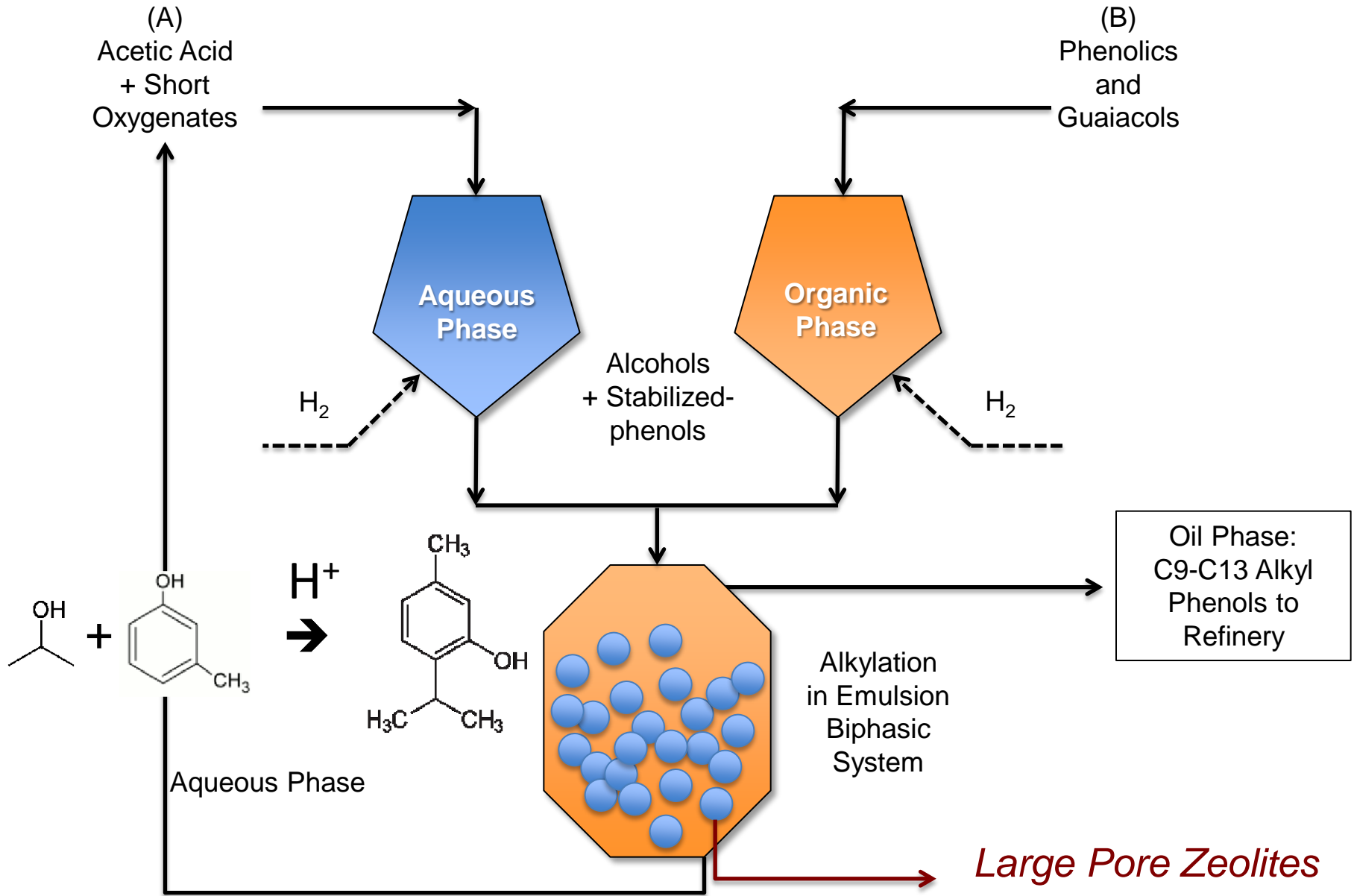
Hydrotreating after aldol - condensation reaction with NaOH.

Reaction was done in presence of Ni-Pt / SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5% Ni 1% Pt).  
3 h at **240°C** and **700 psig H<sub>2</sub>**

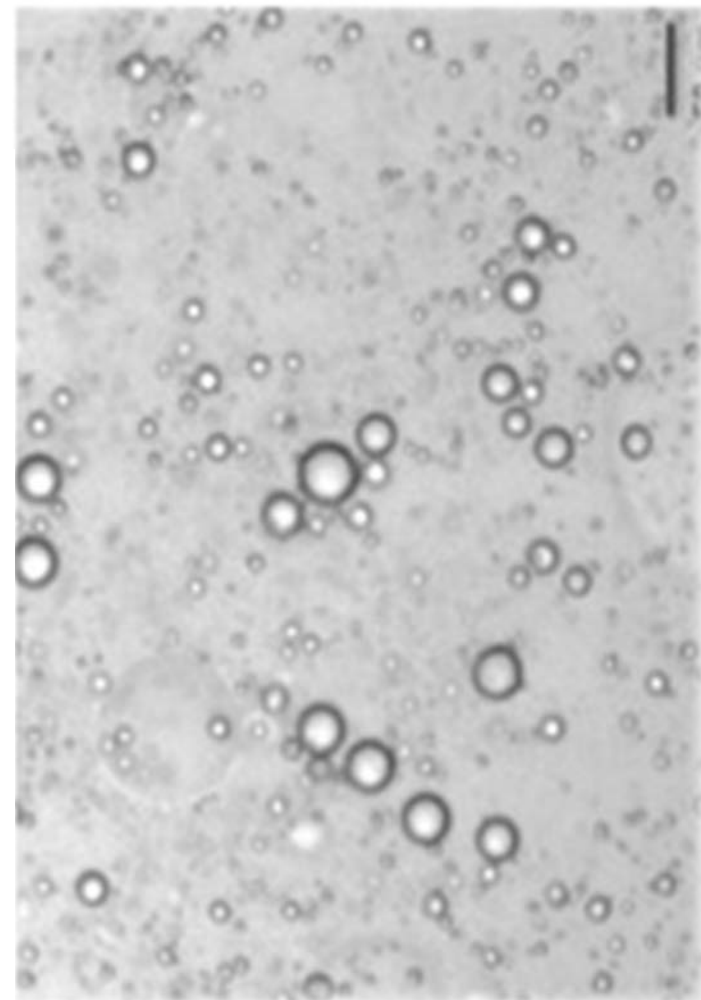
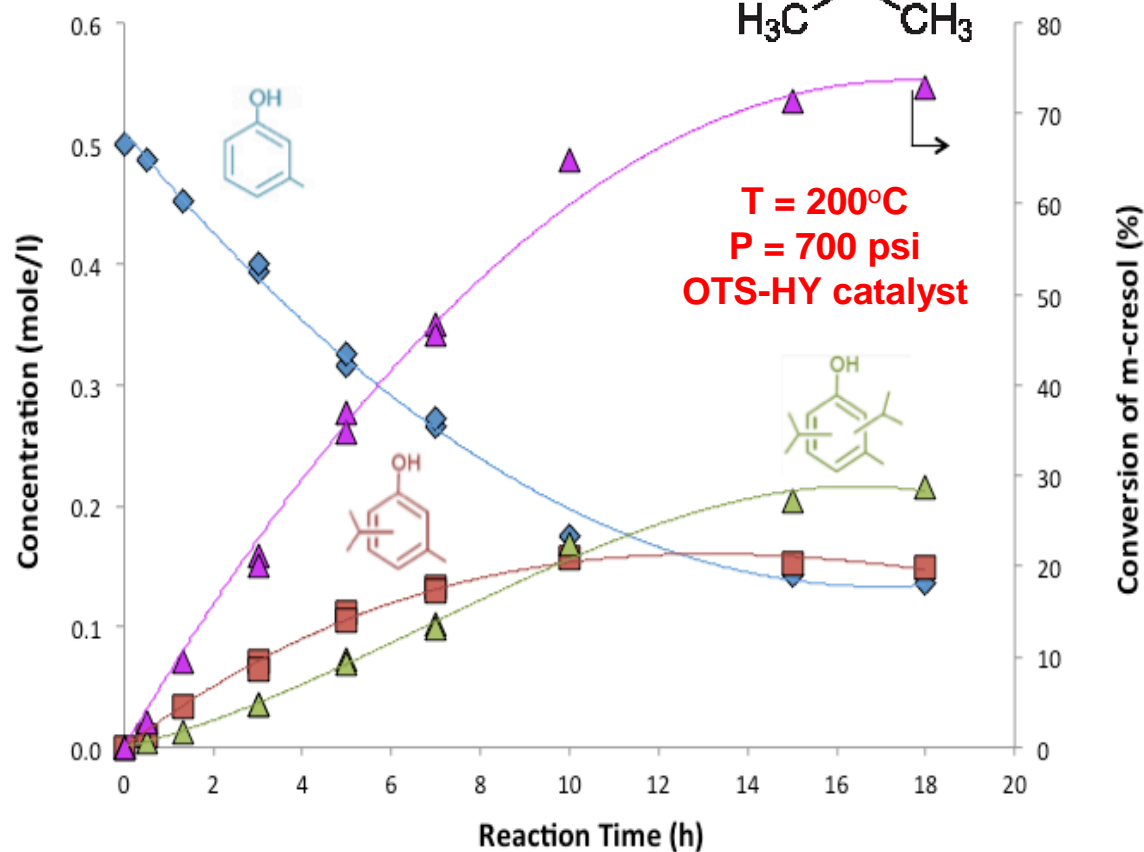
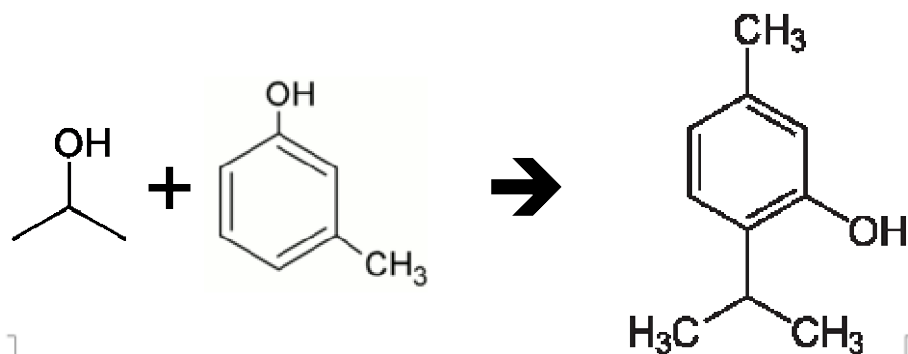
Compound	% (wt)
	34.5
	33.6
	14.0
	4.3
	13.6



