Advanced Analytical Methodologies Enable Feedstock Screening and Correlation to Pyrolysis Yields and Catalytic Upgrading

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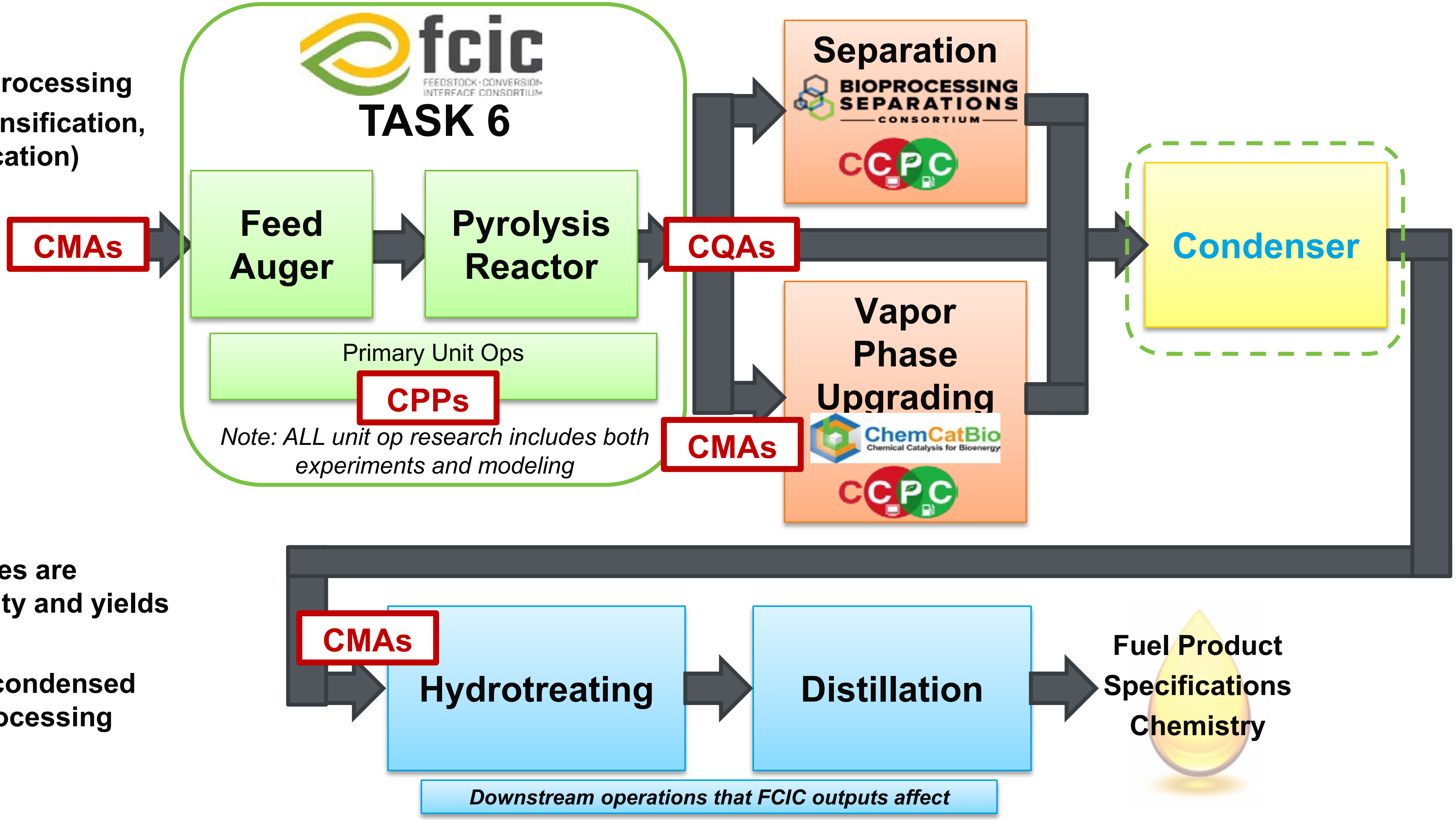
2021 AIChE Annual Meeting

11/15/2021

FCIC Task 6

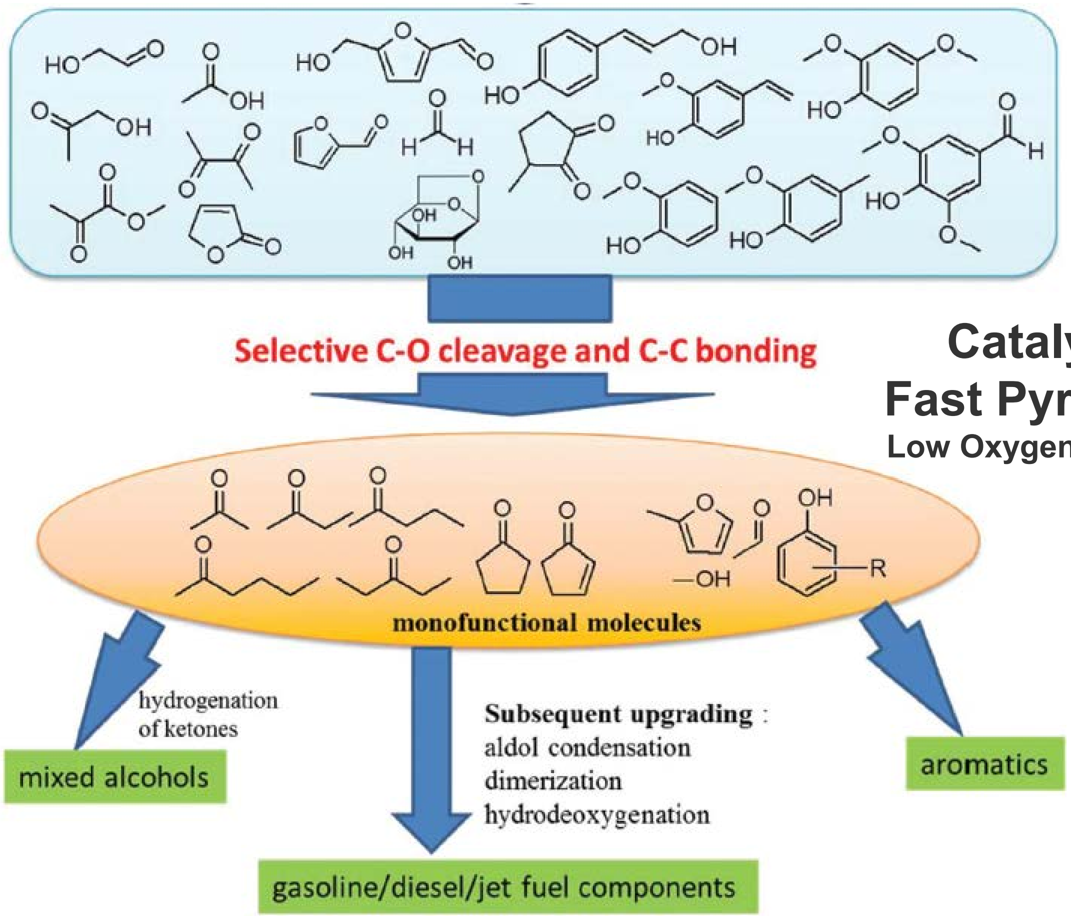
<u>From:</u> Preprocessing (milling, densification, air classification)



- **What feedstock attributes are responsible for oil quality and yields**
- **What properties in the condensed liquids effect further processing**

Pyrolysis of Lignocellulosic Biomass

Fast Pyrolysis
High Oxygen Content



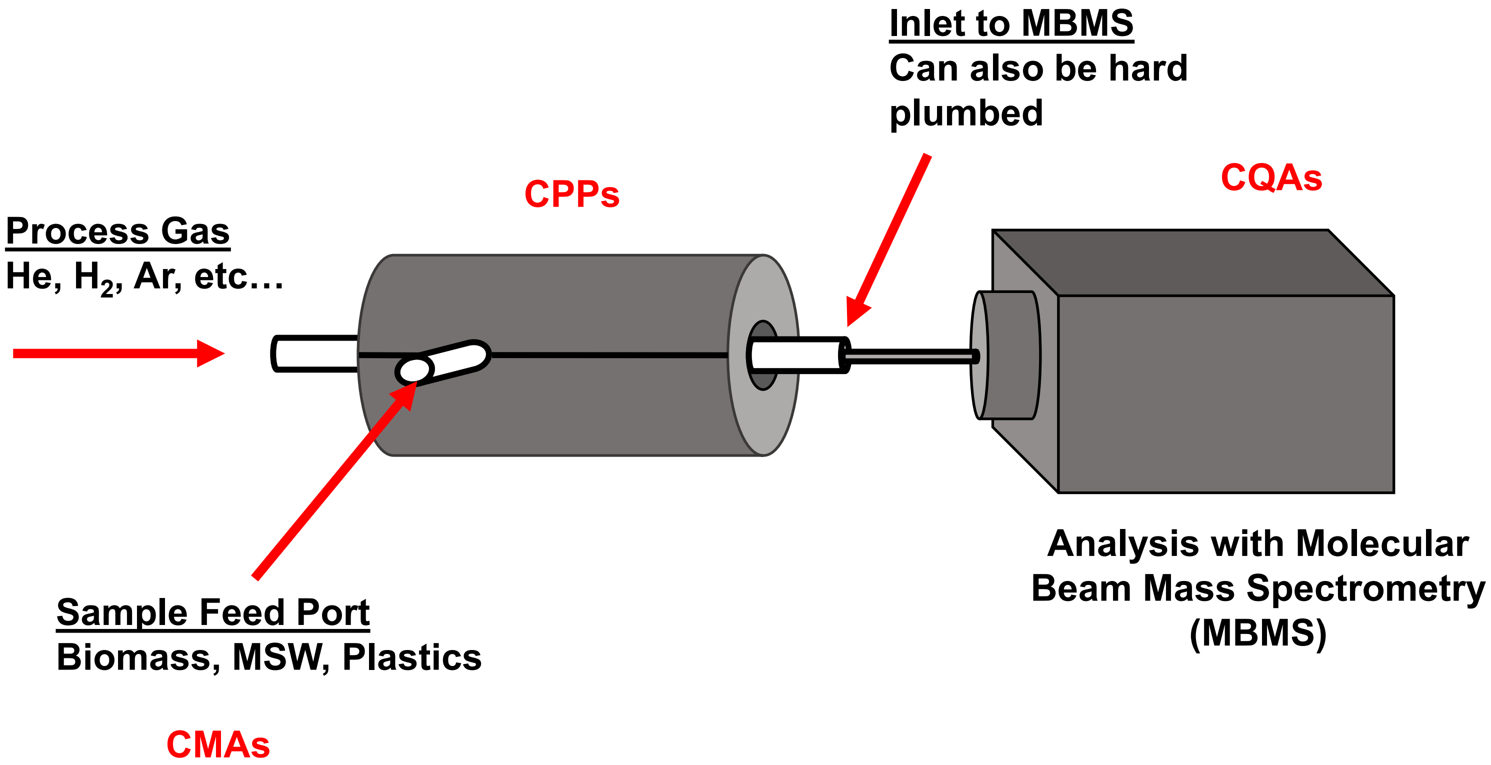
Catalytic Fast Pyrolysis
Low Oxygen Content

