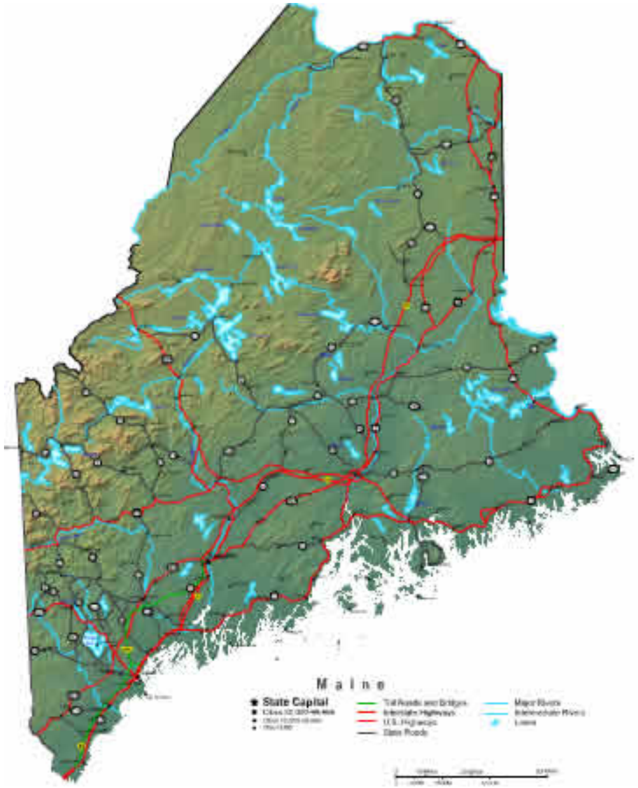
III Latin American Congress
Biorefineries
Ideas for a sustainable world
November 19th to 21st 2012, Pucón, Chile

Formate-assisted fast pyrolysis (FAsP) of woody biomass

William J. DeSisto and M. Clayton Wheeler, University of Maine, Dept. of Chemical Engineering, USA

1865 THE UNIVERSITY OF MAINE
FOREST BIOPRODUCTS RESEARCH INSTITUTE

Maine



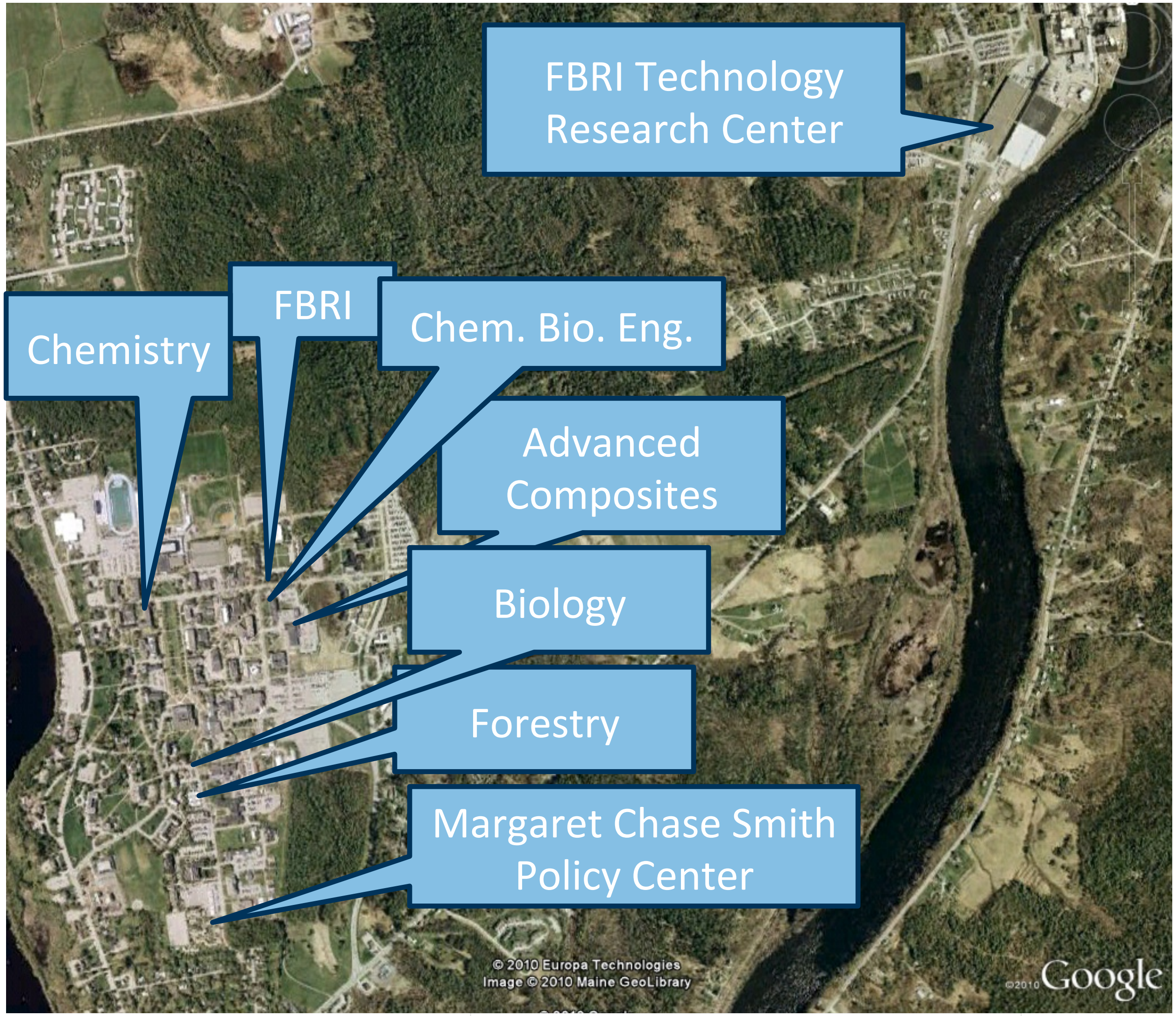
- Most forested state in USA
- Significant pulp and paper production
- Biorefinery opportunities

1865 THE UNIVERSITY OF MAINE

FOREST BIOPRODUCTS RESEARCH INSTITUTE

UMaine Forest Bioproducts Research Institute

http://www.forestbioproducts.umaine.edu/



1865 THE UNIVERSITY OF MAINE

FOREST BIOPRODUCTS RESEARCH INSTITUTE

FBRI Technology Research Center

1865 THE UNIVERSITY OF MAINE

FOREST BIOPRODUCTS RESEARCH INSTITUTE

FBRI TRC

- 40,000 sqft
- 3-50gal fermenters
- 20L HT HP Parr reactor
- 40 L TDO reactor
- Distillation column
- Vacuum evaporator

Forest Bioproducts Thermal Conversion Group at the University of Maine

- **Pyrolysis processes**
  - **Improve bio-oil quality, stability *before* upgrading**
- Pyrolysis oil characterization
  - Liquid and solid state NMR
  - Stability testing
- Catalytic upgrading of bio-oils through hydrodeoxygenation
  - Ru catalysts
  - Mo_2N catalysts (with Nestor Escalona, UdeC)