# Alkylation in Biphasic (emulsion) System

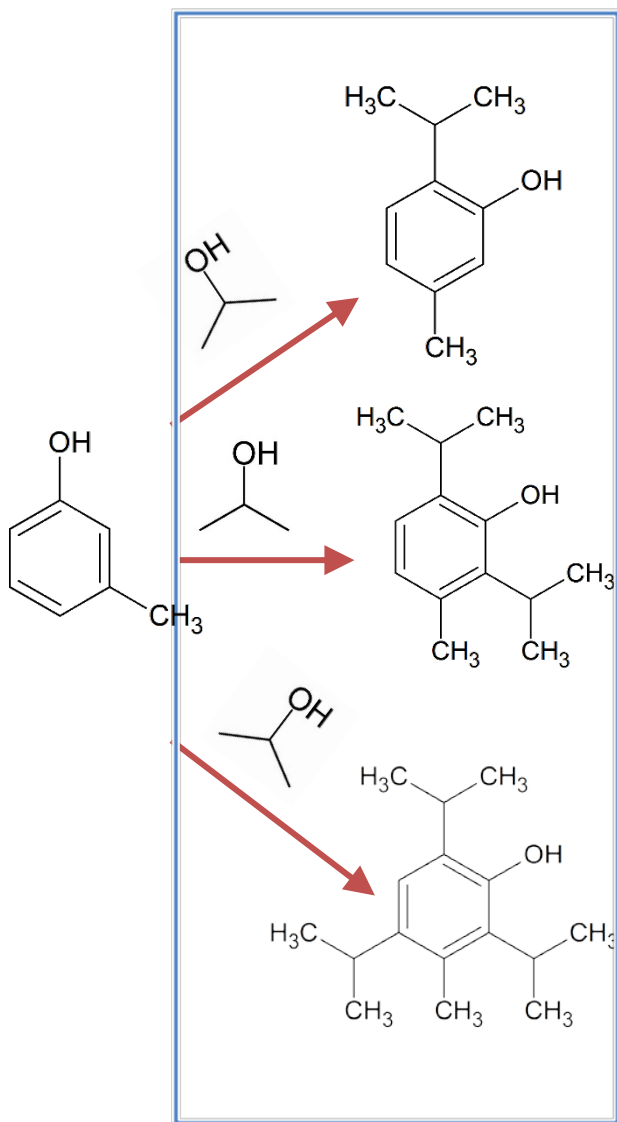


# Alkylation in Biphasic (emulsion) System



*J. Am. Chem. Soc.*, 2012 134, 8570–8578

# HDO and RC/RO of Alkylated Cresols in the Liquid Phase



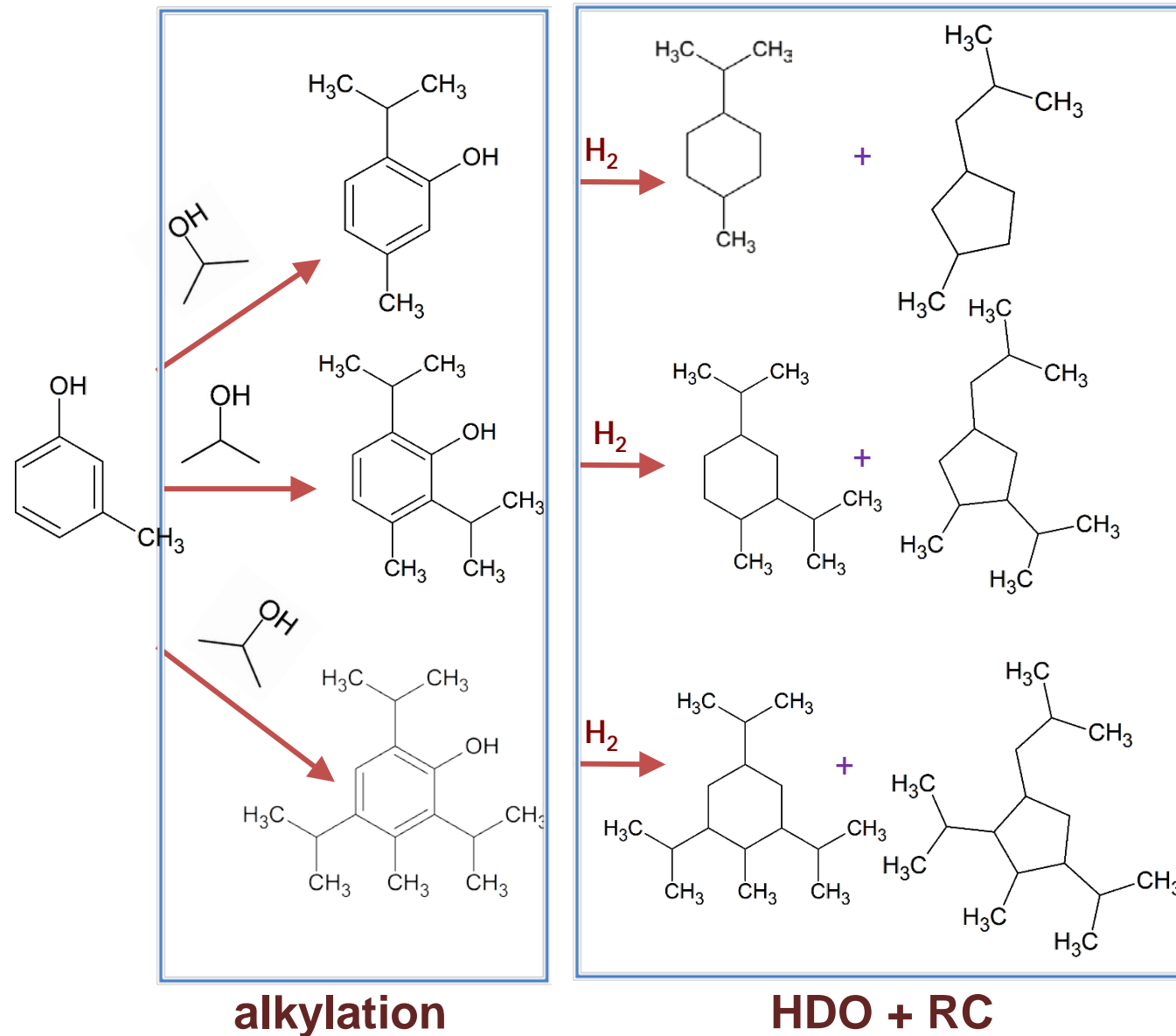
**alkylation**

## ***Advantages:***

- Incorporate the small oxygenates into the fuel pool
- Depending on degree of alkylation, gasoline/diesel fuel range can be selected



# HDO and RC/RO of Alkylated Cresols in the Liquid Phase

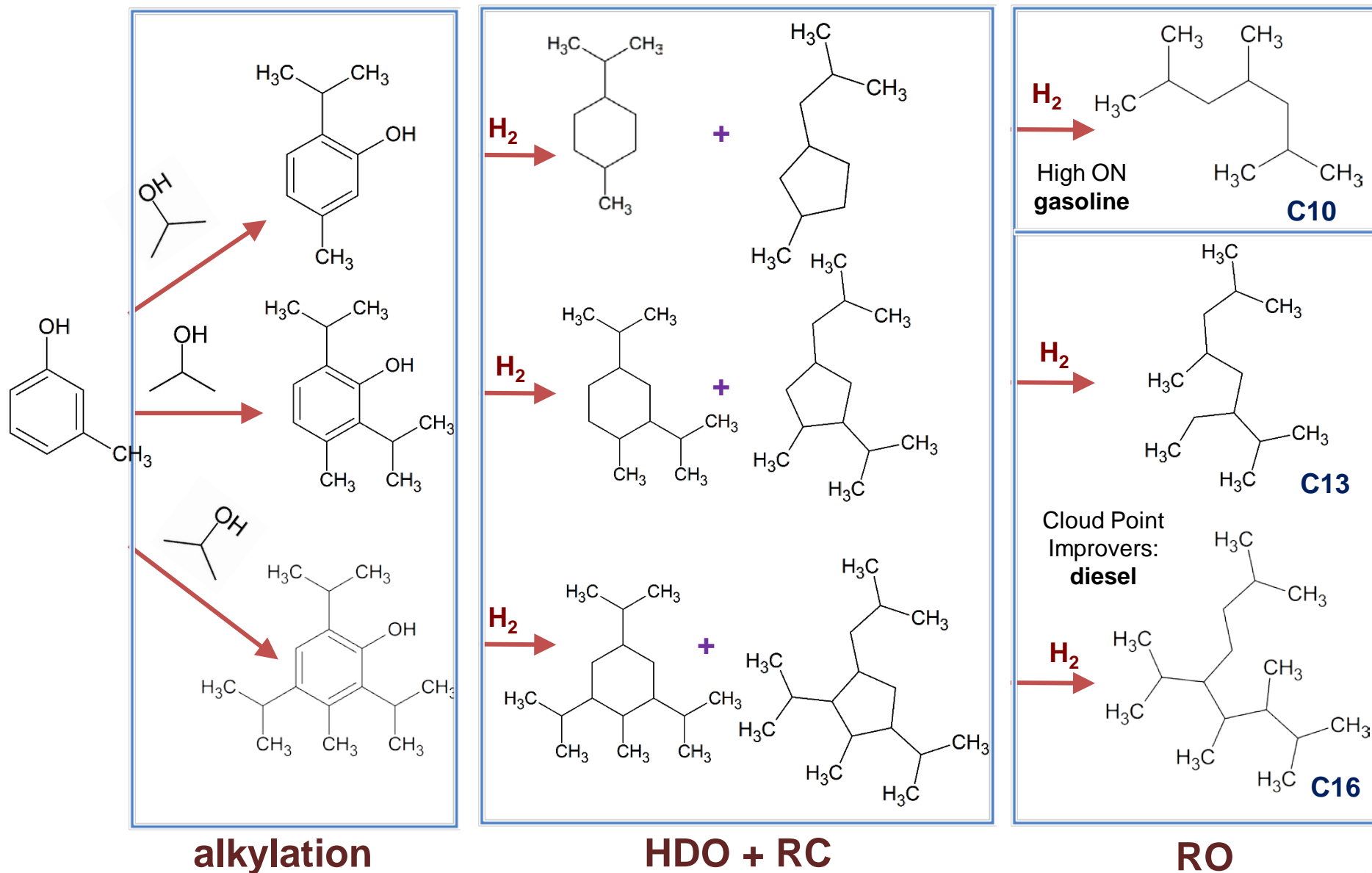


## Advantages:

- HDO removes oxygen while aromatics content is reduced
- Ring contraction produces C5-member rings with good fuel properties (e.g. lower sooting tendency)
- They can be ring-opened