Less than half of carbon balance is accounted for by GC methods

Direct mass spectral analysis can provide insight into unaccounted-for components of vapors and oils.

Mante, O. D., *et al.*, *Green Chem.*, 2015, 17, 2362-2368

Direct Analysis of Pyrolysis Vapors



Can do pyrolysis with or without catalyst
Multi-zone furnace allows for a range of pyrolysis and upgrading temps.

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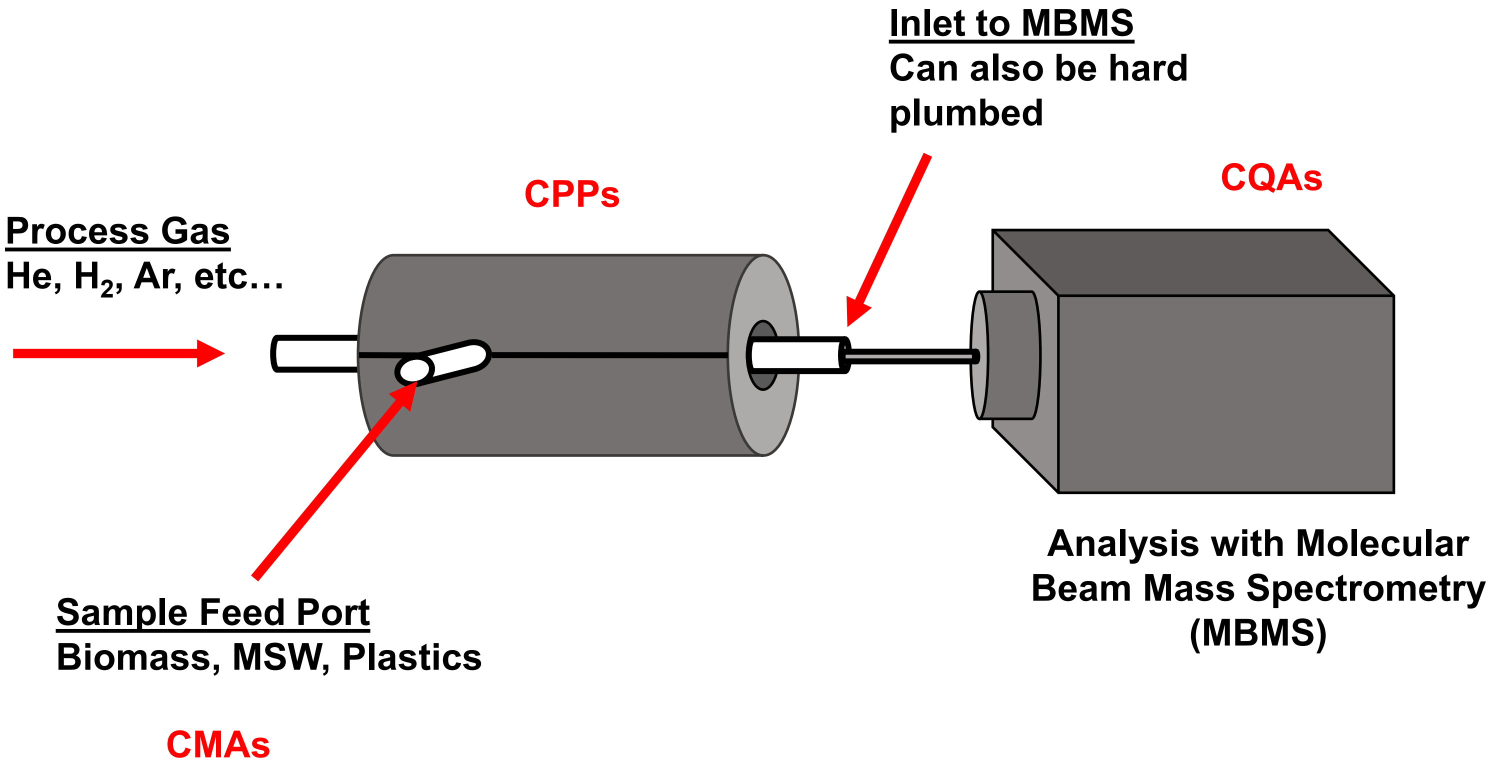
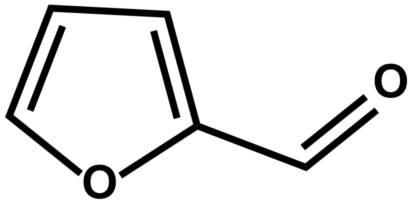


Can do pyrolysis with or without catalyst
Multi-zone furnace allows for a range of pyrolysis and upgrading temps.
Direct analysis without GC addresses limitations of mass yield