1865 THE UNIVERSITY OF MAINE

FOREST BIOPRODUCTS RESEARCH INSTITUTE

New pyrolysis strategies

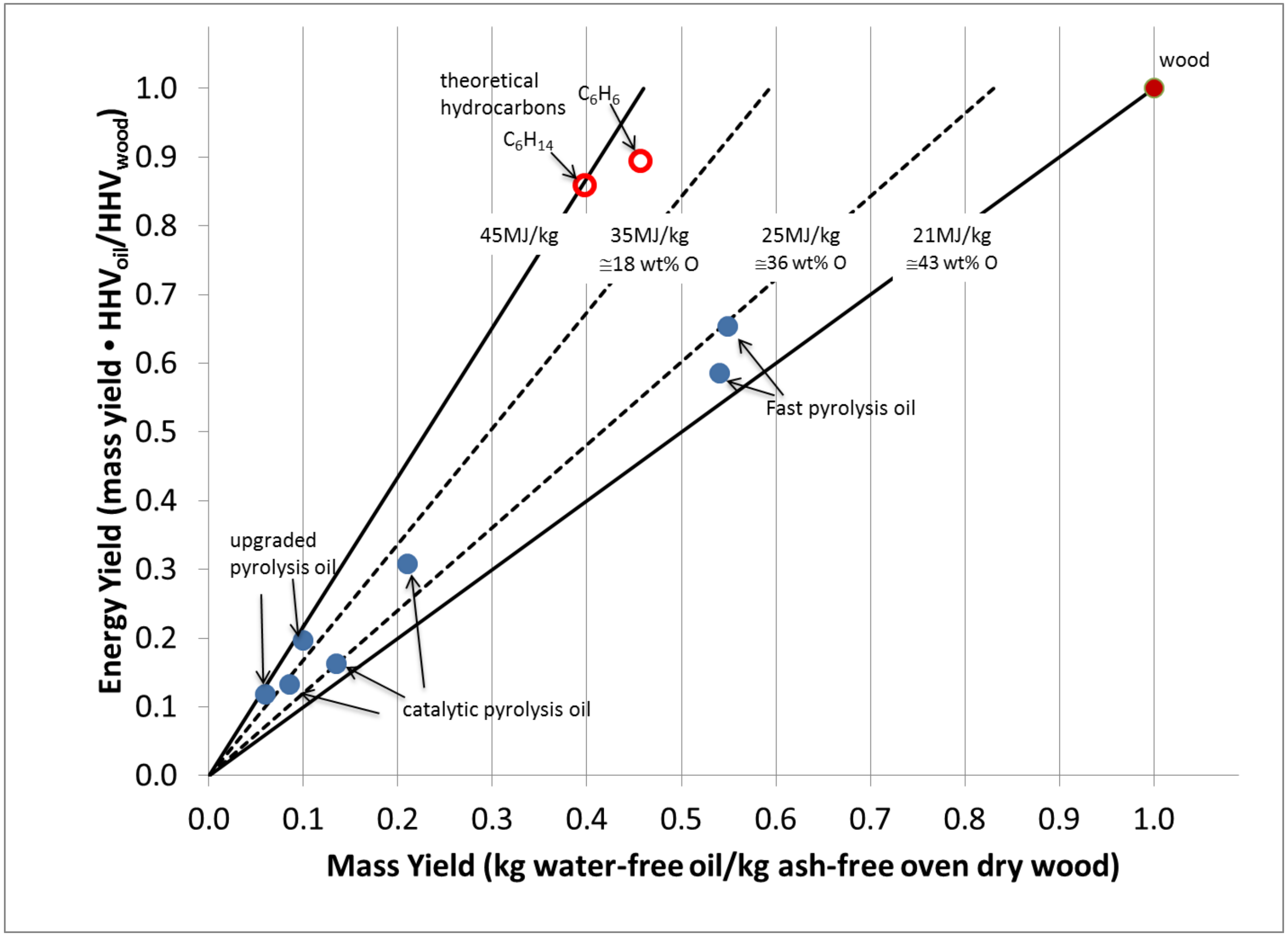
- Improving quality requires oxygen removal
- ***Can oxygen be removed while maintaining high energy yields in the liquid product?***

Biomass (wood) → hydrocarbons

$$CH_{1.5}O_{0.65} \rightarrow 0.7CH_{2} + 0.3CO_{2} + 0.05H_{2}O$$

$$CH_{1.5}O_{0.65} \rightarrow 0.84CH + 0.16CO_{2} + 0.033H_{2}O$$

Energy yields for pyrolysis and upgrading processes (funnel plot)



Pyrolysis and upgrading process inefficiencies

- Some biomass will inevitably form primary char or coke
- Carbon is lost through non-condensable gases, methane, carbon monoxide, etc.
- Secondary vapor phase reactions can lead to both char and gas formation
- Hydroprocessing and hydrocracking catalytic processes
  - High hydrogen pressures
  - Coking/Deactivation
  - Attrition

Pyrolysis processing strategies

- Two innovative processes at the University of Maine
  - **Thermal deoxygenation of hydrolyzed biomass**
  - **Formate-assisted pyrolysis of biomass**

- Formic acid is known to donate hydrogen
- Formate salts decompose into H_2 and CO at pyrolysis temperatures

$$Ca(HCOO)_2 \xrightarrow[\Delta]{} CaCO_3 + CO + H_2$$

New Method for Biomass to Drop-in Hydrocarbon Fuels: Thermal Deoxygenation

High yields of carbohydrate conversion to oil

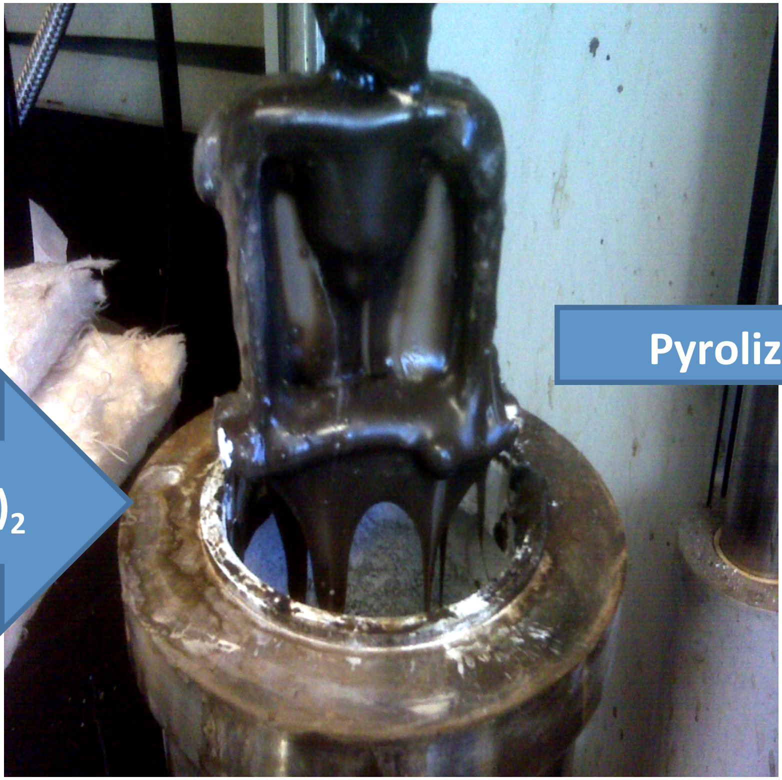
HHV=41MJ/kg

<1% Oxygen

TAN = 1 mgKOH/g

Hydrolysis and Dehydration

Add Ca(OH)$_2$



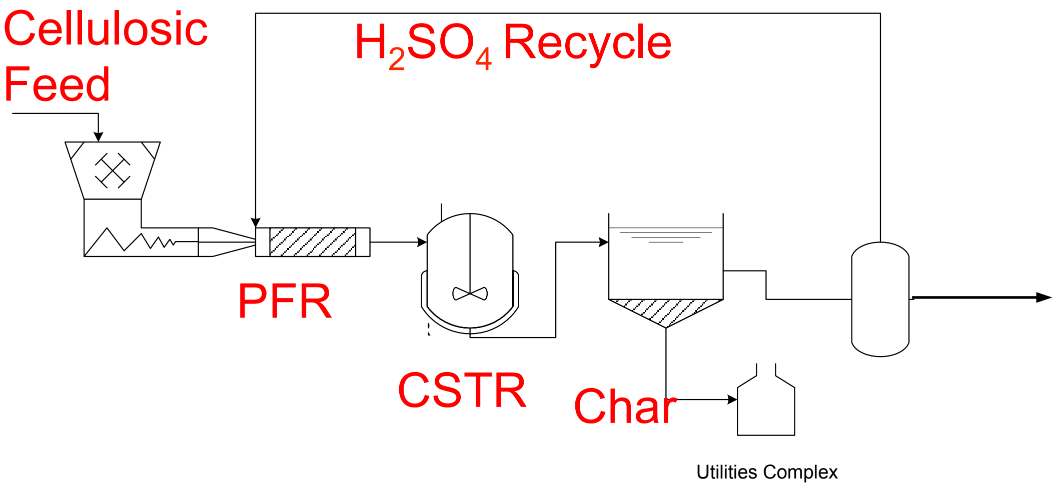
Pyrolize

1865 THE UNIVERSITY OF MAINE

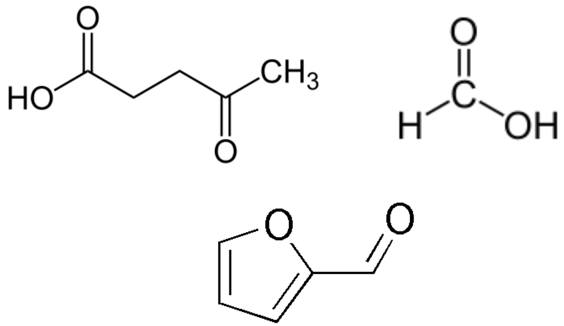
FOREST BIOPRODUCTS RESEARCH INSTITUTE

Hydrolysis + Ketonization

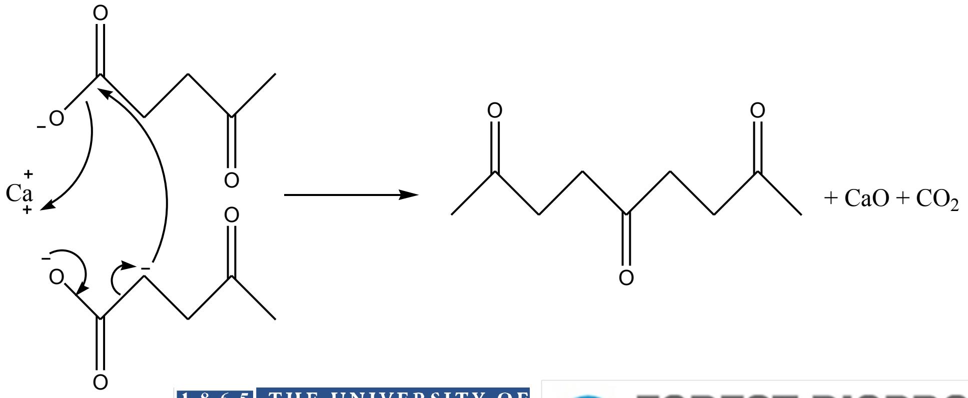
- Biofine Hydrolysis (Fitzpatrick, S.W., U.S. Patents 4,897,497 and 5,608,105)