# HDO and RC/RO of Alkylated Cresols in the Liquid Phase

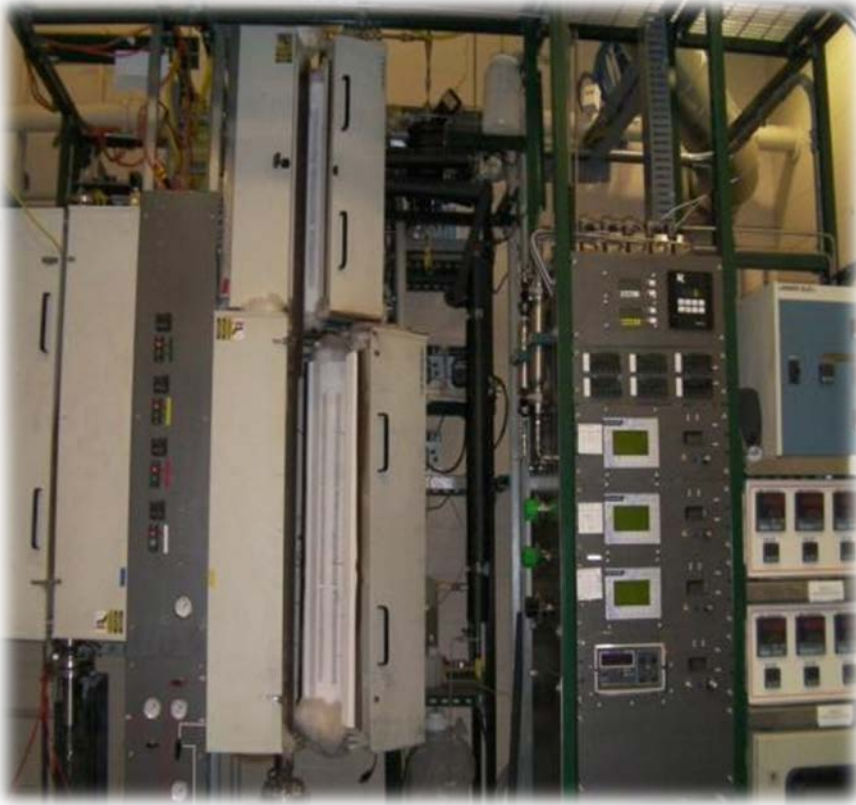
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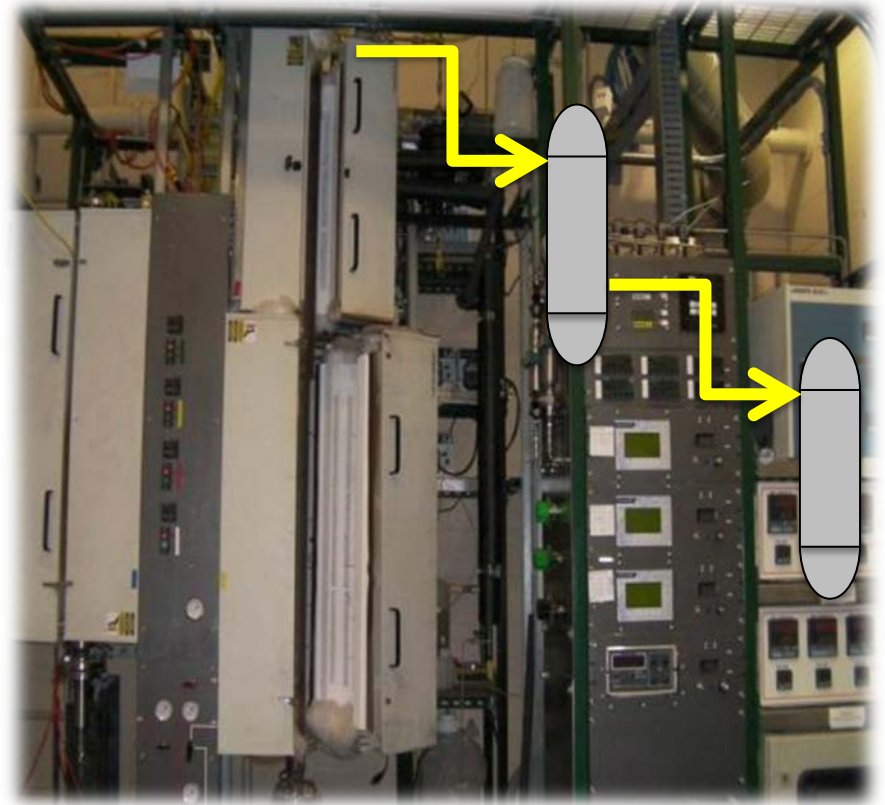
# Conversion of pyrolysis vapors

Conventional  
Pyrolysis + Condensation  
(or sequential condensation)



Product: Bio-oil (or bio-oil fractions)

Pyrolysis or Torrefaction Vapors  
+ Catalytic cascade



Product: Stabilized Bio-oil

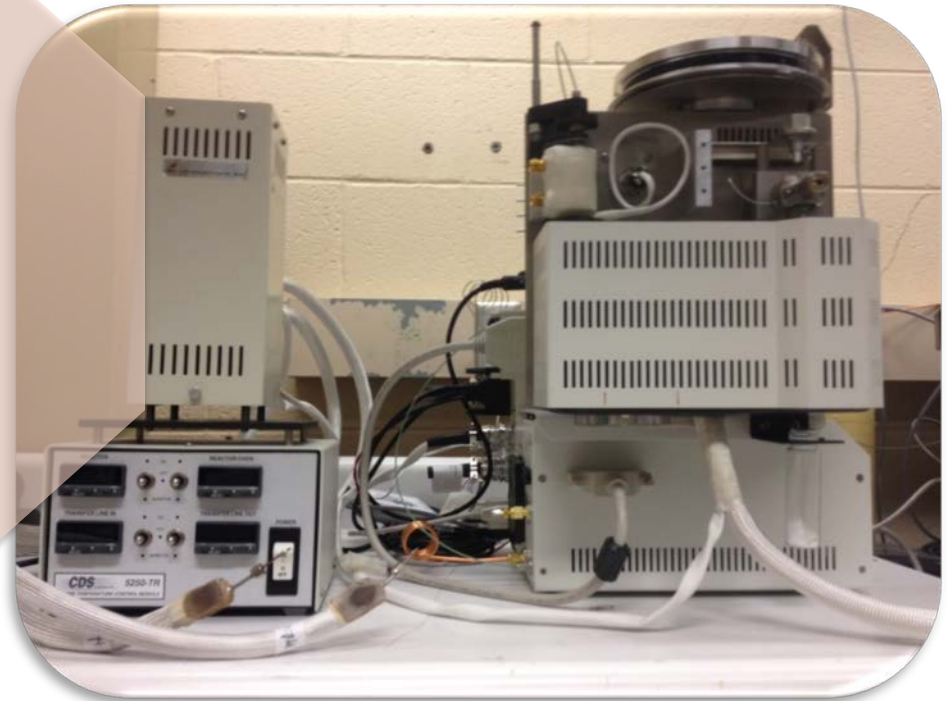
# Conversion of pyrolysis vapors



## WITH SEPARATE CATALYTIC REACTOR:

- study effects of temperature
- study deactivation

- H-ZSM-5 Zeolite
- Ru/TiO<sub>2</sub> (Ketonization)
- Ni-Fe (HDO)

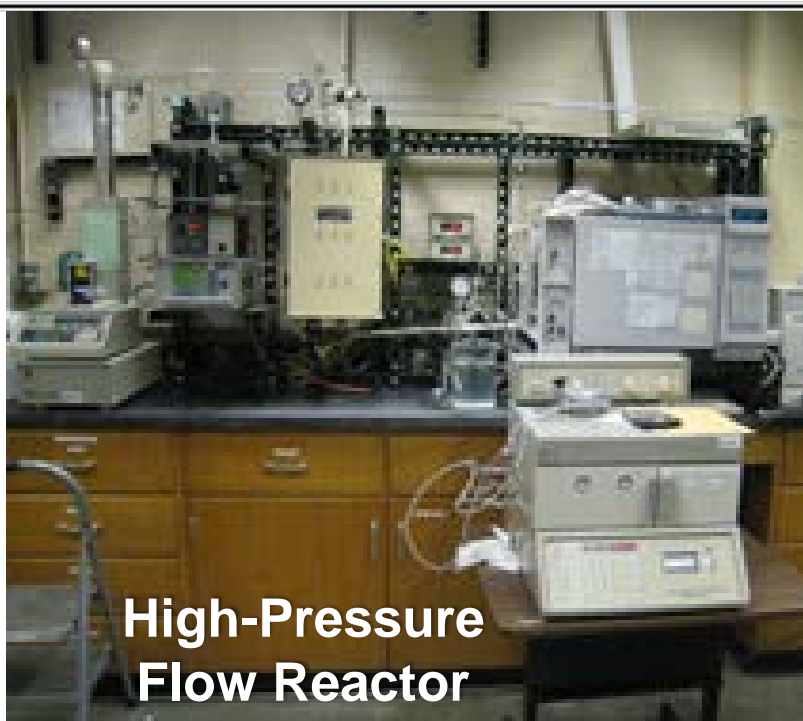


Improvement Vs Catalytic Pyrolysis

# Reactions in the vapor phase



**Low-Pressure  
Flow Reactor**



**High-Pressure  
Flow Reactor**

Reactions in the vapor-phase are conducted in continuous-flow tubular reactors.

From 40 to 1200 psi of pressure and from 50 to 500°C

## ***C-C bond formation reactions:***

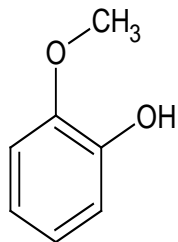
- Ketonization
- Aldol condensation
- Alkylation

## ***C-O bond cleavage reactions:***

- Hydrodeoxygenation of phenolics
- Hydrodeoxygenation of furanics

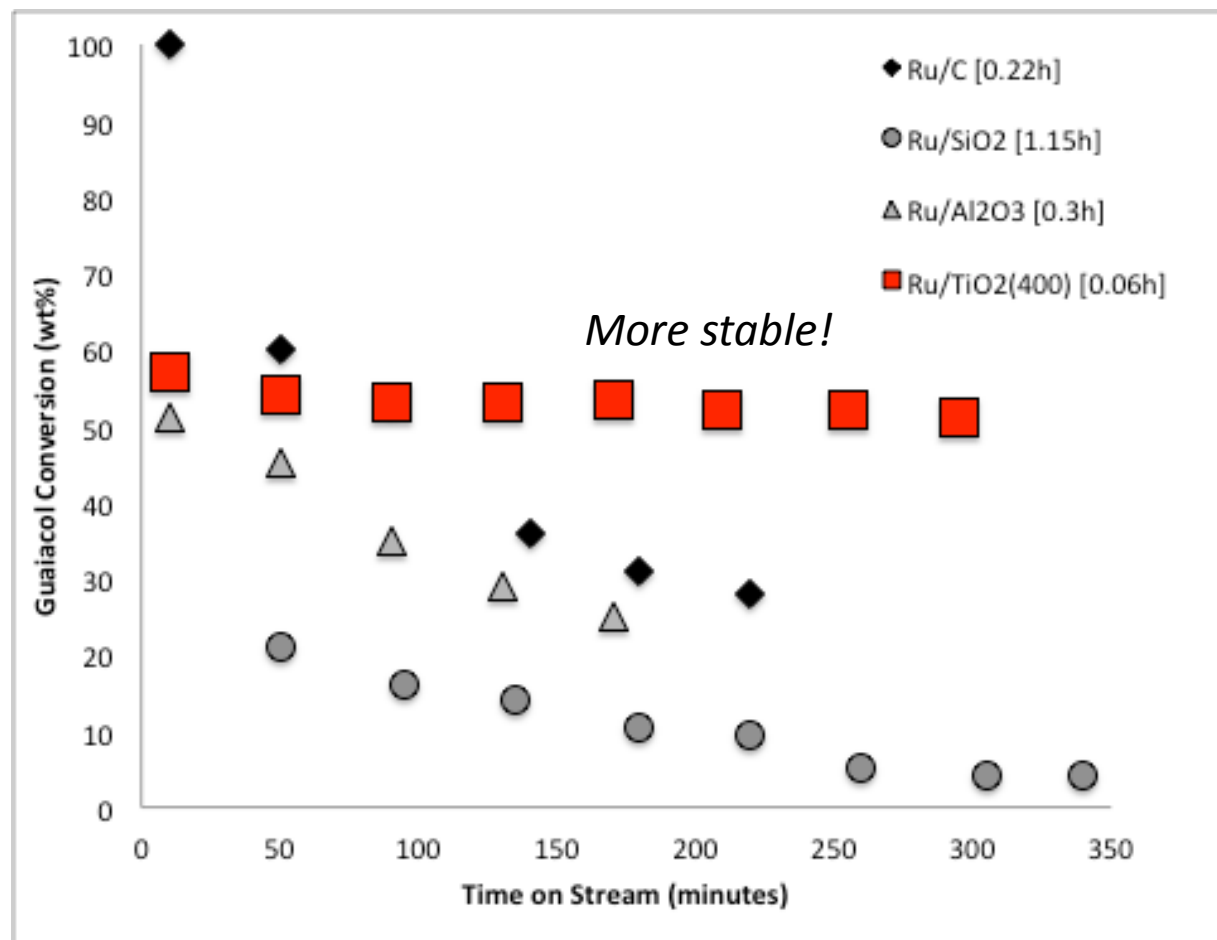
# TiO<sub>2</sub> support produces enhanced activity + stability