Furfural



Mass = 96 g/mol

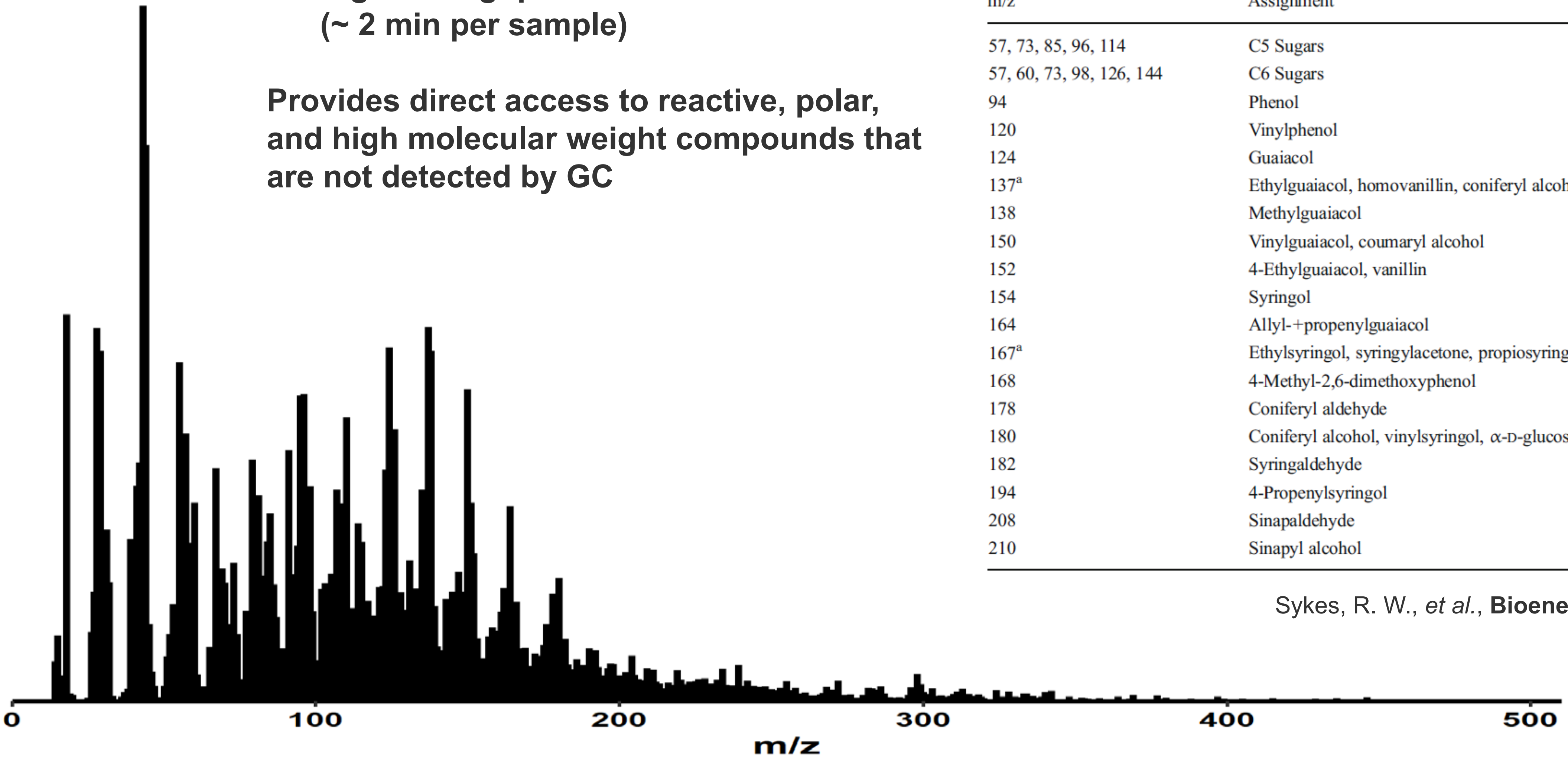
m/z = 96 Th

Vapor Composition From Mass Spectrum

Can detect hundreds of chemical signals simultaneously

- **High throughput data collection (~ 2 min per sample)**

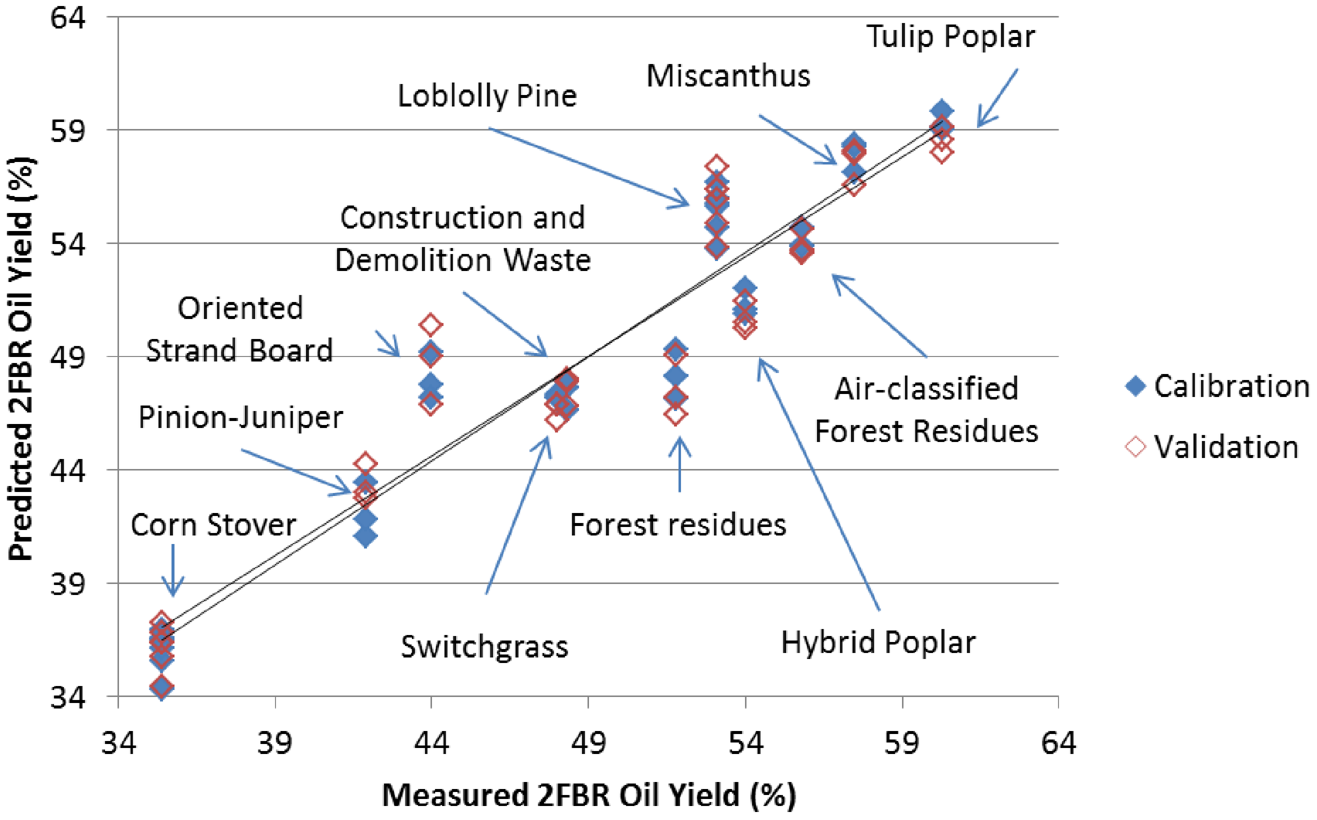
Provides direct access to reactive, polar, and high molecular weight compounds that are not detected by GC



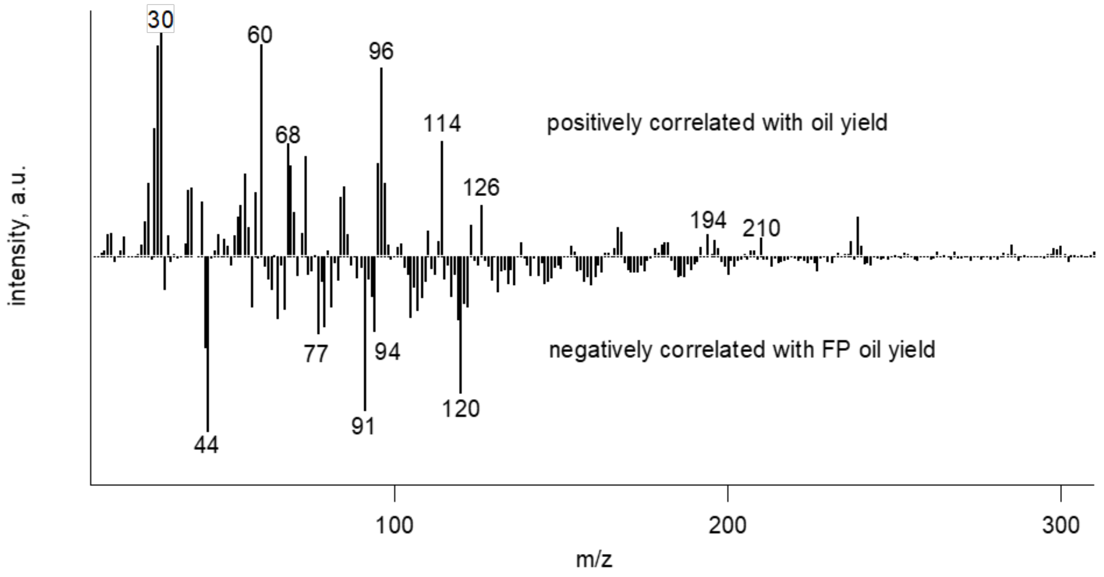
m/z	Assignment	Precursor Type
57, 73, 85, 96, 114	C5 Sugars	
57, 60, 73, 98, 126, 144	C6 Sugars	
94	Phenol	H, S, G
120	Vinylphenol	H, S, G
124	Guaiacol	G
137[a]	Ethylguaiacol, homovanillin, coniferyl alcohol	G
138	Methylguaiacol	G
150	Vinylguaiacol, coumaryl alcohol	G
152	4-Ethylguaiacol, vanillin	G
154	Syringol	S
164	Allyl-+propenylguaiacol	G
167[a]	Ethylsyringol, syringylacetone, propiosyringone	S
168	4-Methyl-2,6-dimethoxyphenol	S
178	Coniferyl aldehyde	G
180	Coniferyl alcohol, vinylsyringol, α-D-glucose	S, G
182	Syringaldehyde	S
194	4-Propenylsyringol	S
208	Sinapaldehyde	S
210	Sinapyl alcohol	S

Sykes, R. W., *et al.*, **Bioenerg. Res.,** 2015, 964-972

Correlation of Vapor to Oil Yield



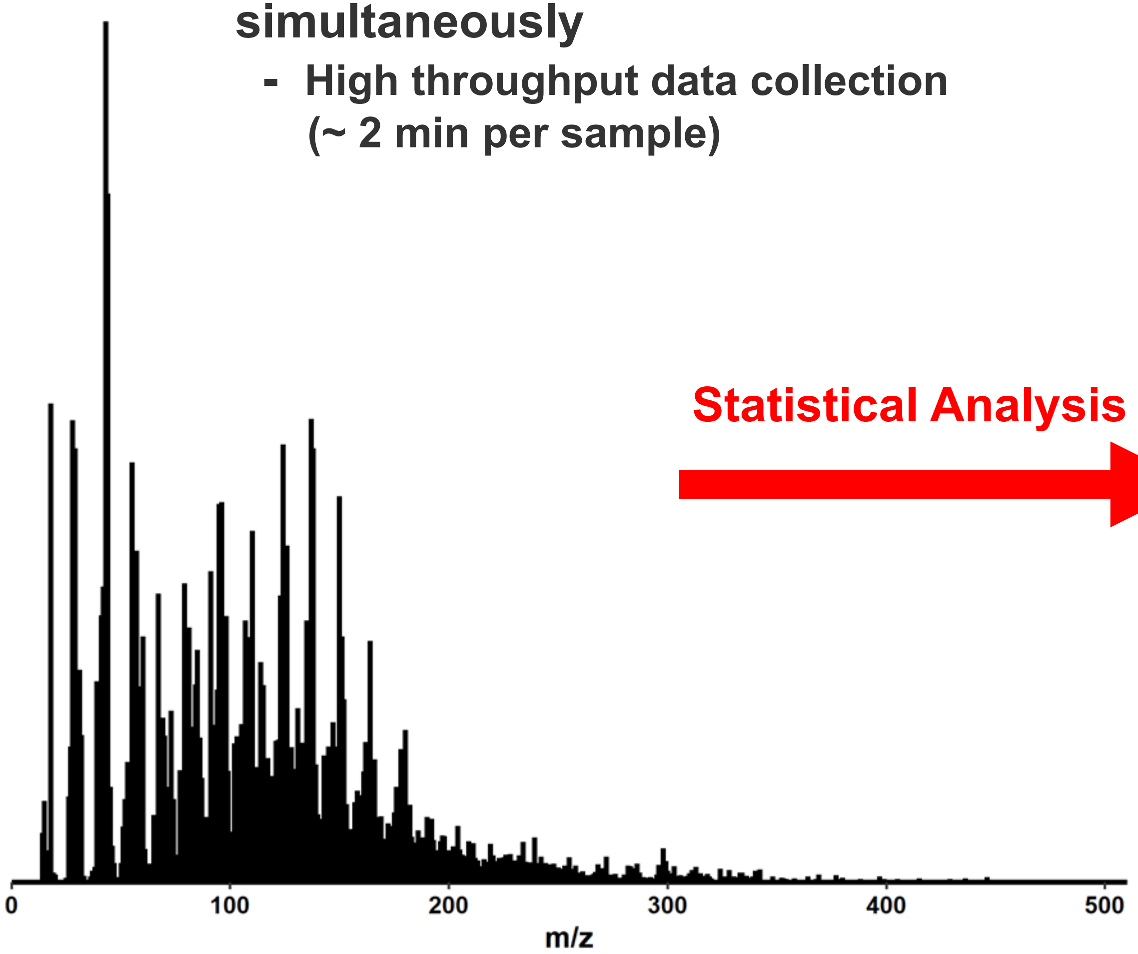
- **PLS regression provides predictive model for oil yield.**
- **Wide range of feedstocks correlate well with predicted values from MBMS analysis**