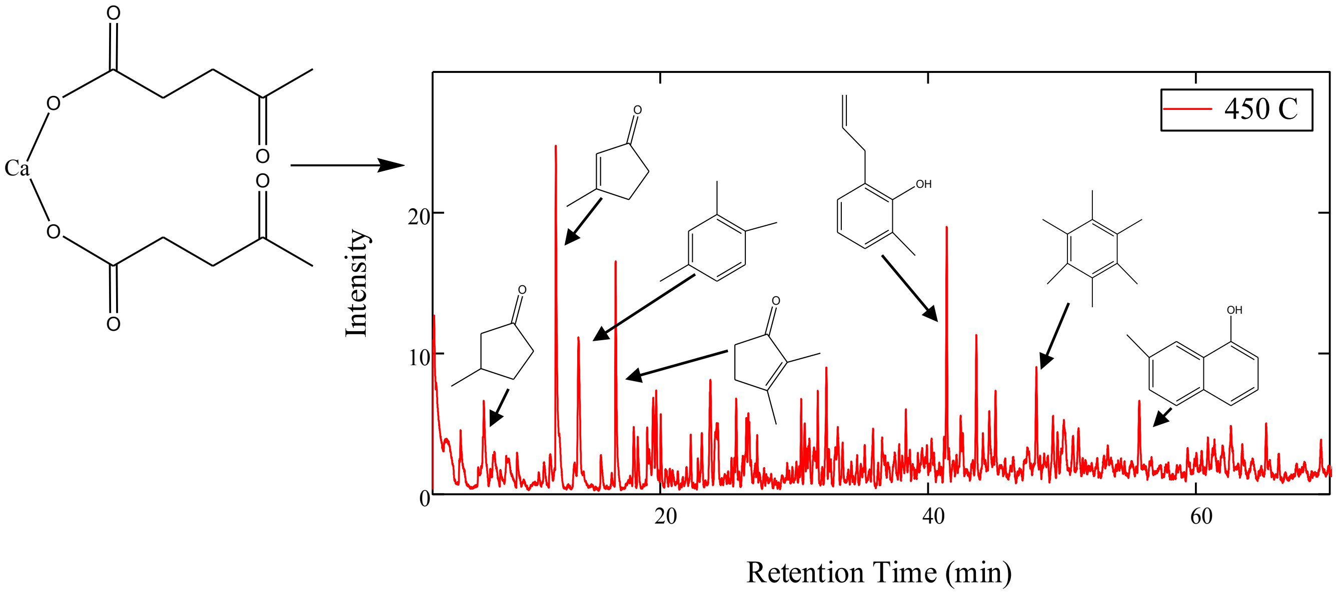
Hydrolysis Products



- Hypothetical Ketonization of Levulinic Acid



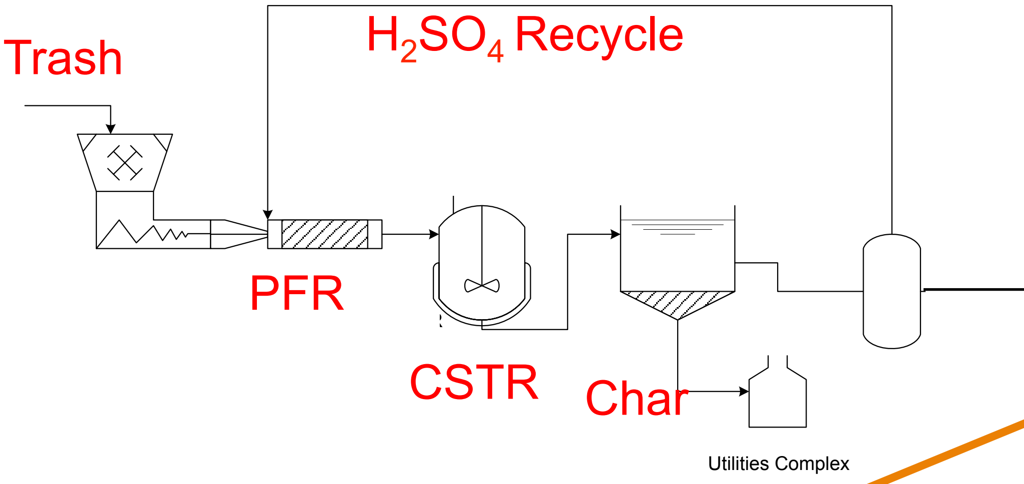
Thermal Deoxygenation (TDO) of Calcium Levulinate



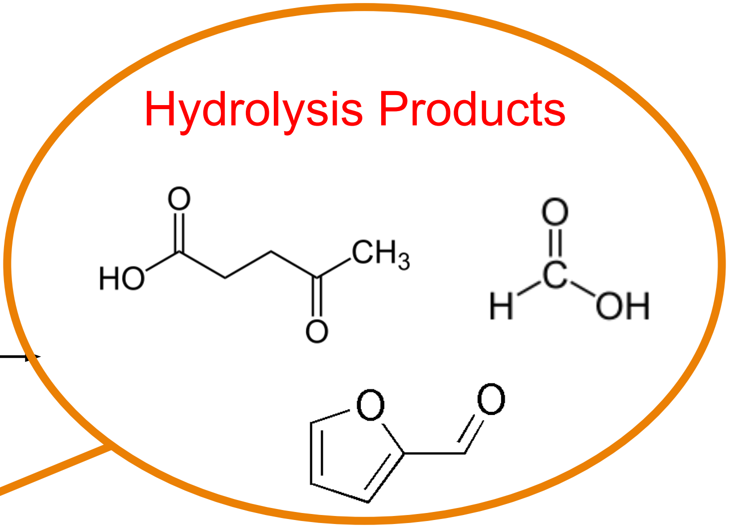
*T. Schwartz, et al., Green Chem., 2010, **12**, 1353–1356.*

- Ramp to 450°C with N_2 purge
- Water soluble products
- No predicted ketone observed
- 35 MJ/kg (calorimetry of extracts)

Next we attempted TDO of Biofine Hydrolyzate



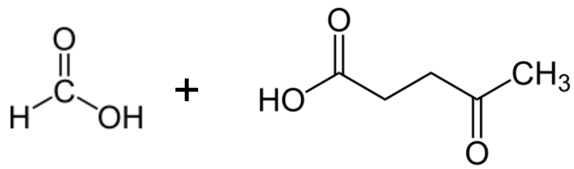
Hydrolysis Products



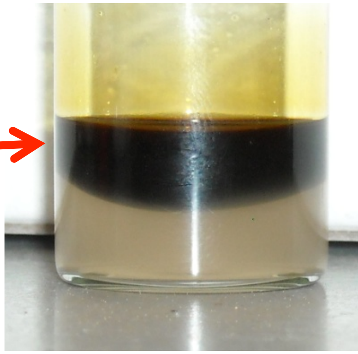
$+ \; Ca(OH)_2 + \Delta \longrightarrow$