Guaiacol (feed)



Catalyst	Conversion	W/F
<i>Ru/C</i>	20	0.035
<i>Ru/SiO<sub>2</sub></i>	23	1.130
<i>Ru/Al<sub>2</sub>O<sub>3</sub></i>	24	0.120
<i>Ru/TiO<sub>2</sub></i>	18	0.011

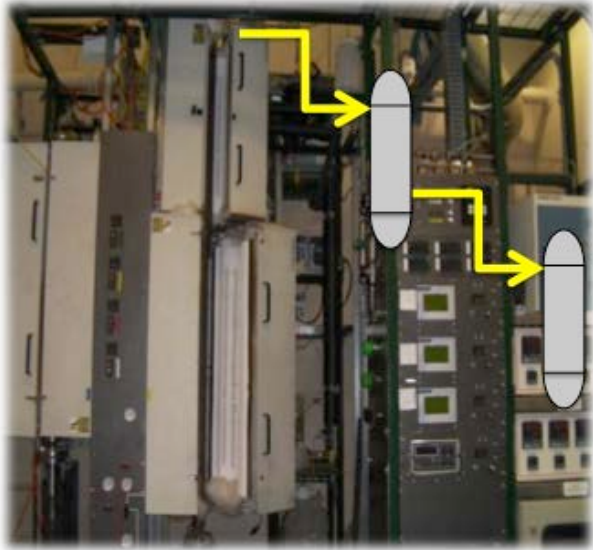
Less catalyst required



W/F (g catalyst/g feed per hour)



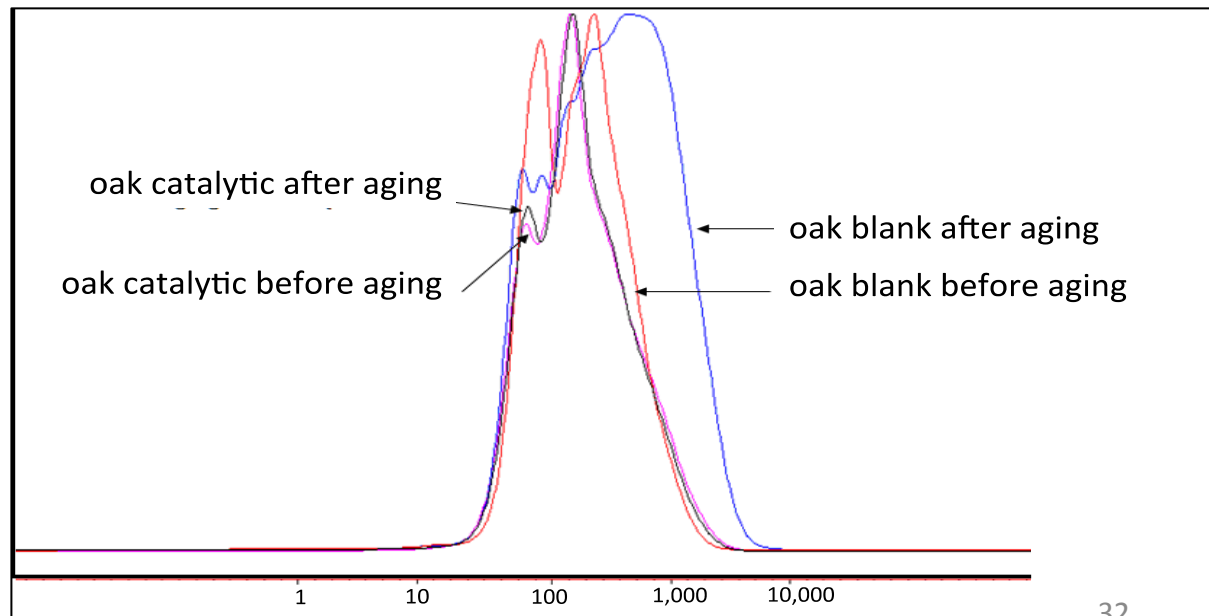
# Conversion of real pyrolysis oil vapors on Ru/TiO<sub>2</sub>



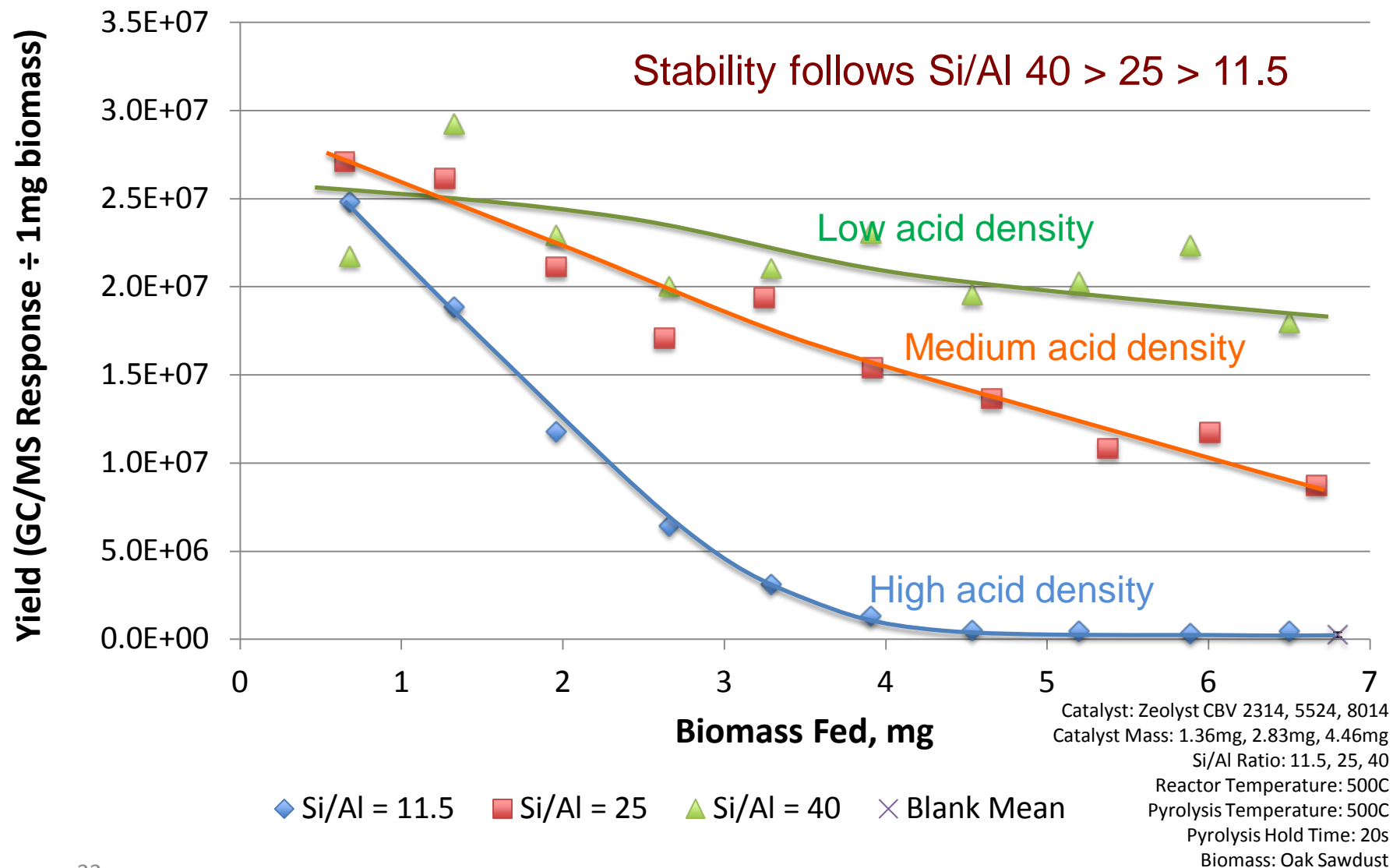
Specific product yields

	oak blank	Ru-TiO <sub>2</sub> 1st run	Ru-TiO <sub>2</sub> 3rd run
acetone	0.3	1.6	0.7
acetic acid	6.3	0.8	2.4

- 4 g Ru/TiO<sub>2</sub>
  - 400°C
  - 1 atm H<sub>2</sub>
- 30 g oak/batch

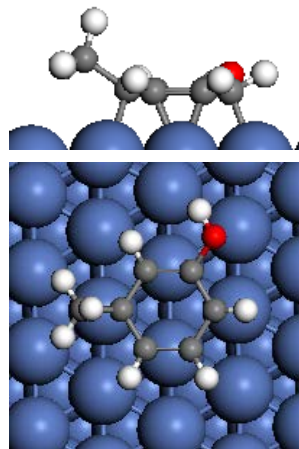
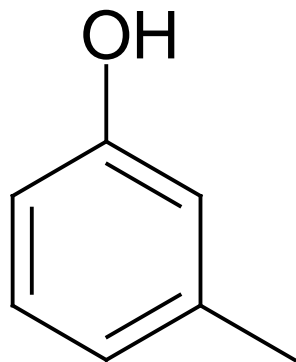


# Acid site density @ constant total acid sites HZSM-5 zeolites with varying acid density

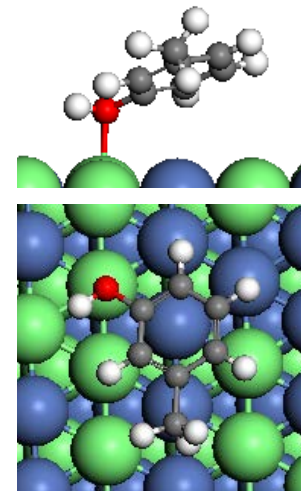
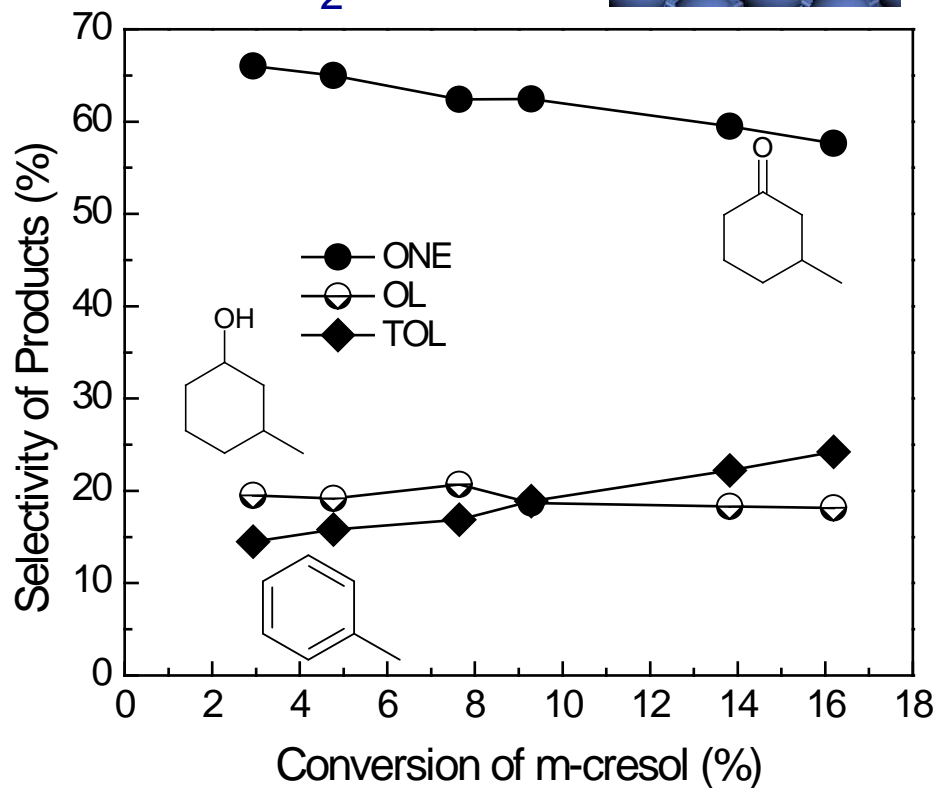