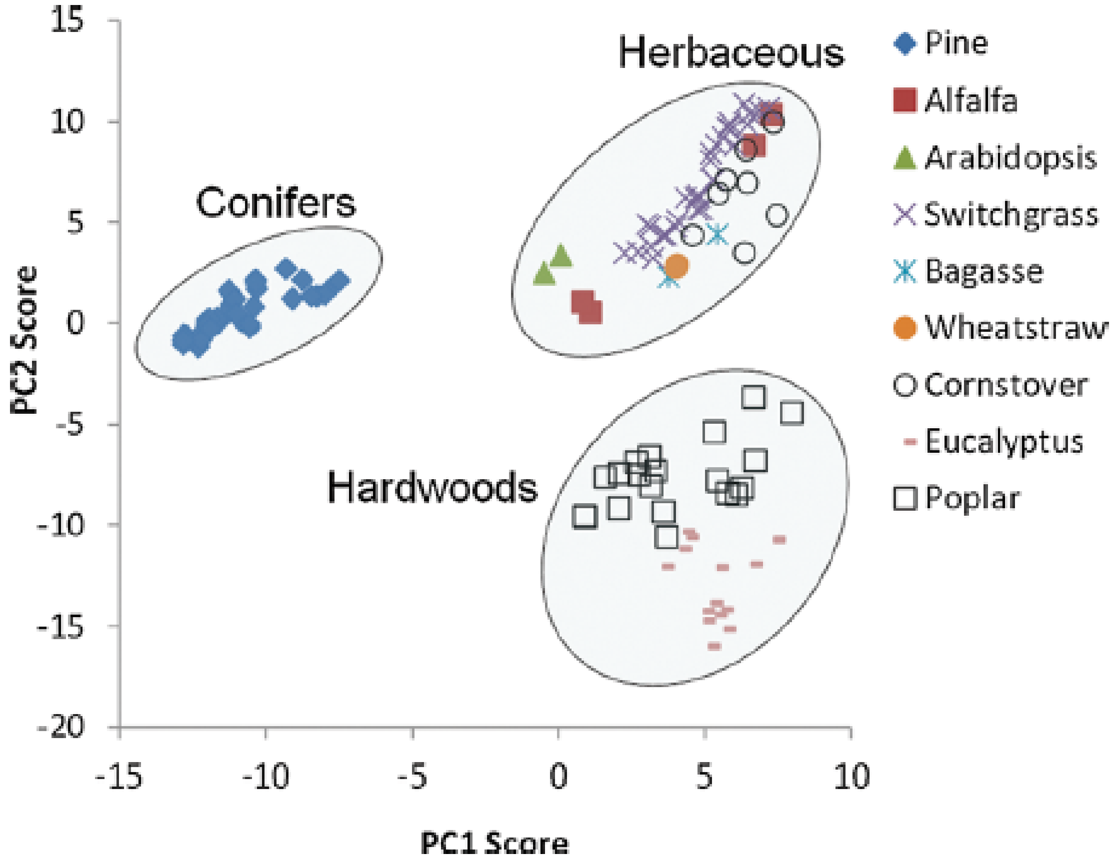
Vapor Composition Based on Feedstocks

Can detect many chemical signals simultaneously

- **High throughput data collection (~ 2 min per sample)**



Statistical Analysis



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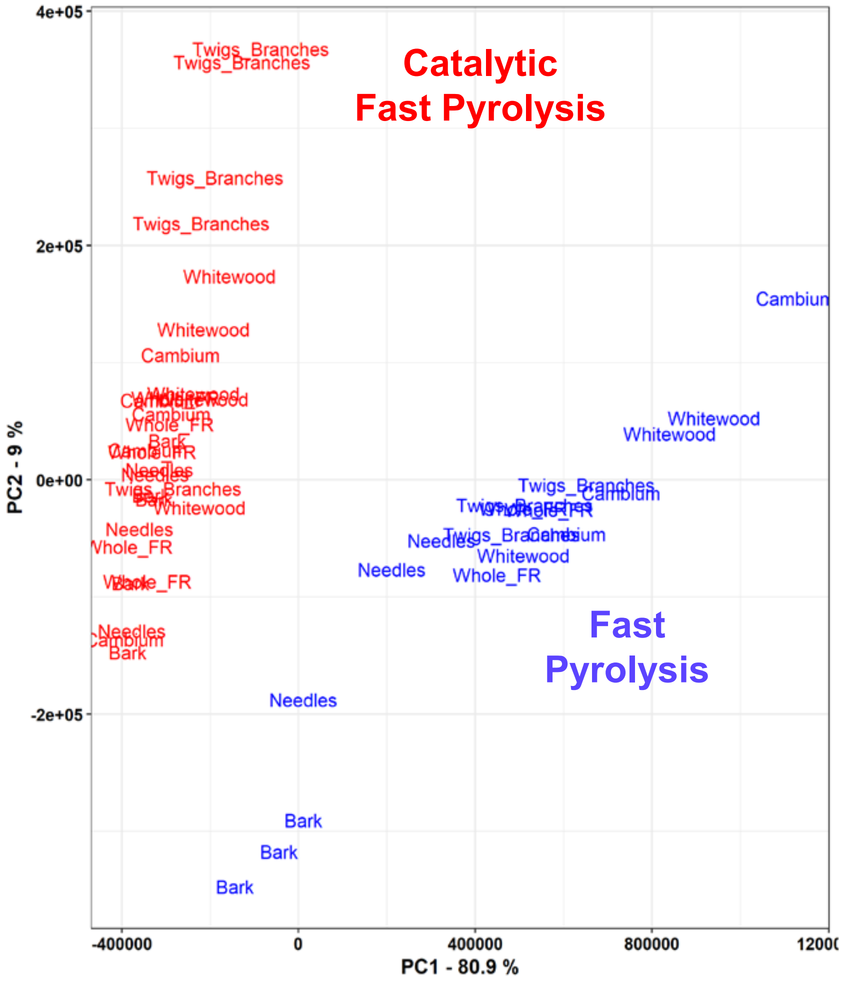
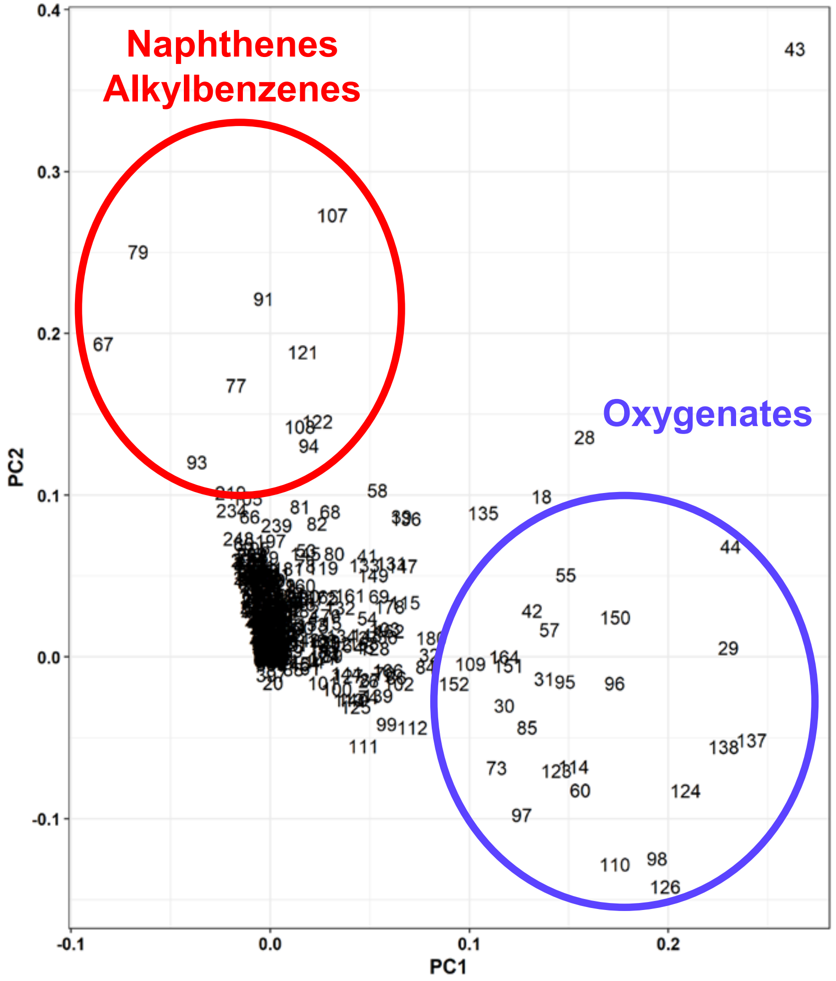
Upgraded Vapor Composition