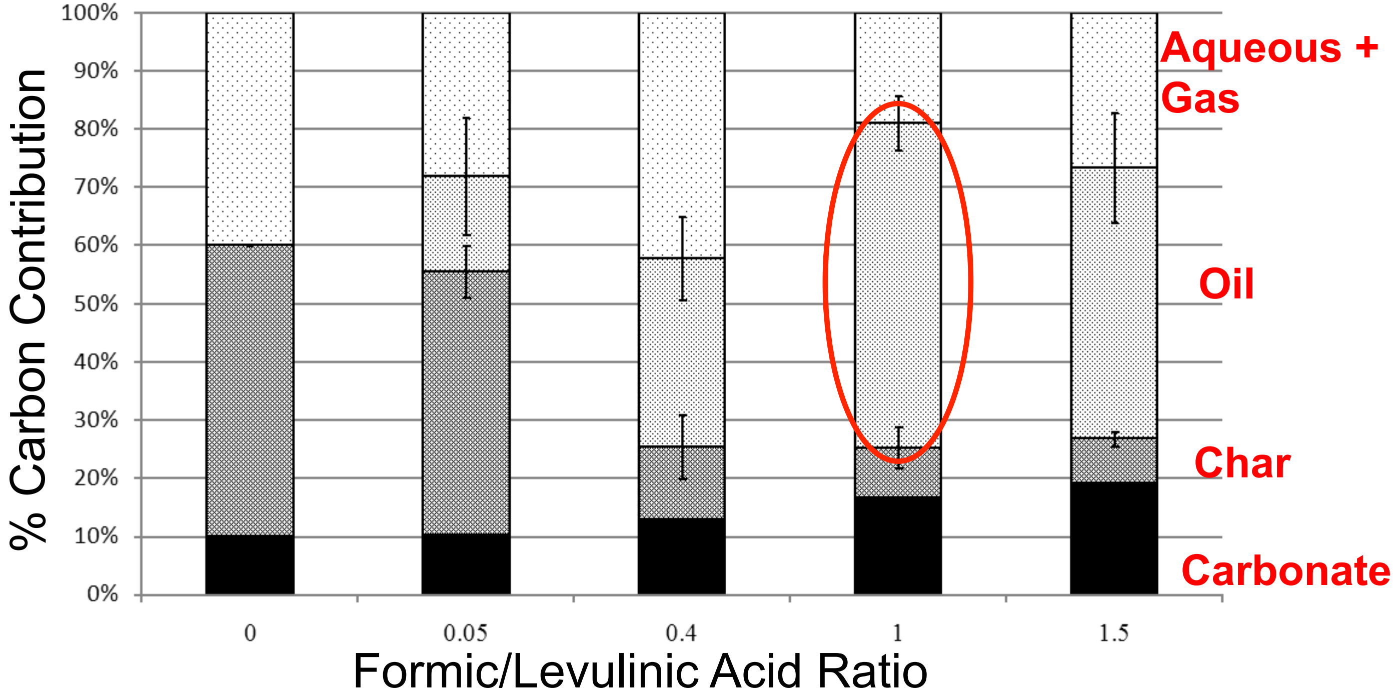
Levulinic Acid + Impurities

Formic Acid is the Key



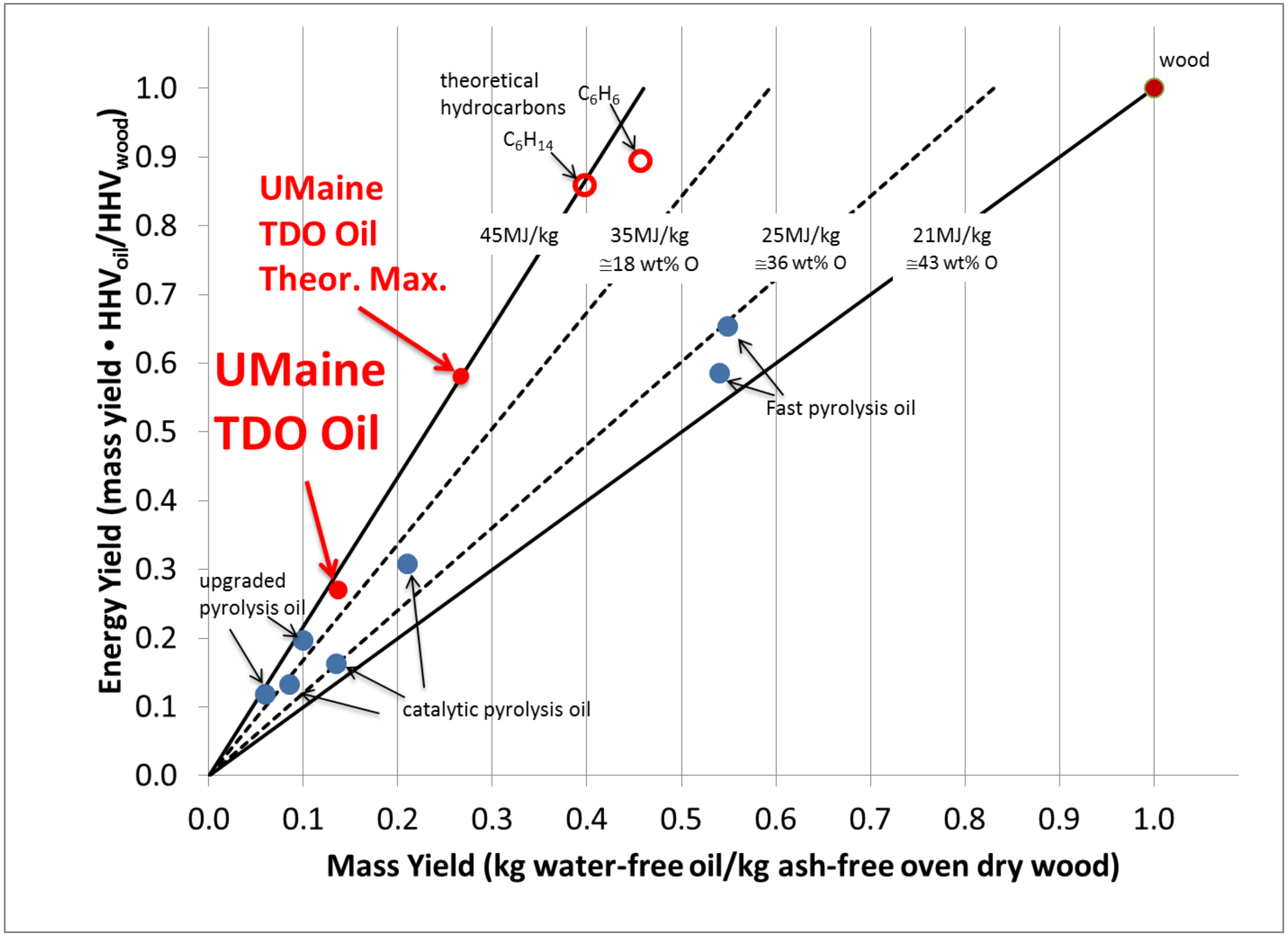
+ $Ca(OH)_2$ + Δ





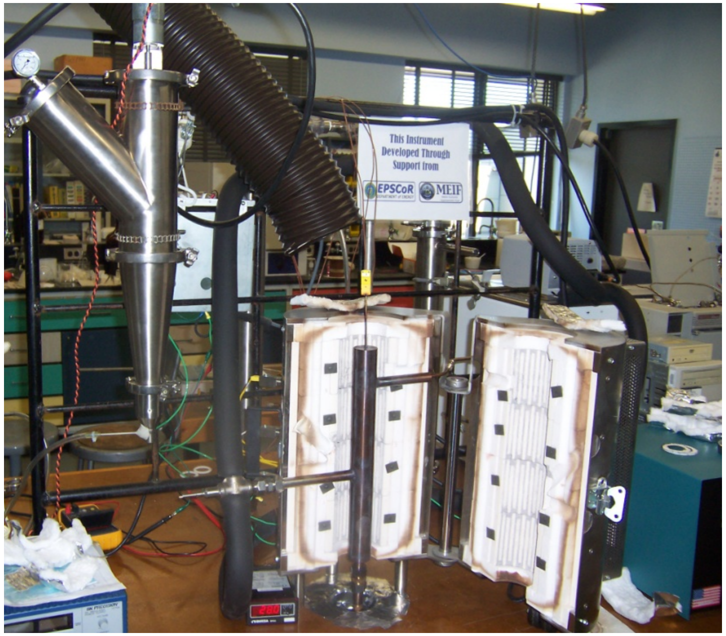
P.A. Case et al., Green Chem. 2012, ***14,*** *85*

TDO efficiency



Co-pyrolyze biomass with formic acid salts

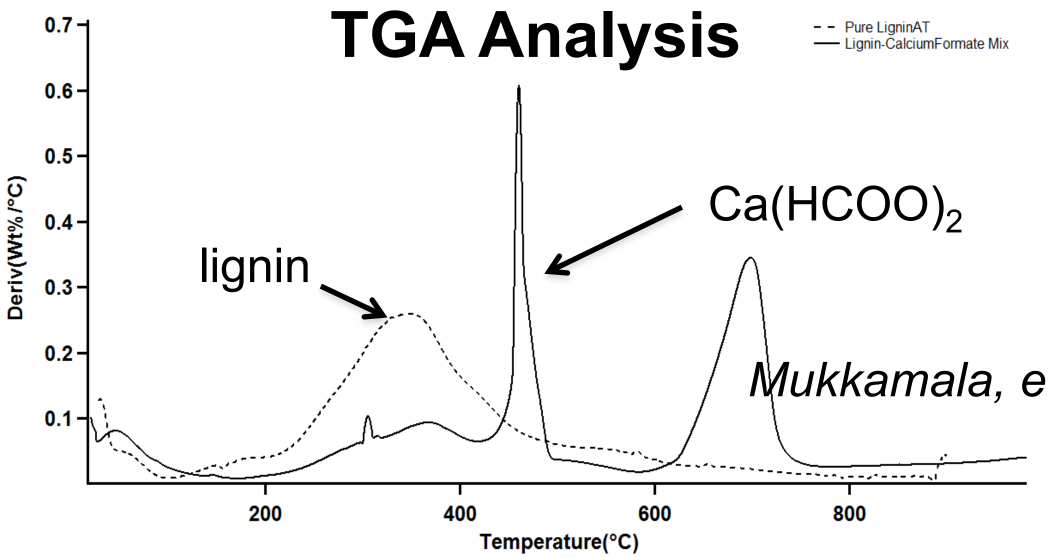
- Apply fast pyrolysis to biomass feedstock pre-mixed with calcium formate (Formate-Assited Pyrolysis, FAsP)
  - Pine sawdust and lignin
  - Eliminate hydrolyzate process
  - Continuous processing at atmospheric pressure and NO precious metal catalysts!