# Remarkably high TOL selectivity @ 300°C on Ni-Fe

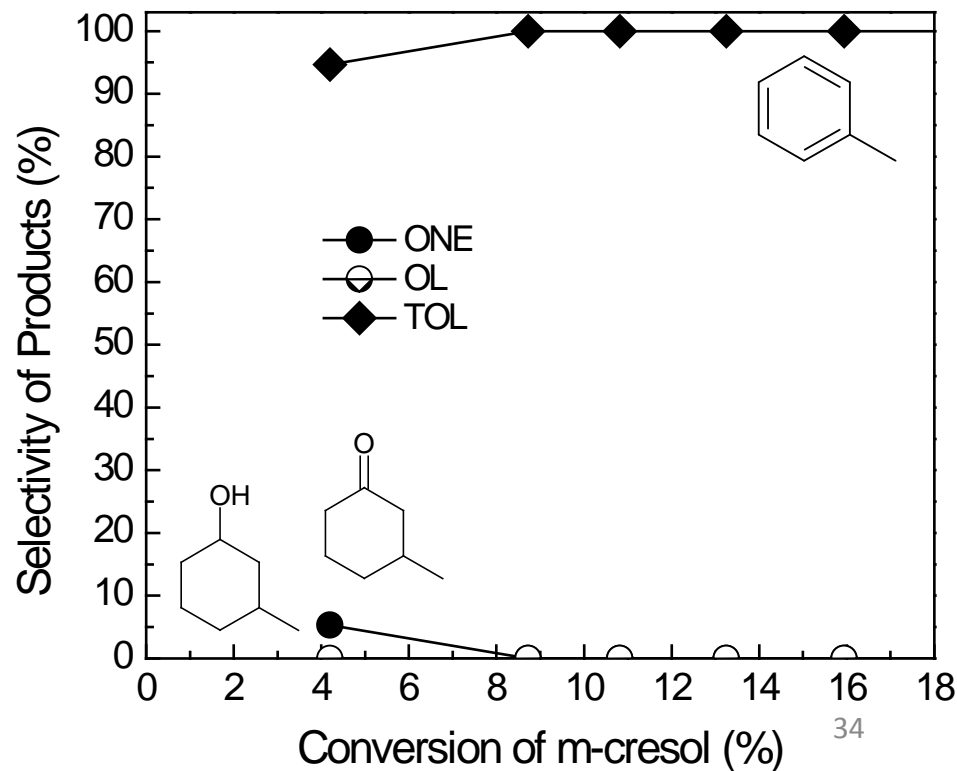
34



Ni/SiO<sub>2</sub>

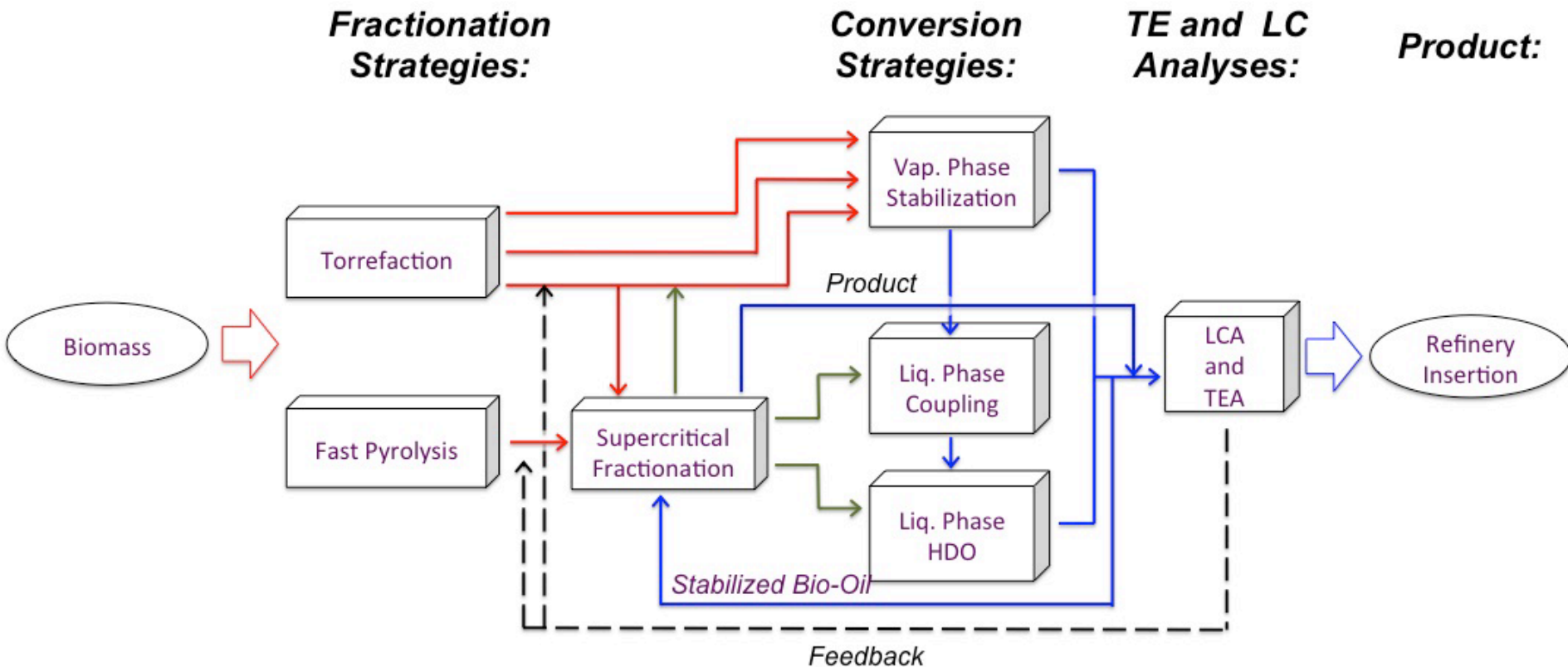


Ni-Fe/SiO<sub>2</sub>



34

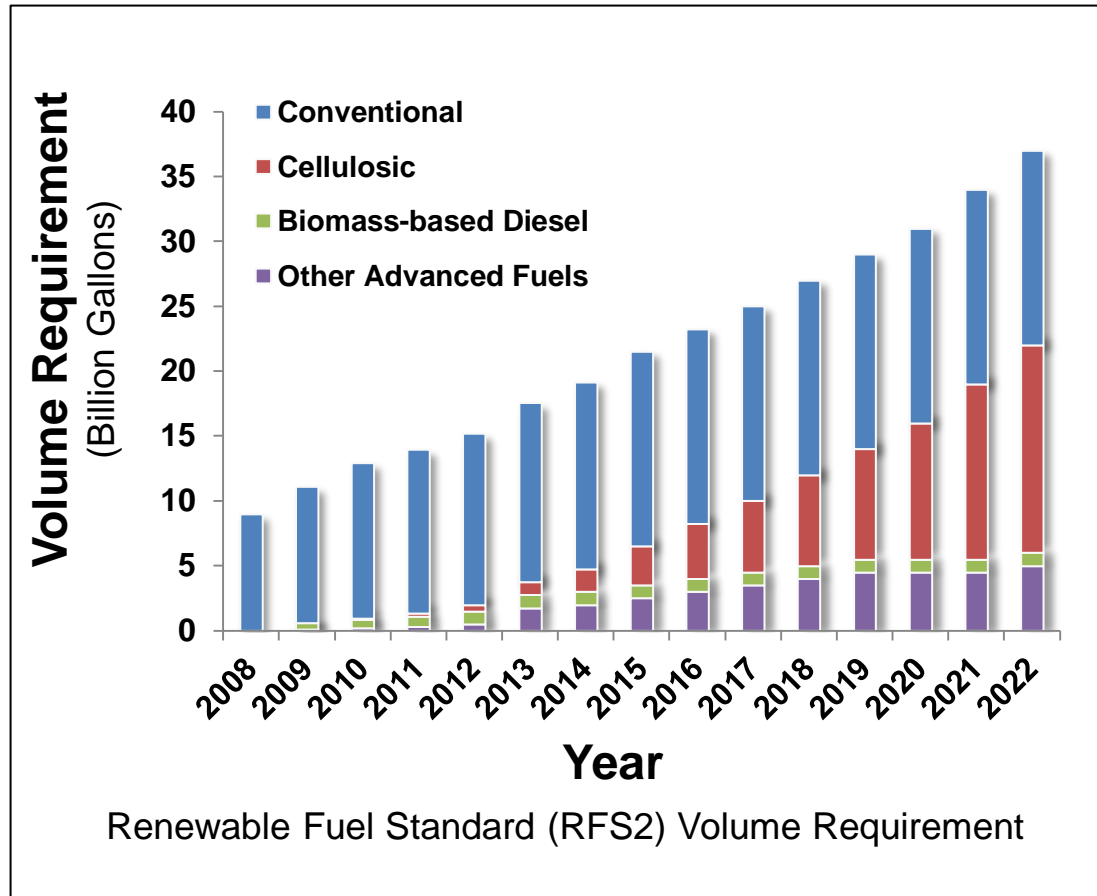
# Approach: Feedback loop with TEA and LCA