Feedstock screening for pine anatomical fractions
- **fast pyrolysis**
- **catalytic fast pyrolysis (Pt/TiO2)**

Primary separator is oxygen content

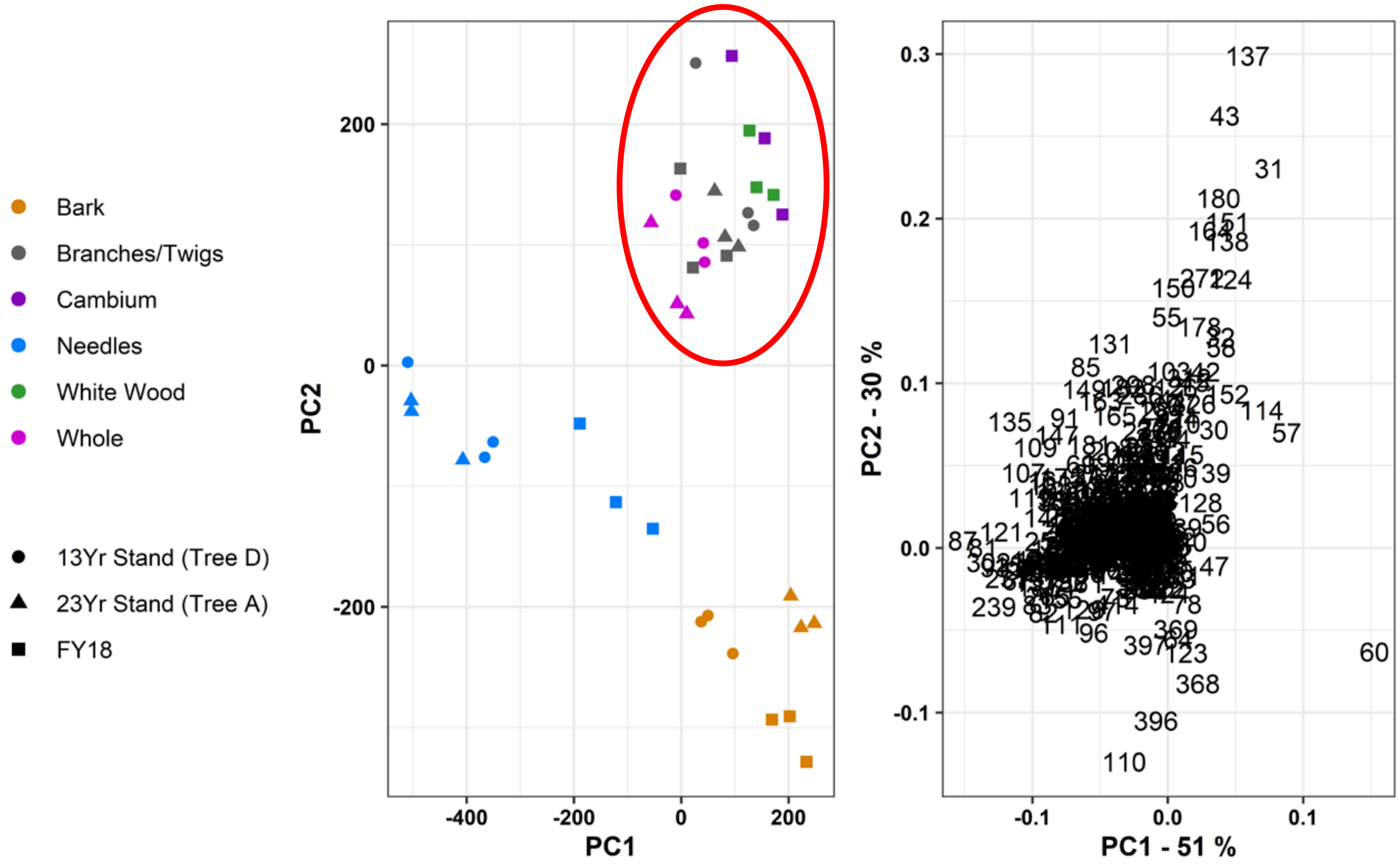
Some secondary separation between anatomical fractions





Direct Analysis of Pyrolysis Vapors

Woody Feedstocks



Fast Pyrolysis

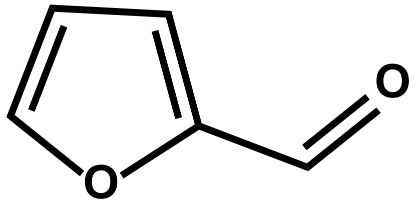
- **Main separation is between woody components and bark/needles**

More difficult to discern

Some secondary separation between anatomical fractions

Need For Better Mass Measurement

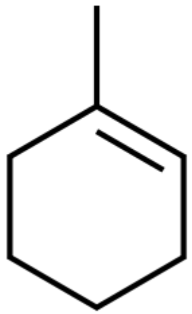
Furfural



m/z = 96 Th

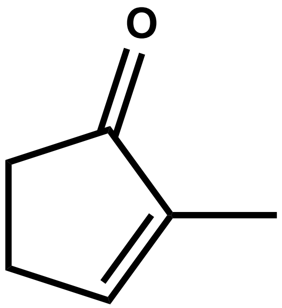
Need For Better Mass Measurement

1-Methylcyclohex-1-ene



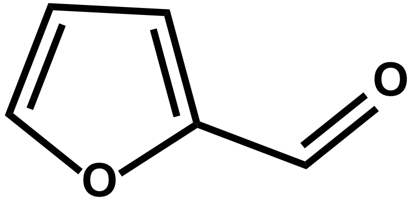
m/z = 96 Th

2-Methyl-2-cyclopentene-1-one



m/z = 96 Th

Furfural



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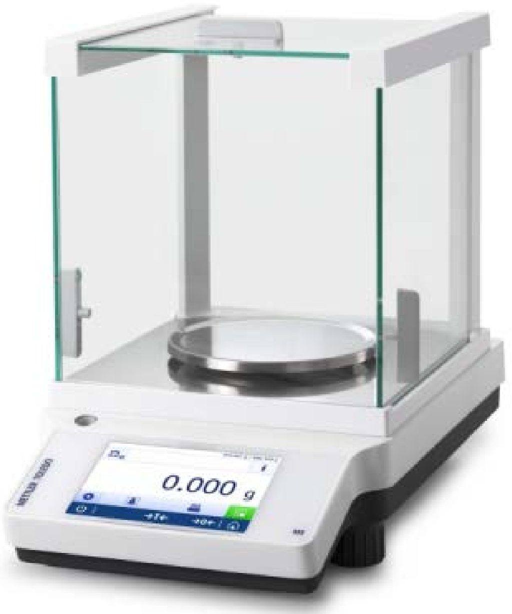
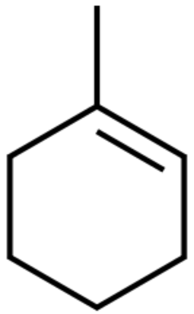
Need For Better Mass Measurement