$$Ca(HCOO)_2 \xrightarrow[\Delta]{} CaCO_3 + CO + H_2$$

Lignin FAsP

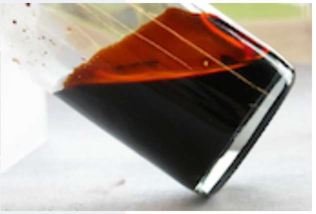
- Indulin AT Lignin (Mead Westvaco)
- Pyrolysis of lignin challenges


TGA Analysis

Mukkamala, et al. Energy Fuels 2012, ***26****, 1380*

Calcium formate increases energy yield in oil with deoxyhydrogenation

Feed	Lignin (Indulin AT)	Lignin/$Ca(OH)_2$	Formate/lignin 0.5gm/gm	Formate/ lignin 1 gm/gm
Liquid yield (wt%)	23	23.3	28.5	**32.5**
C yield in oil (wt%)	21.3	20.4	23.4	**28.6**
Energy yield (%)	24.3	24.5	25.4	**33.0**
O:C	0.19	0.21	0.14	**0.067**
H:C	0.96	0.97	1.23	**1.40**
HHV (MJ/kg)	30.7	32.1	37.2	**41.7**



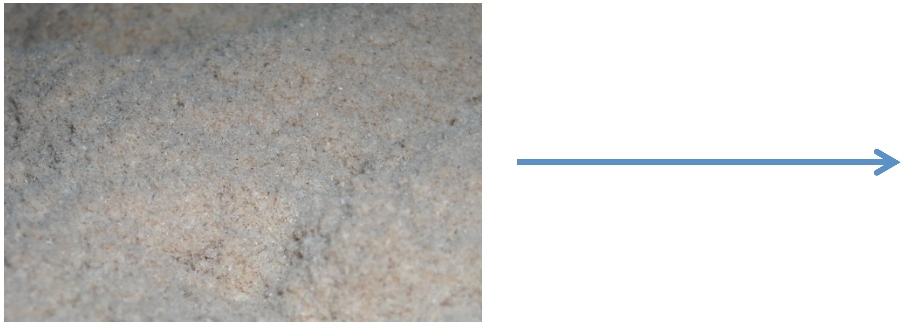
Lignin FAsP

- O:C↓ H:C↑
- Methoxy phenols → alkylated phenols
- Liquid and energy yields increased

- Deoxyhydrogenation from $Ca(HCOO)_2$ reduces char production through stabilizing intermediates
- CO and H_2 are active
  - No hydrogenation catalyst

Pine sawdust FAsP

- Mix pine sawdust with calcium formate
- Continuous fast pyroylsis
  - 500ºC
  - 2-3 sec residence time

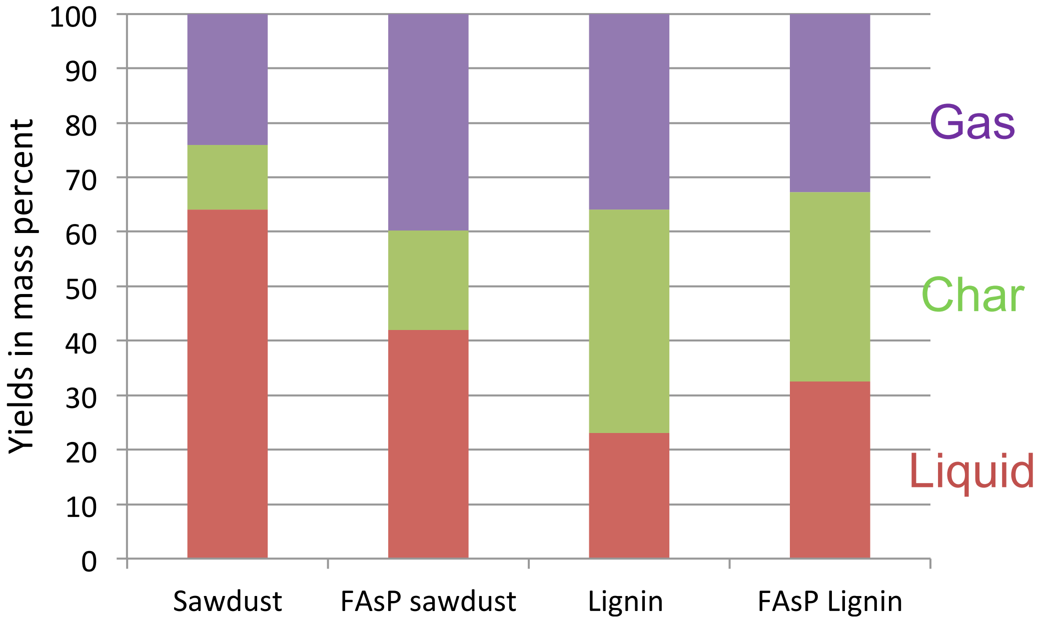


THE UNIVERSITY OF MAINE 1865

FOREST BIOPRODUCTS RESEARCH INSTITUTE

FAsP Oil yields and composition

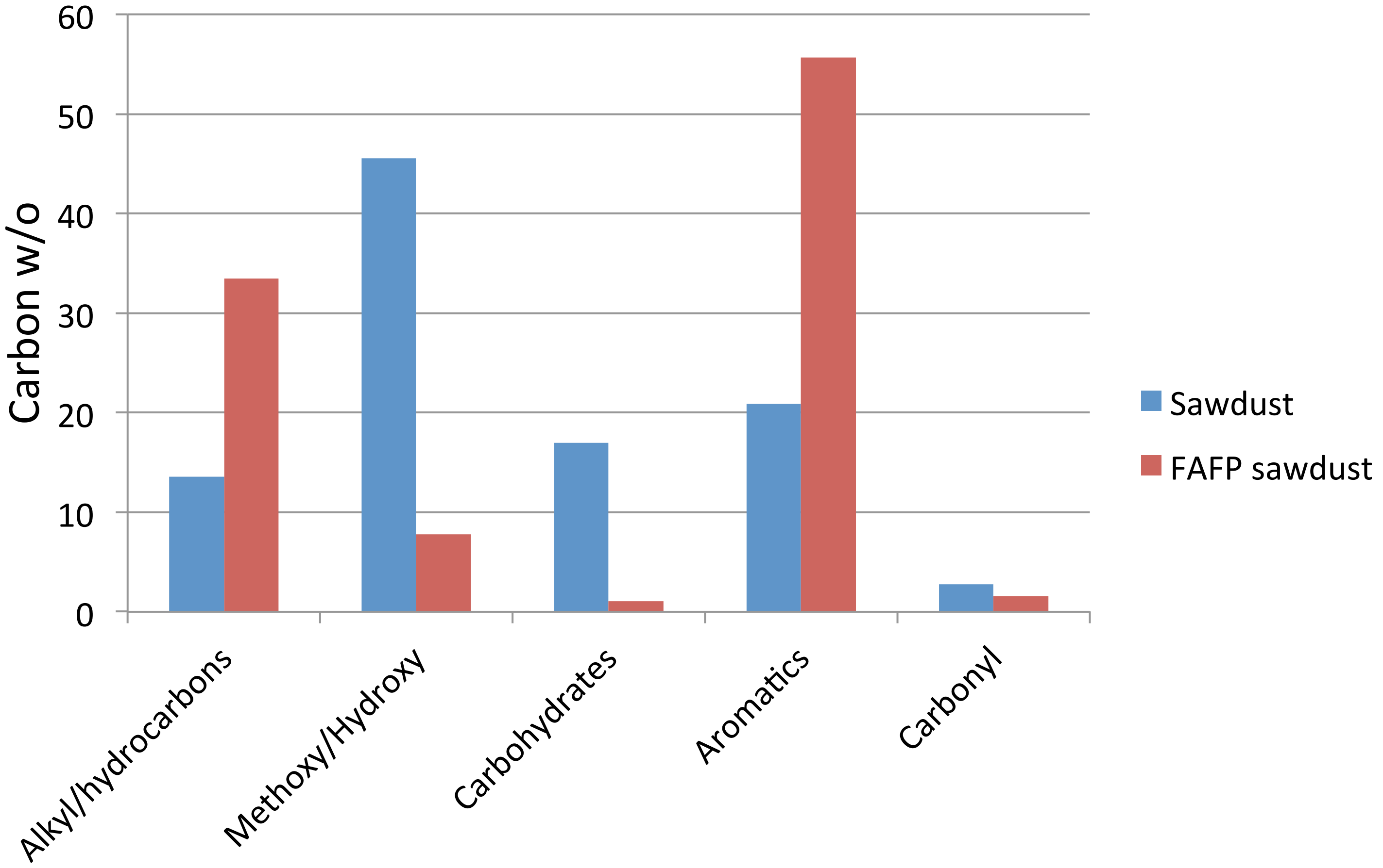
	Pine	FAsP Pine
Liquid yield (%)	64	42
Ash(wt%)	0.11	0.09
C yield wt% in oil	57.5	37.1
O: C	0.29	0.07
H:C	1.0	1.3
HHV(MJ/Kg)	24.3	40.1