*Enables constant evaluation and evolution of strategy*

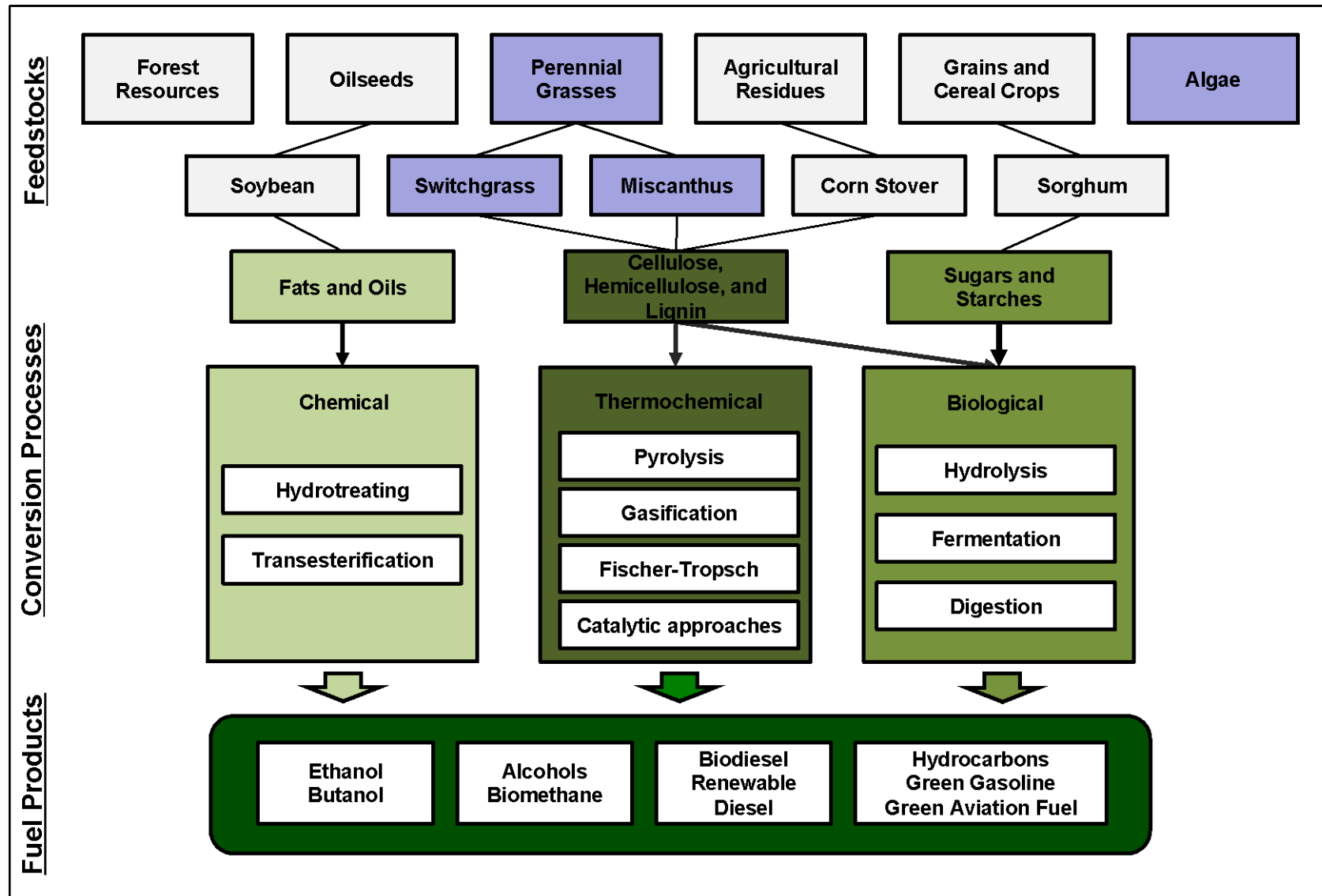
# Biofuels and Life Cycle Greenhouse Gas Emissions

## Renewable Fuel Standard Volumes by Year



- Energy Independence and Security Act (EISA) of 2007
- Minimum lifecycle greenhouse gas (GHG) emissions reduction standards
  - Cellulosic biofuel: 60% reduction
  - Biomass-based diesel: 50% reduction
  - Advanced biofuels: 50% reduction

# Biofeedstocks, Conversion Pathways, Fuel Products



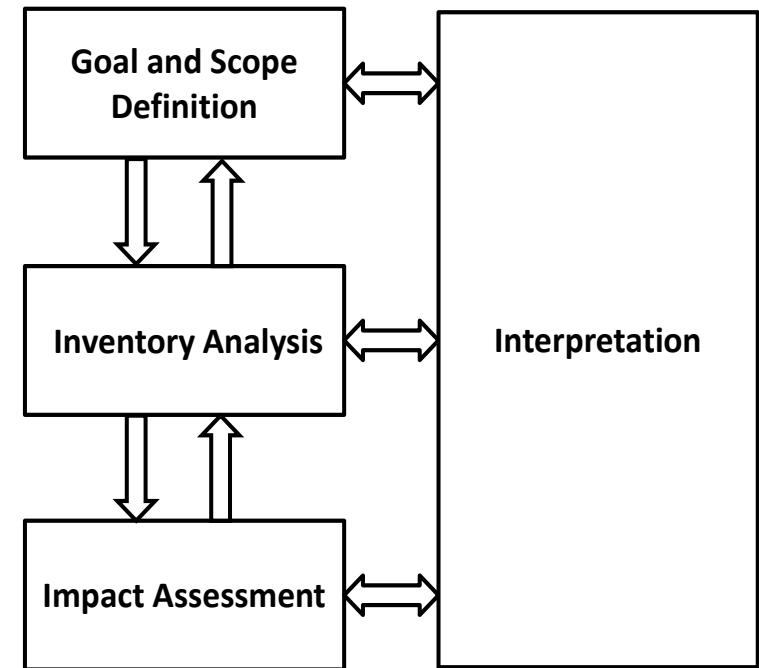
# Issues with first generation biofuels

- Corn-derived ethanol, soybean-derived biodiesel
- Low energy return on investment (EROI)
- Small reduction of greenhouse gas (GHG) emissions from petroleum fuels
- Direct and indirect land use change
- Exert market pressure on food prices
- High water footprint



# Life Cycle Assessment

- Life cycle assessment (LCA) is a methodology used to track and quantify the environmental impacts of a product or service throughout all stages of its life cycle – from raw material extraction to end of life.
- Standardized via ISO 14040 and 14044
- Widely used in the industry
- **Our goal is to use LCA proactively to guide conversion strategies and catalyst development**



ISO 14040 and 14044 LCA Framework

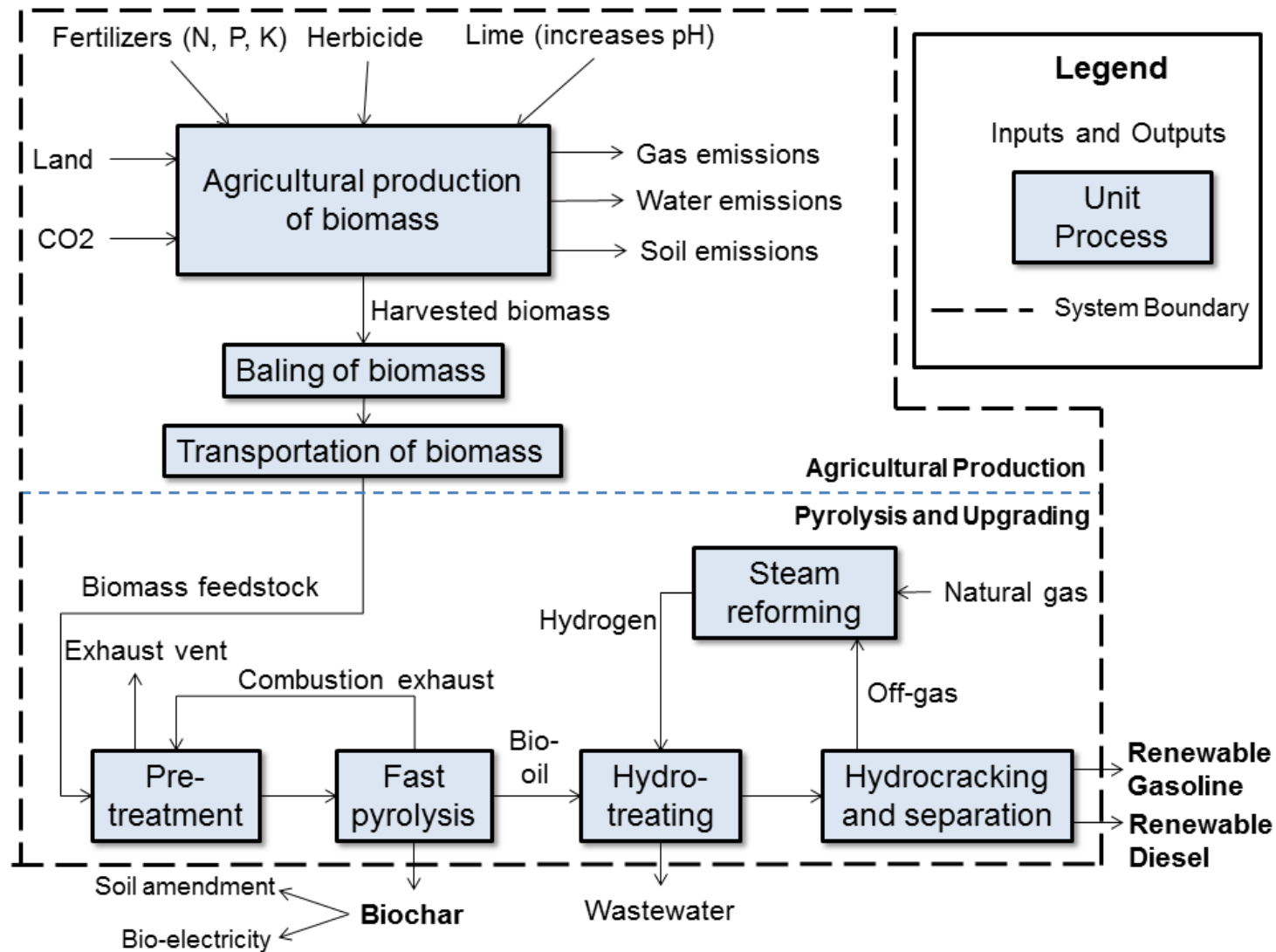
# LCA Objectives

- Develop life cycle assessment (LCA) of biofuels derived via biomass fast pyrolysis to guide biomass processing and conversion strategies
- Compare and contrast the LCA findings for conventional hydrotreating vs our approach (thermal fractionation and catalytic upgrading)
- Evaluate several different combinations of biomass feedstock and conversion pathways
  - Identify pathways satisfying RFS2 standard
  - Compare tradeoffs between biomass cultivars
  - Integrate experimental results in the LCA model
- Evaluate tradeoffs between life cycle environmental impacts (energy, greenhouse gas emissions, water footprint, land use change etc.)

# Methodology

- Develop parameters for crop growth, cultivation, and harvesting
- Aspen models for fast pyrolysis
- Multiple co-product utilization options and production scenarios
- Monte Carlo simulation to quantify statistical uncertainty in life cycle environmental impacts

# Base case: Fast pyrolysis + Hydrotreating of entire bio oil

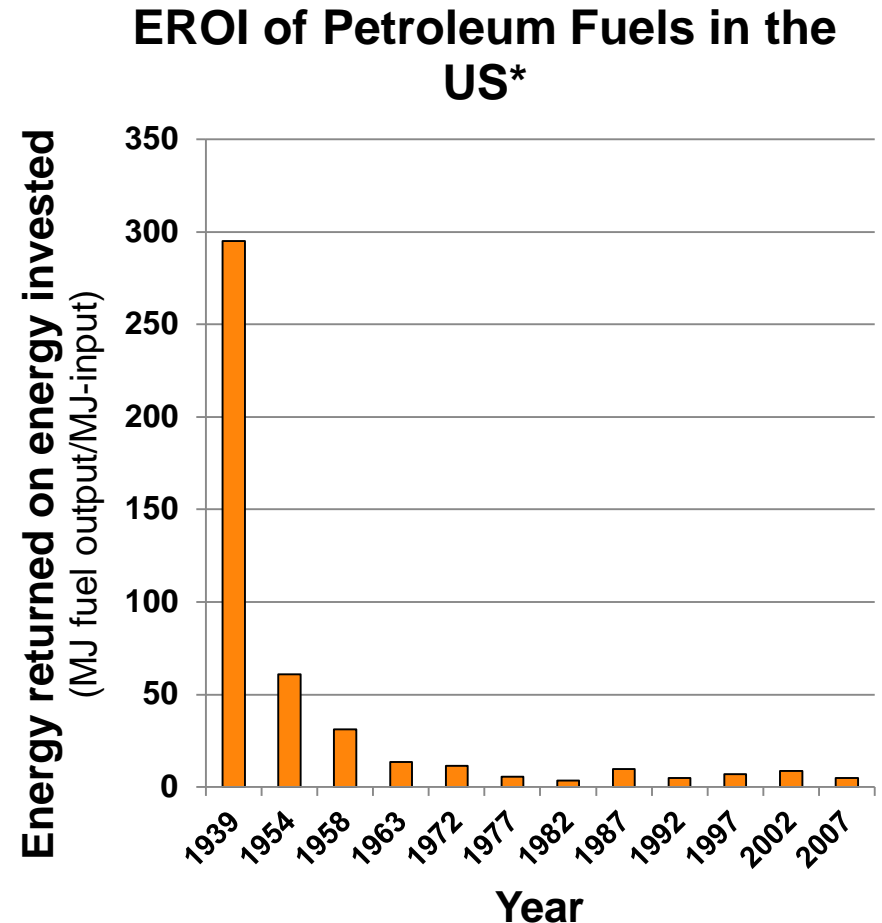


**Elements considered in the biomass to biofuel supply chain**  
**Feedstocks (evaluated so far): Switchgrass, Miscanthus**