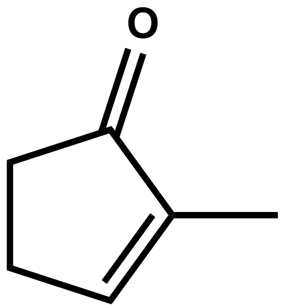


1-Methylcyclohex-1-ene



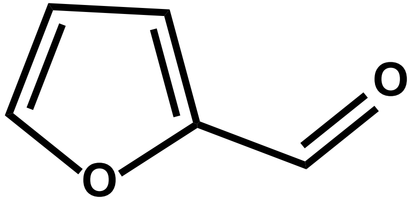
m/z = 96.0939 Th

2-Methyl-2-cyclopentene-1-one



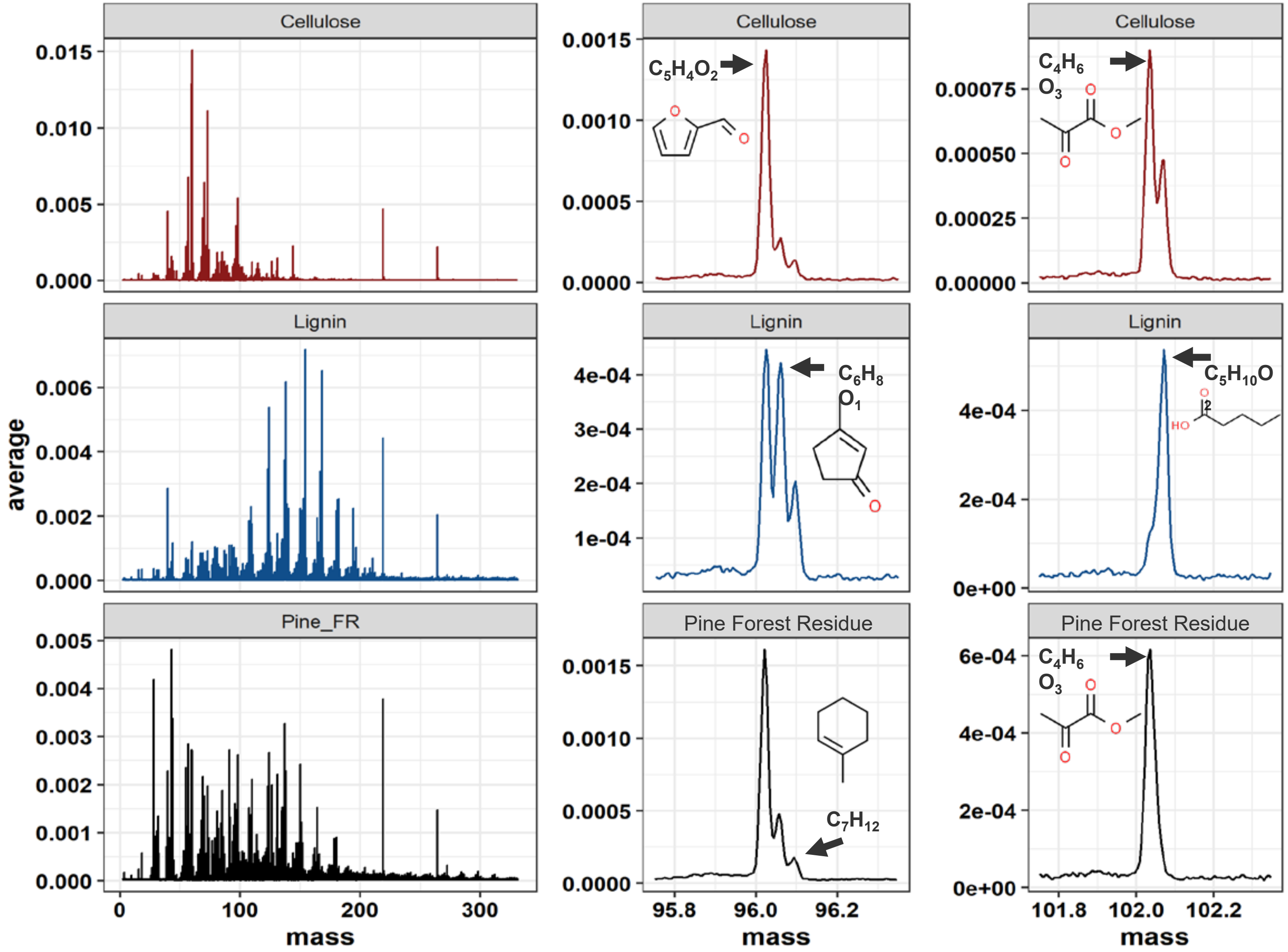
m/z = 96.057518 Th

Furfural

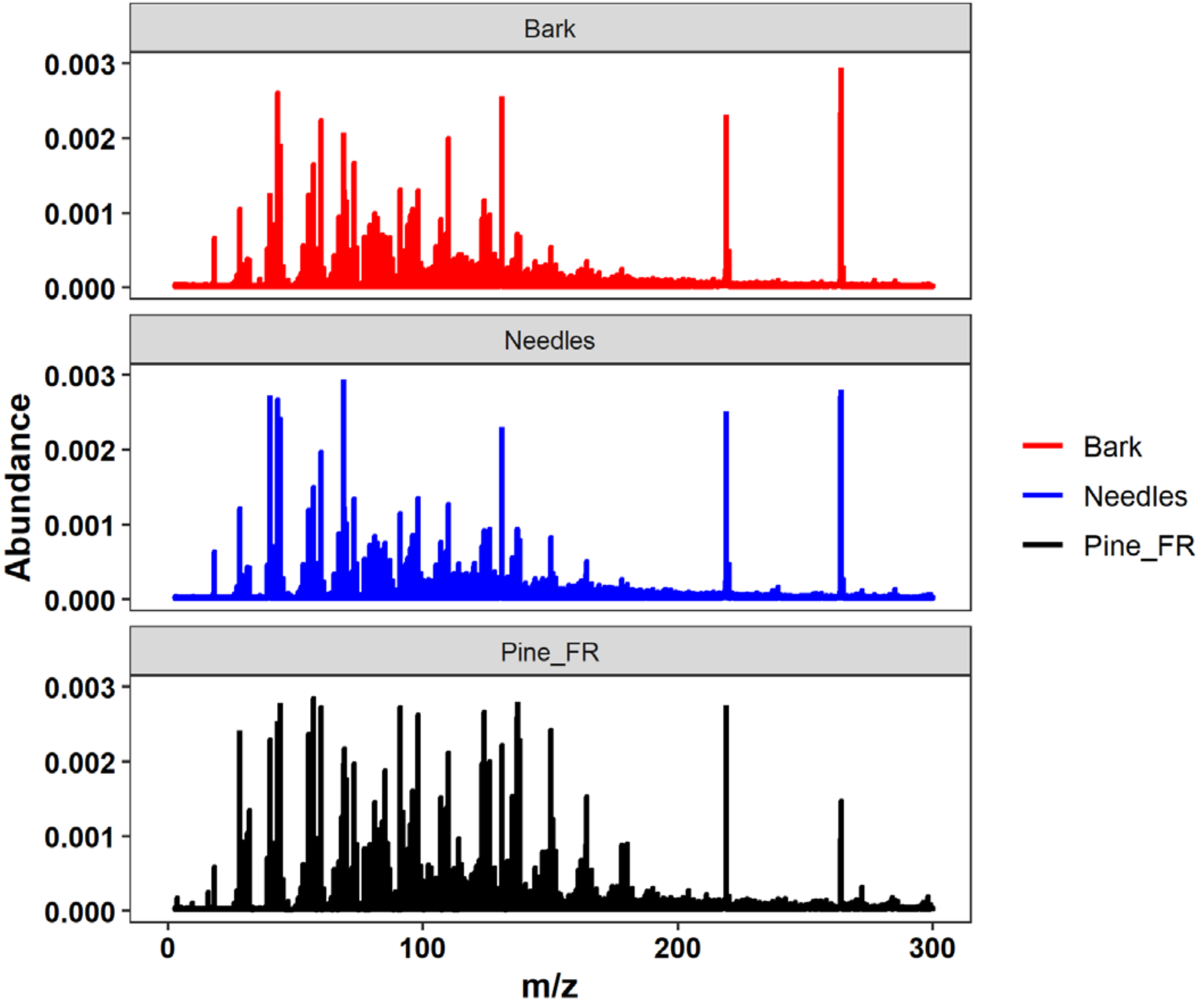


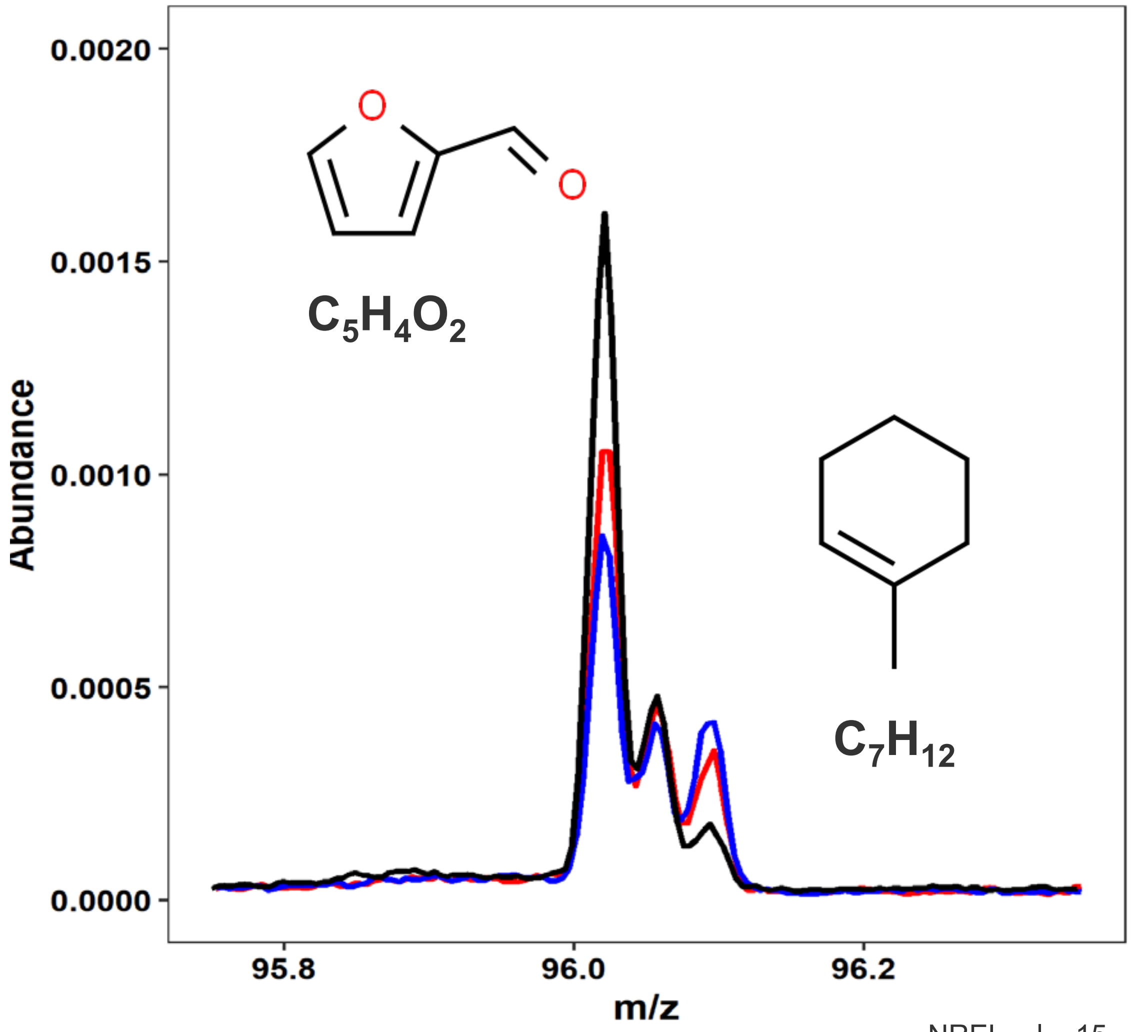
m/z = 96.021126 Th

Direct Analysis of Pyrolysis Vapors



Vapor Screening for Pine Anatomical Fractions





Ultrahigh-Resolution MS for Oil Analysis

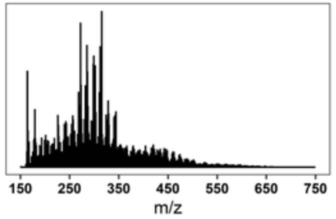
Fast analysis time provides high sample throughput (~10 min/sample)