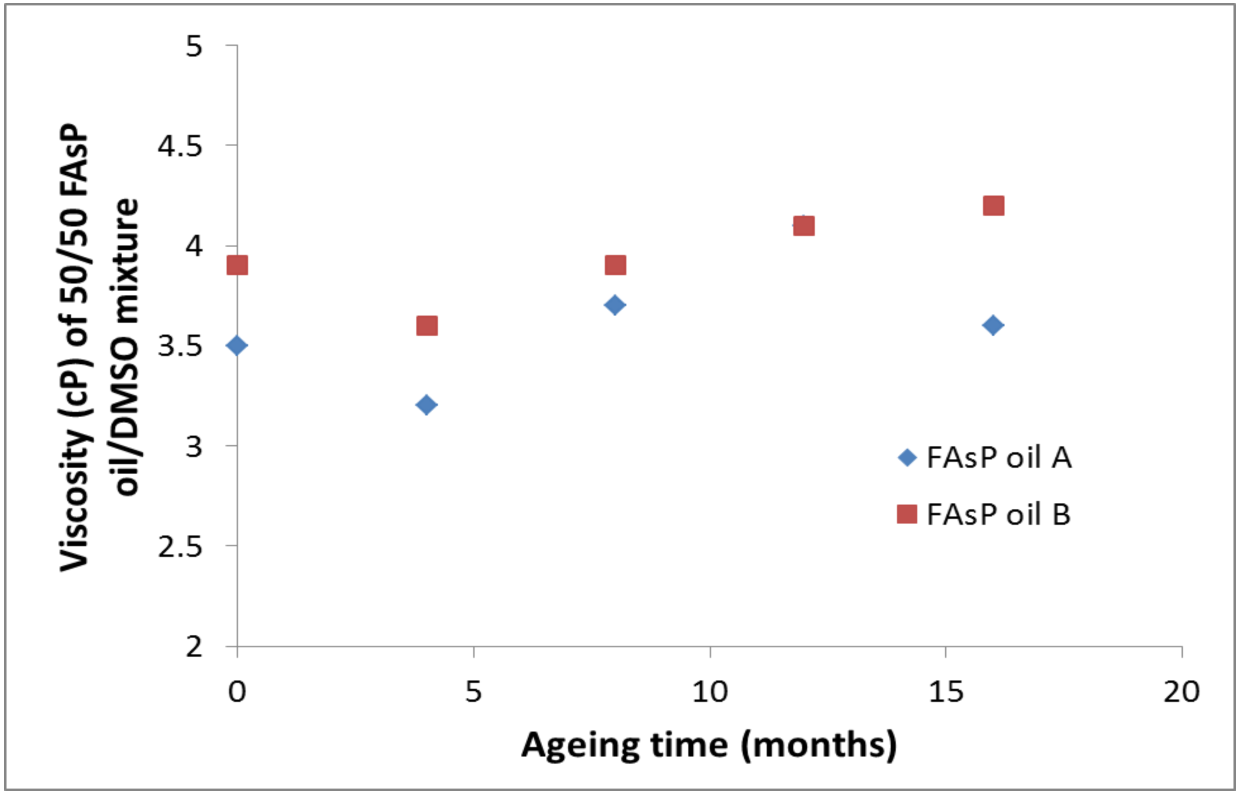
Temperature 500°C

Feed 1gm/min

^{13}C NMR Analysis

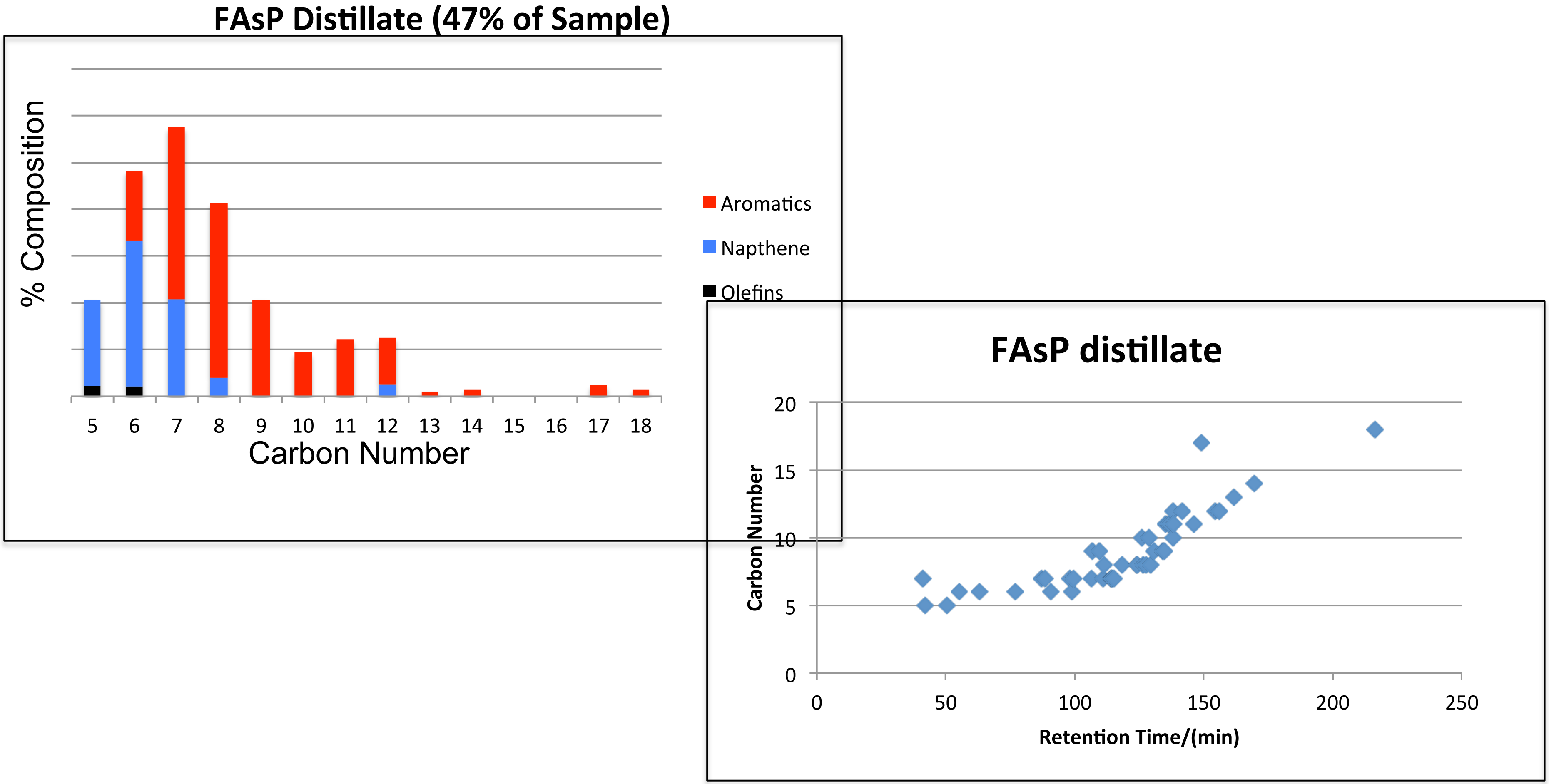


FAsP Pine stability

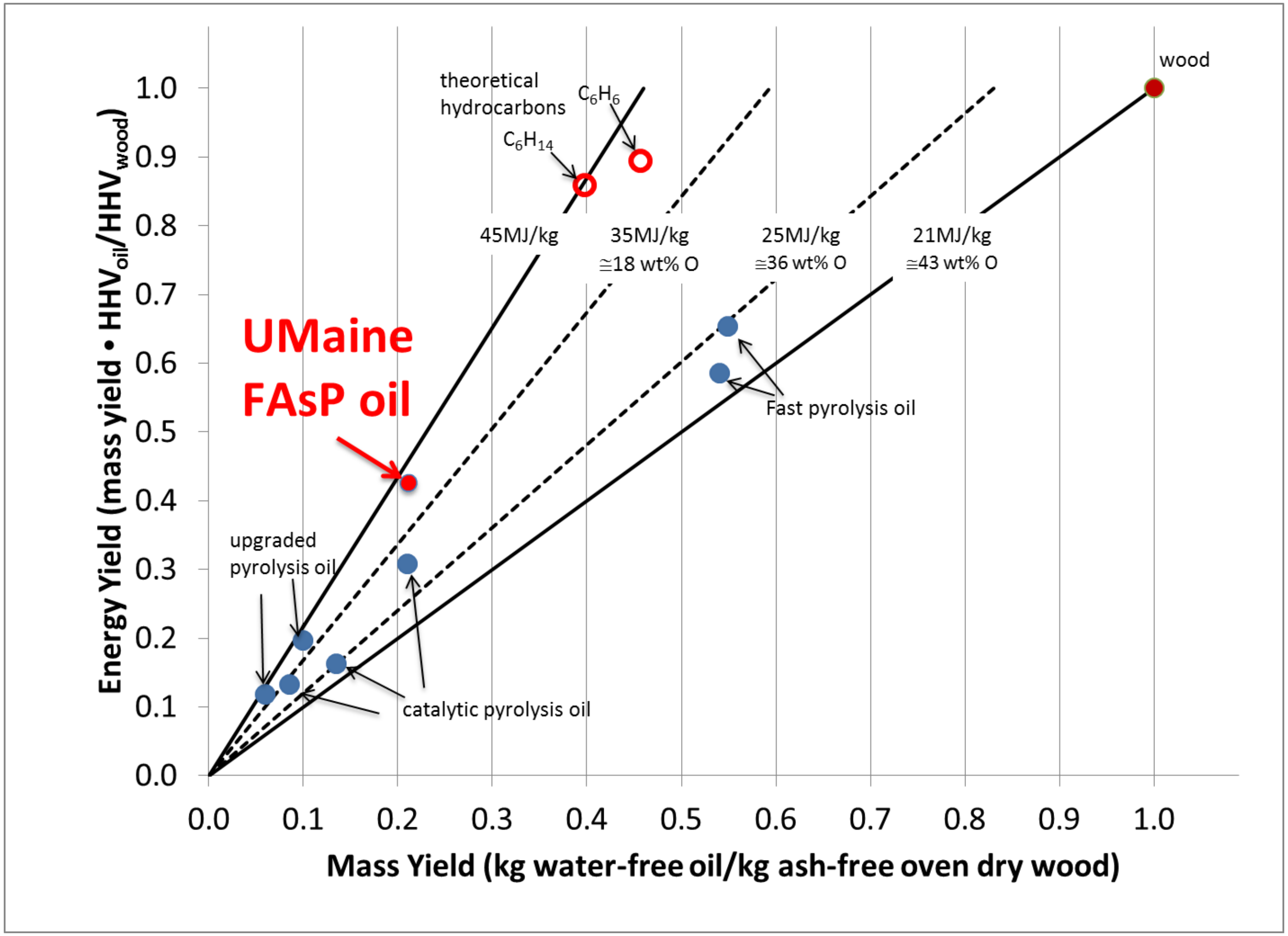


C13 NMR integration values				
	Corrected areas			
		Sample A		Sample B	
types of C	ppm	0m aged	16m aged	0m aged	16m aged
alkyl	0-54	36.1%	39.4%	34.2%	35.2%
methoxy/hydroxy	54-70	2.5%	2.3%	5.9%	5.6%
carbohydrate	70-103	1.3%	1.1%	2.5%	2.4%
aromatic	103-163	51.7%	52.3%	49.7%	49.3%
carbonyl	163-215	8.4%	5.0%	7.7%	7.5%

Preliminary PONA analysis of FAsP bio-oil



FAsP improves energy yield



FAsP challenges

- Metal formate and formic acid requirements
  - Reduce loading to 11%, similar mass yield at HHV 36 MJ/kg (lower energy yield)
  - Feedstock costs
    - ~$80/bbl at current yields with $70/dry ton biomass and $500/ton calcium formate (11%)
    - Integrated production of formate