# Energy Return On Investment (EROI)

$$EROI = \frac{\text{Fuel Energy Output}}{\text{Life Cycle Energy Input}}$$

- Why look at EROI?
  - $EROI > 1$ : Net energy positive
  - $EROI = 1$ : Break-even
  - $EROI < 1$ : Net energy negative
- EROI of petroleum fuels over time

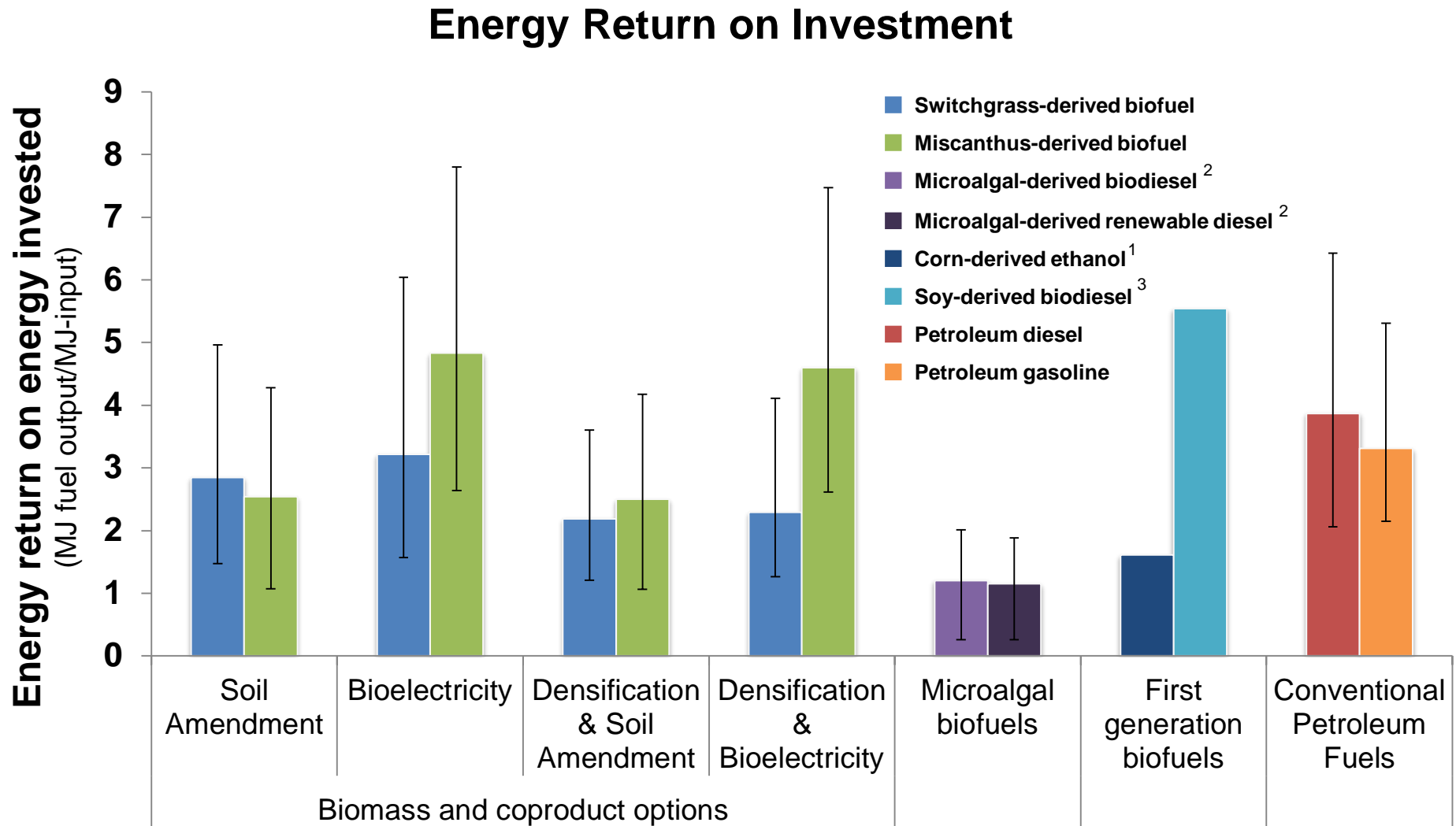


# Cultivation and Harvesting of Biomass

- Establishment and seeding
- Fertilizers and herbicides
- Growth cycles
  - Miscanthus: 15 years
  - Switchgrass: 20 years
- Harvesting options
  - Baling
  - Chopping
- Densification
- Transportation
  - Assume local biorefinery



# Preliminary results: Energy Return on Investment (EROI)



<sup>1</sup>Wang et al. *Environmental Research Letters* 7.4 (2012): 045905.

<sup>2</sup>Zaimes and Khanna, *Environmental Progress & Sustainable Energy* **2013**, published online

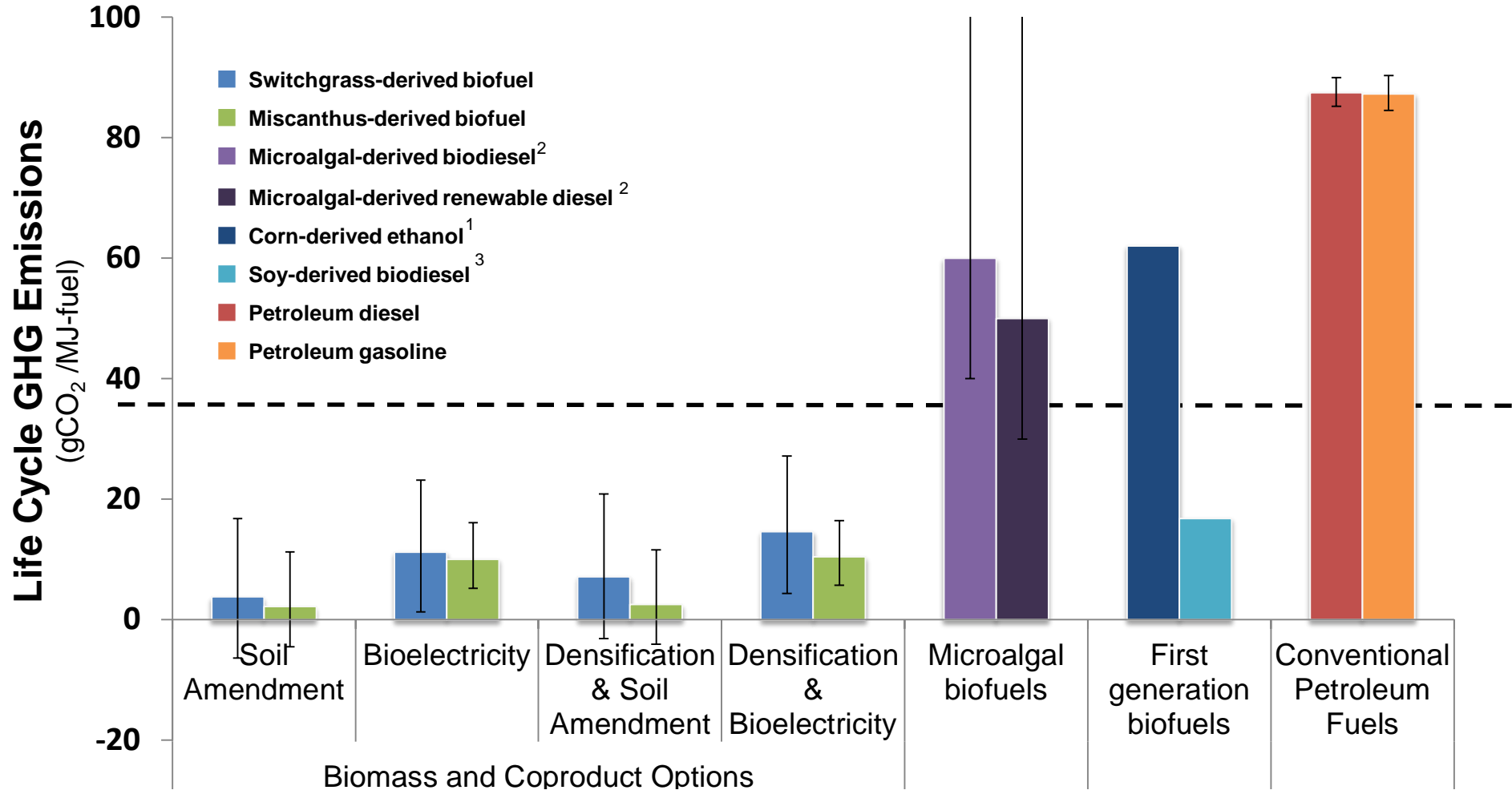
<sup>3</sup>Pradhan et al. *Transactions of the ASABE* **2012**, 55 (6), 2257-2264.