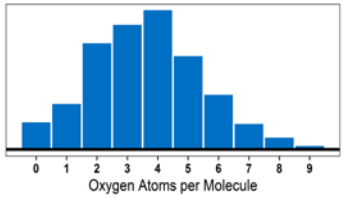
Interface with ambient ionization enables analysis of large polar molecules

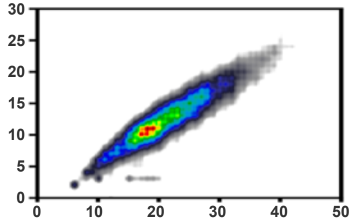
High resolution and mass accuracy limits the need for chromatographic separations for screening applications

Tolerates oils from a wide range of feedstocks

Can resolve sulfur- and nitrogen-containing compounds as well as oxygenates

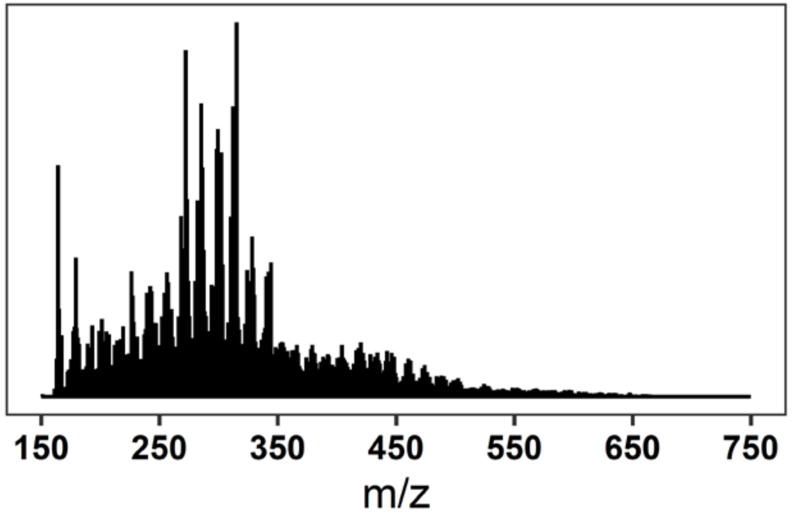






FT-ICR MS Analysis

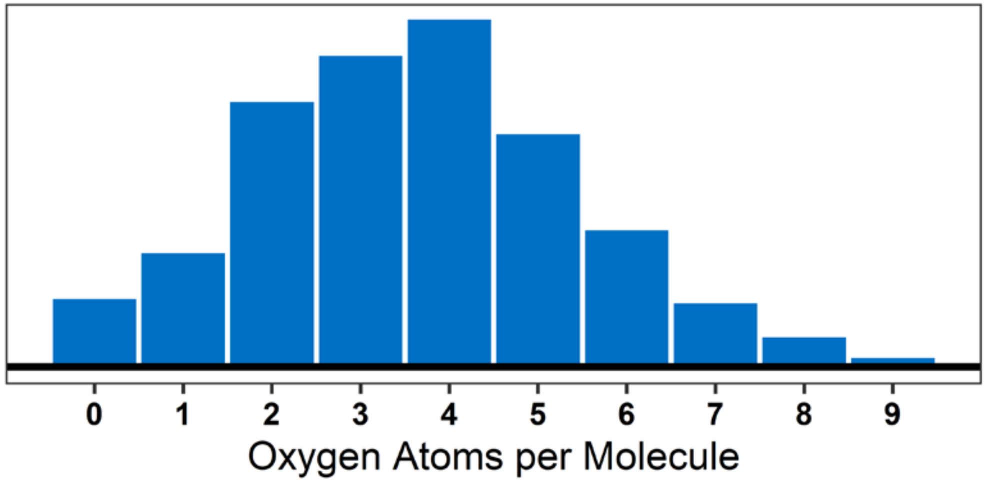
Mass Spectrum



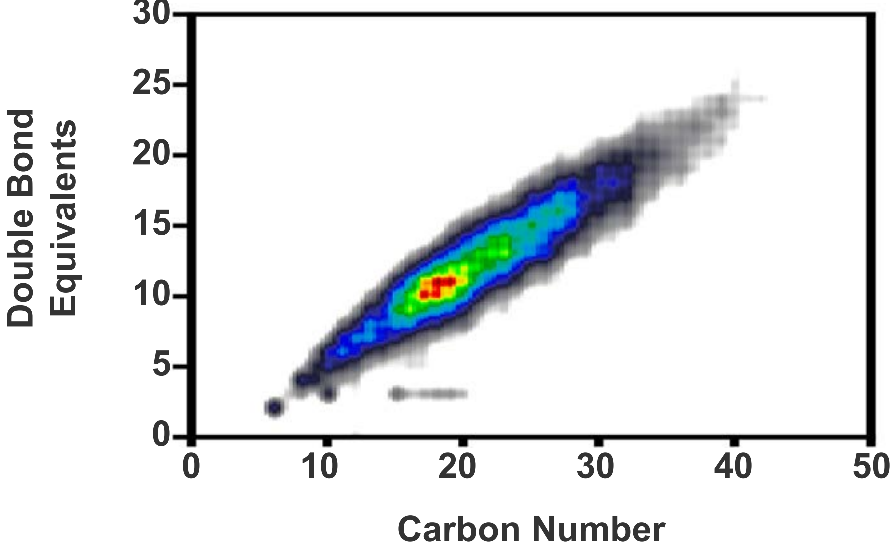
Elemental Composition

Elemental Composition	Measured Mass	Calculated Mass	Error (ppm)
C10 H10 O3	179.07027	179.070271	0.0035
C15 H14 O3	243.10157	243.101571	0.0031
C18 H16 O4	281.11723	281.117221	-0.0326
C9 H10 O4	183.06518	183.065185	0.0287
C12 H12 O4	221.08084	221.080835	-0.0212
C16 H14 O4	271.09649	271.096485	-0.0170
C19 H16 O4	309.11213	309.112135	0.0176
C6 H10 O5	163.0601	163.060100	-0.0008
C13 H14 O5	251.09141	251.091400	-0.0398
C17 H16 O5	301.10705	301.107050	0.0002
C23 H20 O5	377.13835	377.138350	0.0005