- Fundamental processes
  - Mass transfer limitations
  - Catalytic effects of the metal oxide
  - Critical factors in increasing mass yields (avoid the funnel)
  - Balance between dehydration/hydrogenation

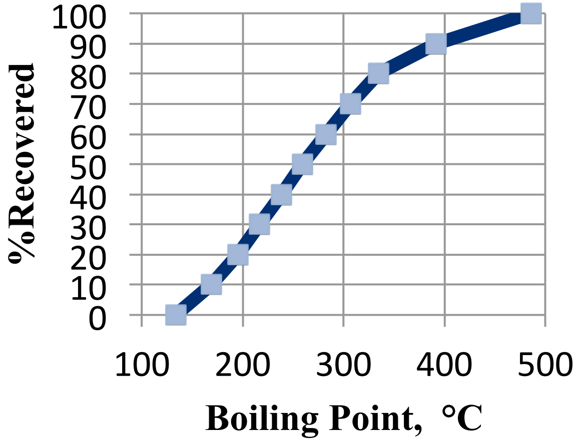
Independent Testing of Washed Crude TDO Oil Produced from Biomass Hydrolyzate

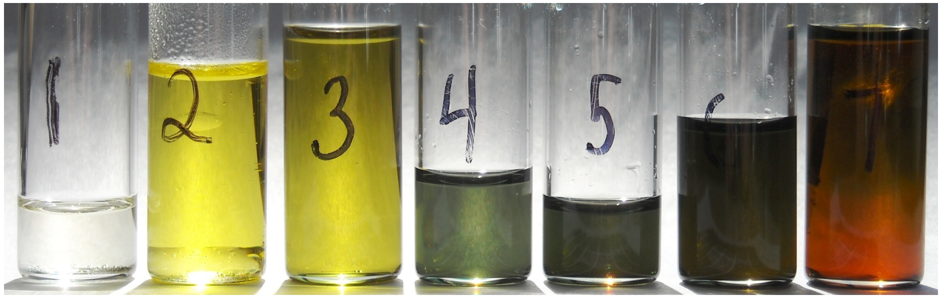
Total Acid Number	1.02 mg KOH/g
Ramsbottom Carbon Residue	0.48 wt%

OXYGENATES (0.86%) GC Low Ox method (ppm)	
Acetaldehyde	43
Methanol	18
Ethanol	53
Propanols	44
n-Butanol	14
Butyraldehyde	16
Methyl T-Butyl Ether	24
Ally Alcohol	4
tert-Amyl Alcohol	15
Vinyl Acetate	8338

TRACE METALS	ICP (ppm)
Aluminum	<0.1
Arsenic	<0.1
Barium	<0.1
Beryllium	<0.1
Bismuth	<0.1
Boron	<0.1
Cadmium	<0.1
Calcium	4.5
Chromium	<0.1
Cobalt	<0.1
Copper	0.4
Iron	8.8
Lead	0.3
Magnesium	<0.1
Potassium	0.2
Sodium	0.2

Boiling Point Distribution
(ASTM D7169)