Zaimes and Khanna, *Biotechnology for Biofuels*, 6(88), 2013



# Life Cycle GHG emissions

## Life Cycle Greenhouse Gas Emissions



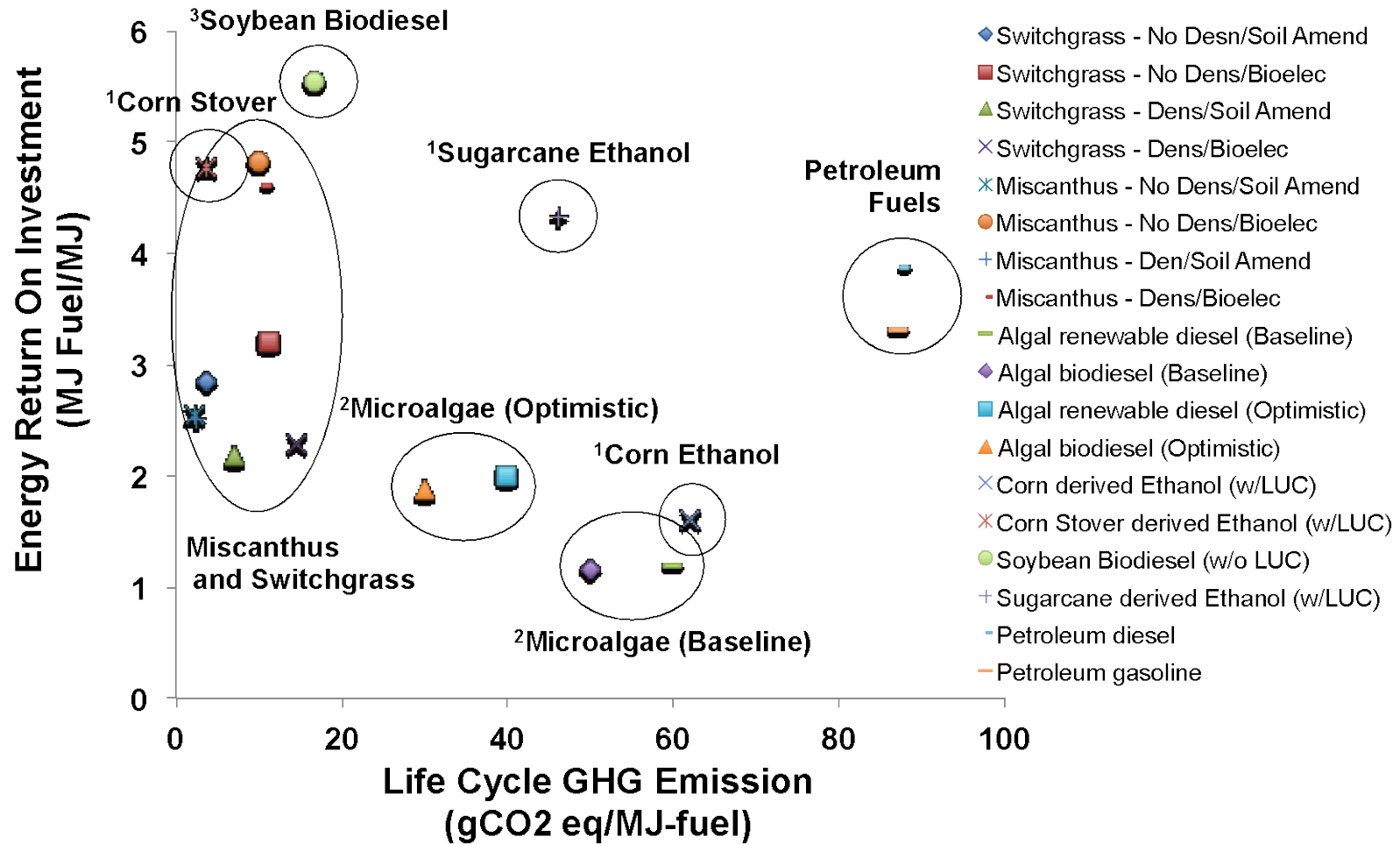
<sup>1</sup>Wang et al. *Environmental Research Letters* 7.4 (2012): 045905.

<sup>2</sup>Zaimes and Khanna, *Environmental Progress & Sustainable Energy* **2013**, published online

<sup>3</sup>Pradhan et al. *Transactions of the ASABE* **2012**, 55 (6), 2257-2264.

Zaimes and Khanna, *Biotechnology for Biofuels*, 6(88), 2013

# EROI VS GHG Emissions



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# Existing vs Our Approach: Implications for LCA

## Issues with 1-step hydrotreating approach

- Loss of carbon and reduced liquid yield (small oxygenates converted to lower alkanes, higher life cycle GHG emissions )
- Higher hydrogen requirement (hence increased life cycle GHG emissions)
- Severe hydrotreating conditions translate into higher utility consumption (higher life cycle GHG emissions)

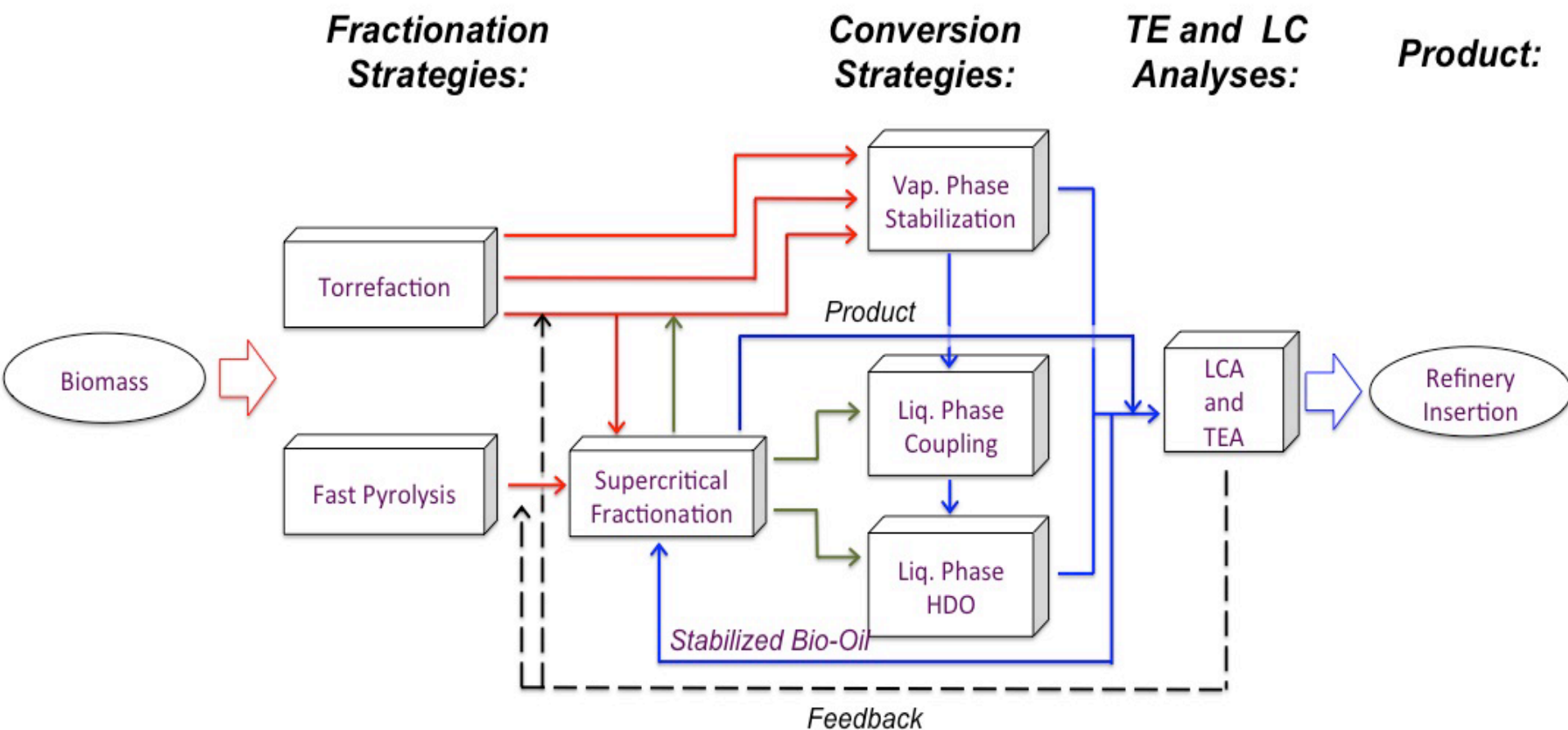
## Proposed approach and implications for LCA

- C-C bond formation before HDO will increase liquid yield (lower life cycle GHG emissions per fuel output)
- Multistage pyrolysis coupled with different upgrading strategies for each fraction will lead to reduced fossil hydrogen requirement (reduction in life cycle GHG emissions)
- Net improvement in yield and catalyst lifetimes due to tailored strategies for upgrading separate bio-oil fraction (improved GHG emission profile)

# Ongoing and Future Work

- Analyze variants of fast pyrolysis
  - Thermal fractionation + ex-situ catalytic fast pyrolysis
  - Thermal fractionation, supercritical fluid extraction and biphasic upgrading
- Detailed Aspen models for the above
- Water footprint of biofuel production
- Analyze direct and indirect land use change
- Additional biomass feedstocks and address spatial variation in life cycle environmental impacts

# Summary



# Gantt Chart

		Year-->	1				2				3			
		Quarter-->	I	II	III	IV	I	II	III	IV	I	II	III	IV
<b>Task 1</b>	<b>Thermal fractionation</b>													
1.1	Staged thermal conversion of biomass at various temperatures and heating times													
1.2	Chromatographic analysis of different fractions					◆								
1.3	Optimization to maximize liquid yield and species separation (A, B, C)									◆				
1.4	Production of fractions A, B, and C for vapor-phase and liquid-phase reactions					◆								
<b>Task 2</b>	<b>Supercritical Fluid Extraction of Torrefaction and Pyrolysis Oils</b>													
2.1	Development of SCF separation and analysis of different fractions													
2.2	Application of SCF extraction to full bio-oil obtained from fast pyrolysis					◆								
2.3	Application of SCF to different fractions of the thermal fractionation process									◆				
2.4	Production of fractions D, E, F, and G for vapor-phase and liquid-phase reactions					◆								
<b>Task 3</b>	<b>Design of novel catalysts</b>													
3.1	Synthesis of basic/acid oxides (reducible and mixed oxides) – e.g. TiO <sub>2</sub> , Ce-ZrO <sub>2</sub>		◆											
3.2	Synthesis of acidic zeolites (HY, H-ZSM5, H-ZSM22, H-beta)			◆										
3.3	Synthesis of metal catalysts supported on basic/acid oxides – Ni, Ru, Ni-Fe				◆									
3.4	Characterization of acidity, metal dispersion, surface area, XRD, TEM, SEM.													

Purple:

Planned activity

Green:

Activity dependent on input from Orange

Orange:

Output to help decision making to Green

Diamonds:

Go / No-Go decisions

# Gantt Chart

		Year-->	1				2				3			
		Quarter-->	I	II	III	IV	I	II	III	IV	I	II	III	IV
<b>Task 4</b>	<b>Reactions in Vapor Phase</b>													
4.1	Ketonization/aldol condensation of vapors over acid/based catalysts				♦					♦				
4.2	Aldol condensation combined w/hydrodeoxygenation (metals+acid/base)					♦					♦			
4.3	Hydrodeoxygenation of vapors over metals with added H <sub>2</sub>					♦					♦			
4.4	Quantification of deactivation rates and evaluation of regeneration potential								♦			♦		
<b>Task 5</b>	<b>Reactions in Liquid Phase</b>													
5.1	Condensation reactions of liquids from fractions rich in small oxygenates				♦					♦				
5.2	Condensation reactions of liquids from fractions rich in furfurals and other dehydrated sugars					♦					♦			
5.3	Hydrodeoxygenation of liquids from fractions rich in phenolics and oligomers						♦				♦			
5.4	Quantification of deactivation and catalyst regeneration.								♦				♦	
<b>Task 6</b>	<b>LCA</b>													
6.1	Develop inventory modules for production of bio-oil fractions and upgrading					♦								
6.2	Perform multiscale hybrid LCAs for the different fractionation / conversion strategies.					♦						♦		
6.3	Sensitivity and uncertainty analysis						♦							
6.4	Give feedback to improve overall economics of the process and identify bottlenecks					♦								
<b>Task 7</b>	<b>TEA</b>													
7.1	Develop integrated processes for the various upgrading strategies.					♦								
7.2	Develop process simulation models for all alternative processes					♦						♦		
7.3	Perform technoeconomic evaluations and sensitivity analysis studies.						♦							
7.4	Location and capacity of the facility Vs. economics of the various strategies					♦								
7.5	Give feedback to improve overall economics of the process.													