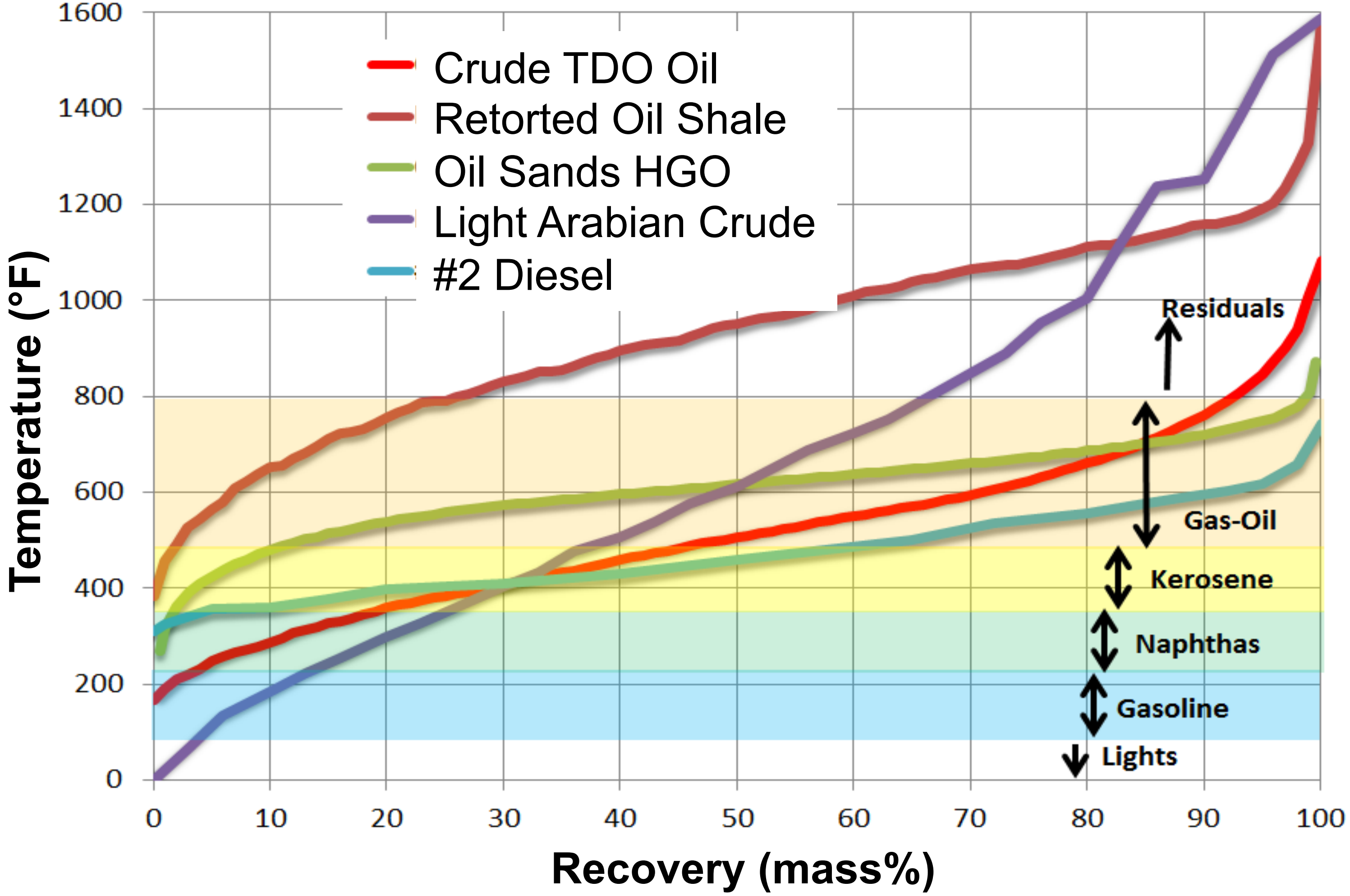




1865 THE UNIVERSITY OF MAINE

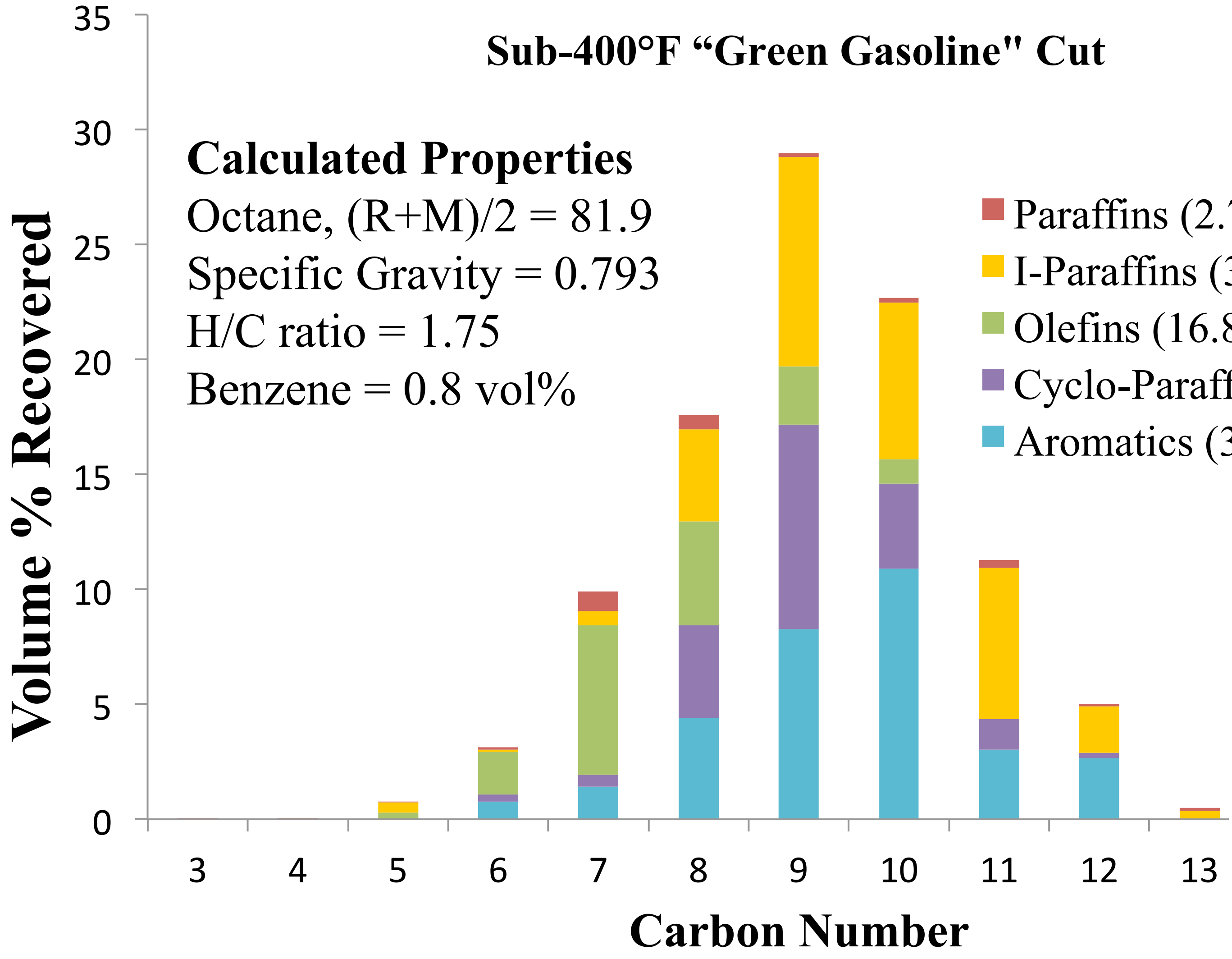
FOREST BIOPRODUCTS RESEARCH INSTITUTE

Comparison of Boiling Point Distributions



> ~80% Overlap with #2 diesel

PONA Analysis (ASTM D6730)



Calculated Properties

Octane, (R+M)/2 = 81.9

Specific Gravity = 0.793

H/C ratio = 1.75

Benzene = 0.8 vol%

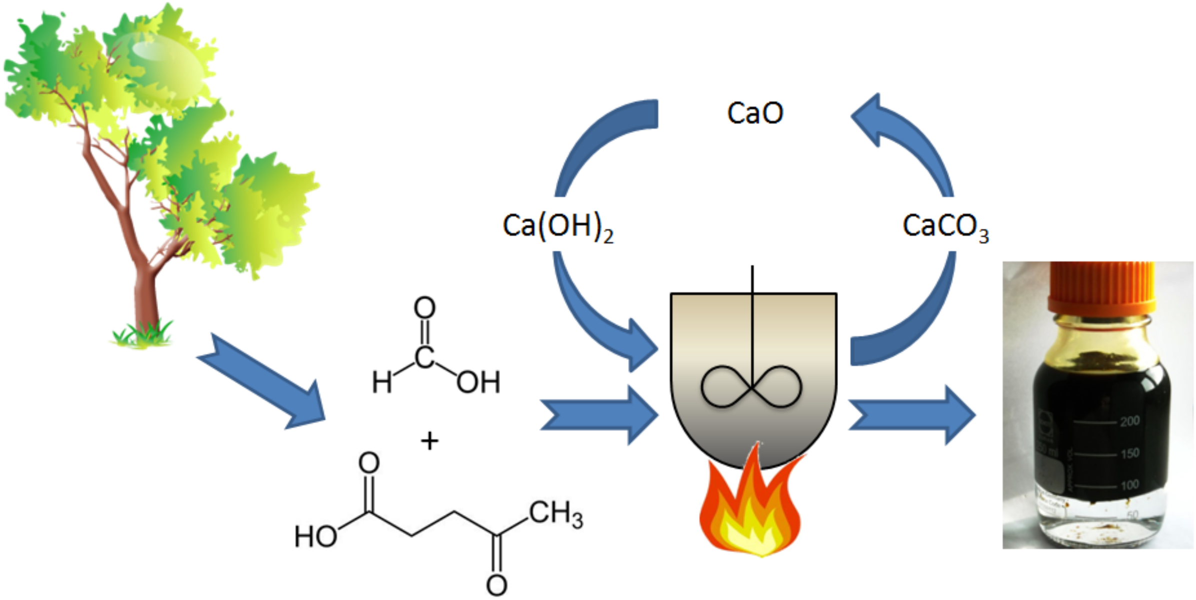
1865 THE UNIVERSITY OF MAINE

FOREST BIOPRODUCTS RESEARCH INSTITUTE

Conclusions/Implications

- Atmospheric pressure TDO and FAsP processes for producing deoxyhydrogenated generated bio-oils
- No hydrogen
- No precious metal catalysts
- Cation may be regenerated in pulp-mill-based biorefinery
- Pyrolytic “deoxyhydrogenation” tolerant to impurities

Acknowledgements



- Co-Authors and Collaborators
  - Adriaan van Heiningen
  - Brian Frederick
  - Nestor Escalona
  - Cristina Segura
  - Rachel Austin
  - Hemant Pendse
  - Peter van Walsum
  - Elizabeth Stemmler

- Students
  - Paige Case
  - Scott Eaton
  - Tyrone Ghampson
  - Jincy Joseph
  - Lina Kong
  - Katherine Leiva
  - Daniel Moberg
  - Cody Newman
  - Ta-Hsuan Ong
  - Saikrishna Mukkamala
  - Eric Pier
  - Rachel Pollock
  - Brenna Walsh
  - Thomas Schwartz
  - Catherine Sepulveda
  - Timothy Thibodeau
  - Joshua Wright

- Nick Hill
- Funding
  - UMaine Forest Bioproducts Research Institute
  - U.S. Dept. of Energy DE-FG02-07ER46373 and DE-FG36-08GO18165

1865 THE UNIVERSITY OF MAINE

FOREST BIOPRODUCTS RESEARCH INSTITUTE

Questions?