Heteroatom Distribution



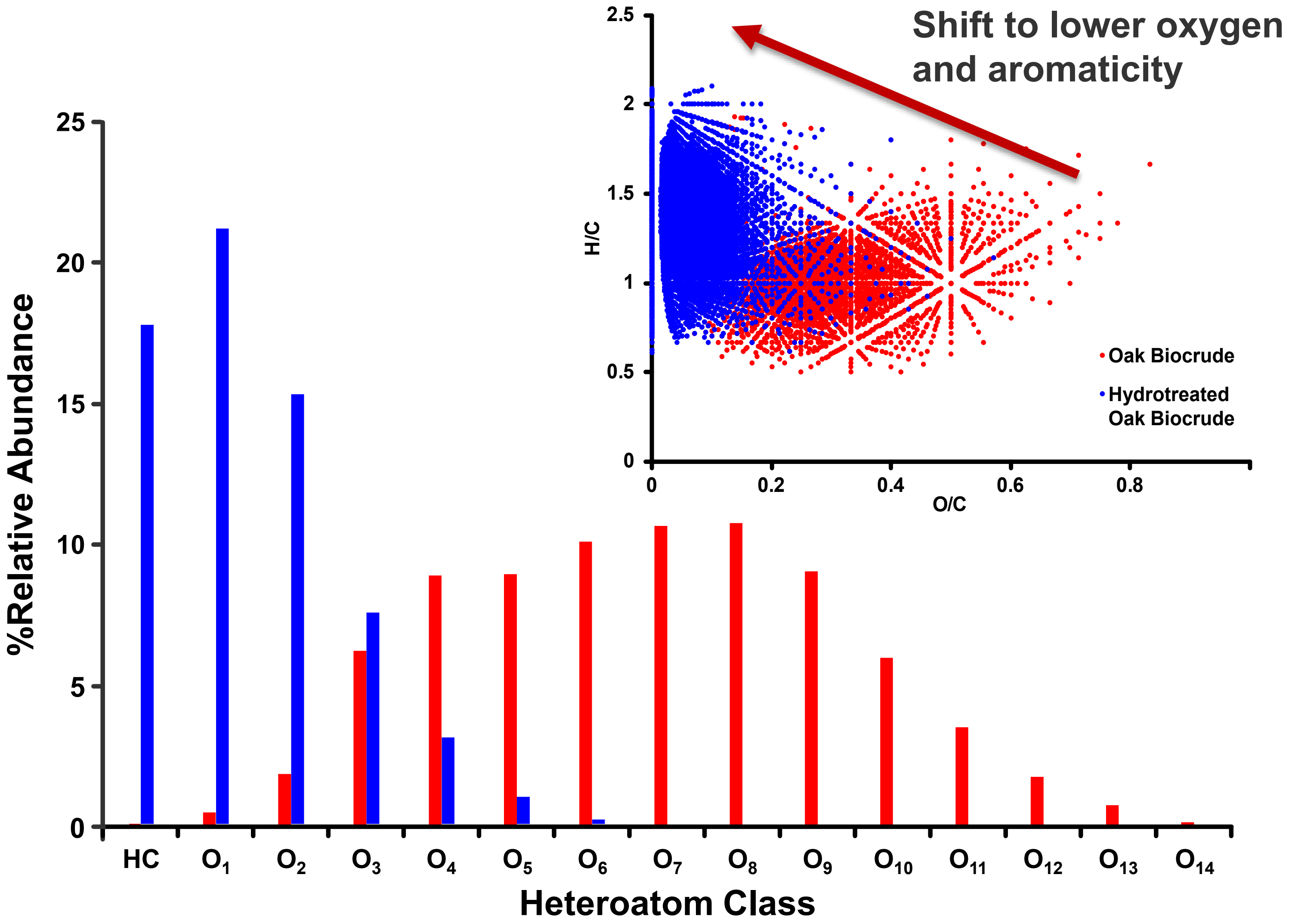
Structural Complexity



Applications of FT-ICR MS

Determination of Hydrotreating results

- Chemical composition shows shifts at the molecular level
- Although oxygen content reduced from ~40% to 5%, there are remaining high oxygen species compared to petroleum
- Van Krevelen plot shows shift from crude bio-crude composition to oil-compatible composition



Ware, R. L., *et al.*, Sustainable Energy Fuels, 2020, 4, 2404–2410

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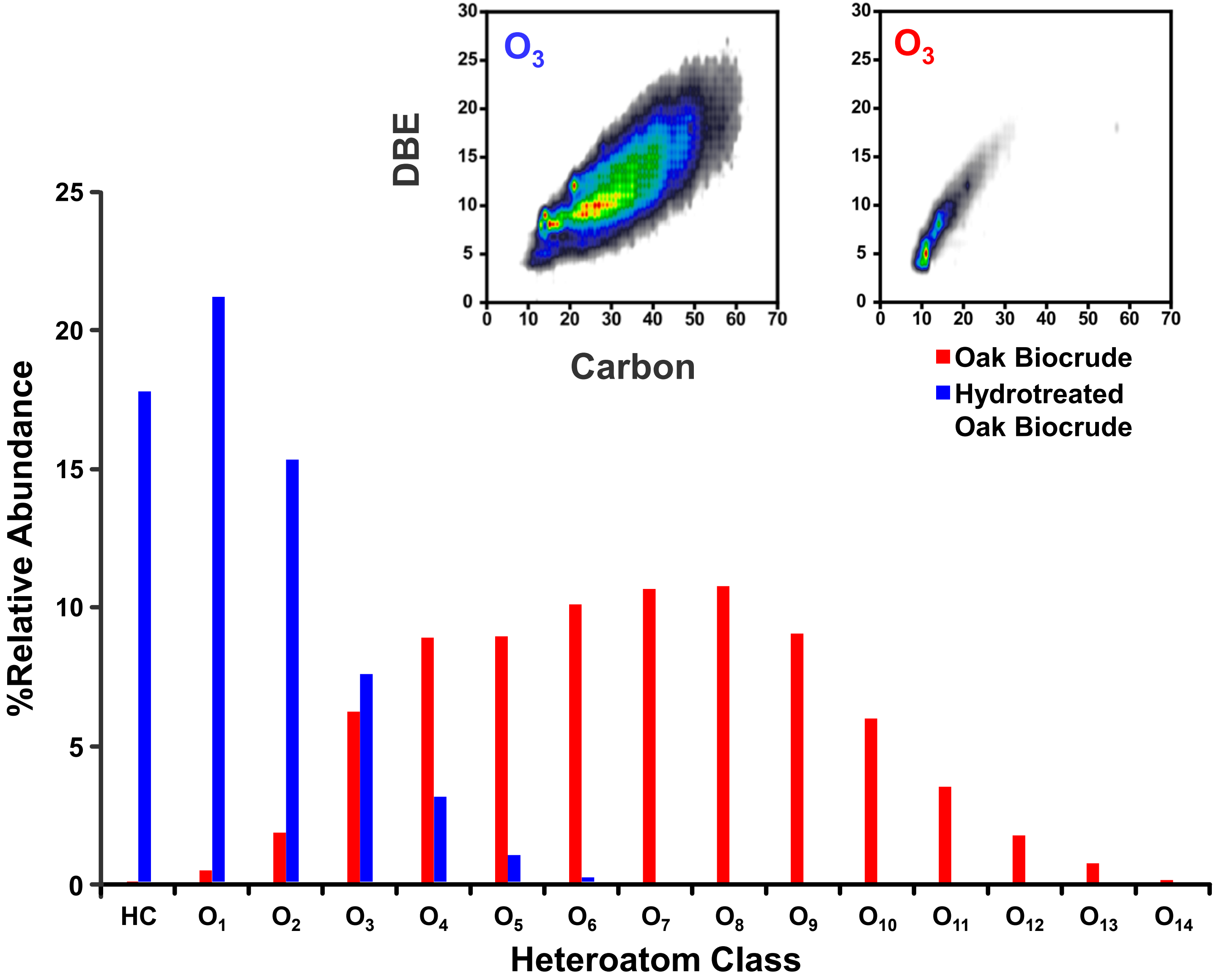

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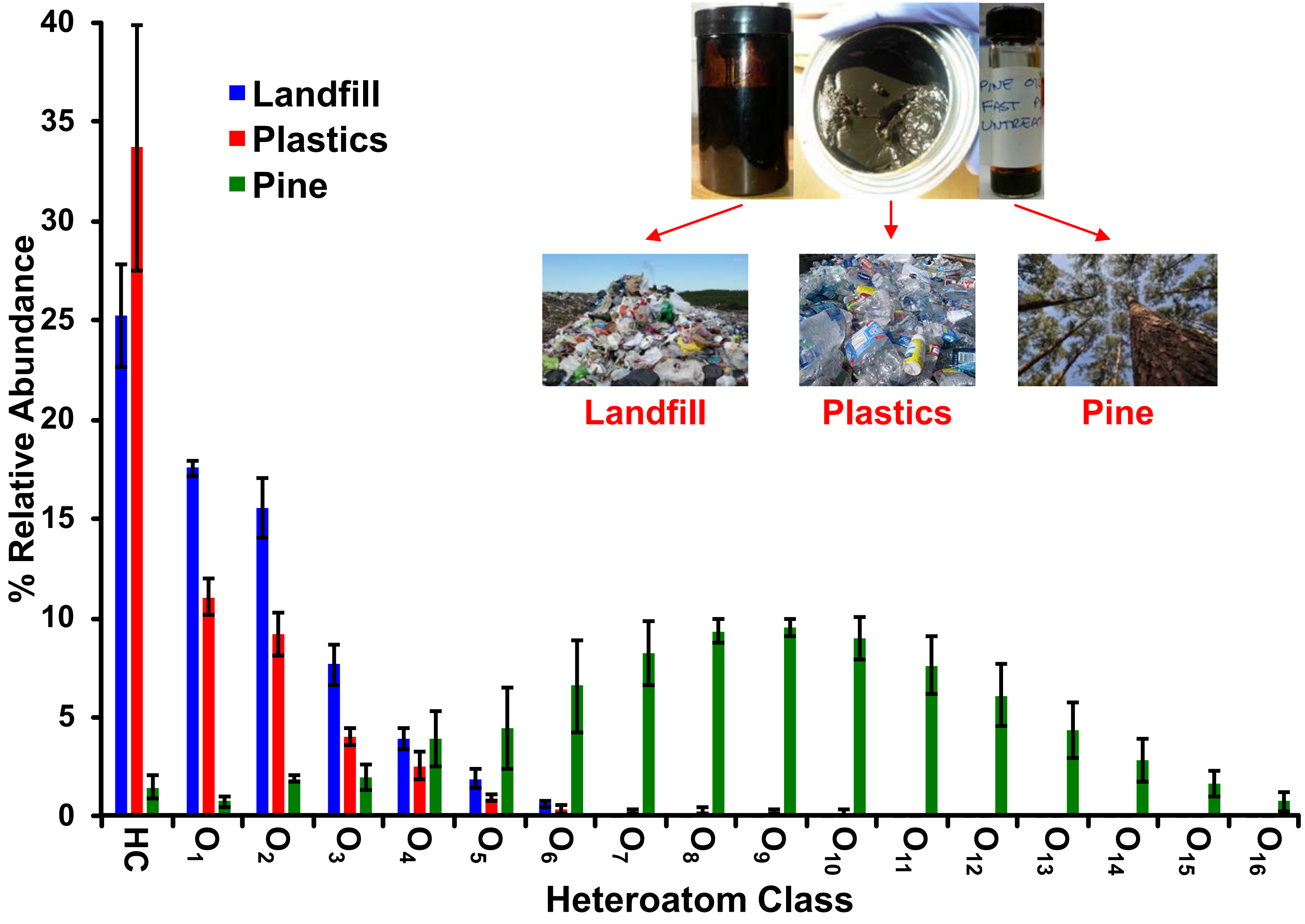
Applications of FT-ICR MS

Influence of Feedstocks

- Comparison of oil from landfill, plastics, and pine feedstocks
- Landfill and plastics waste show similar distribution of oxygenates

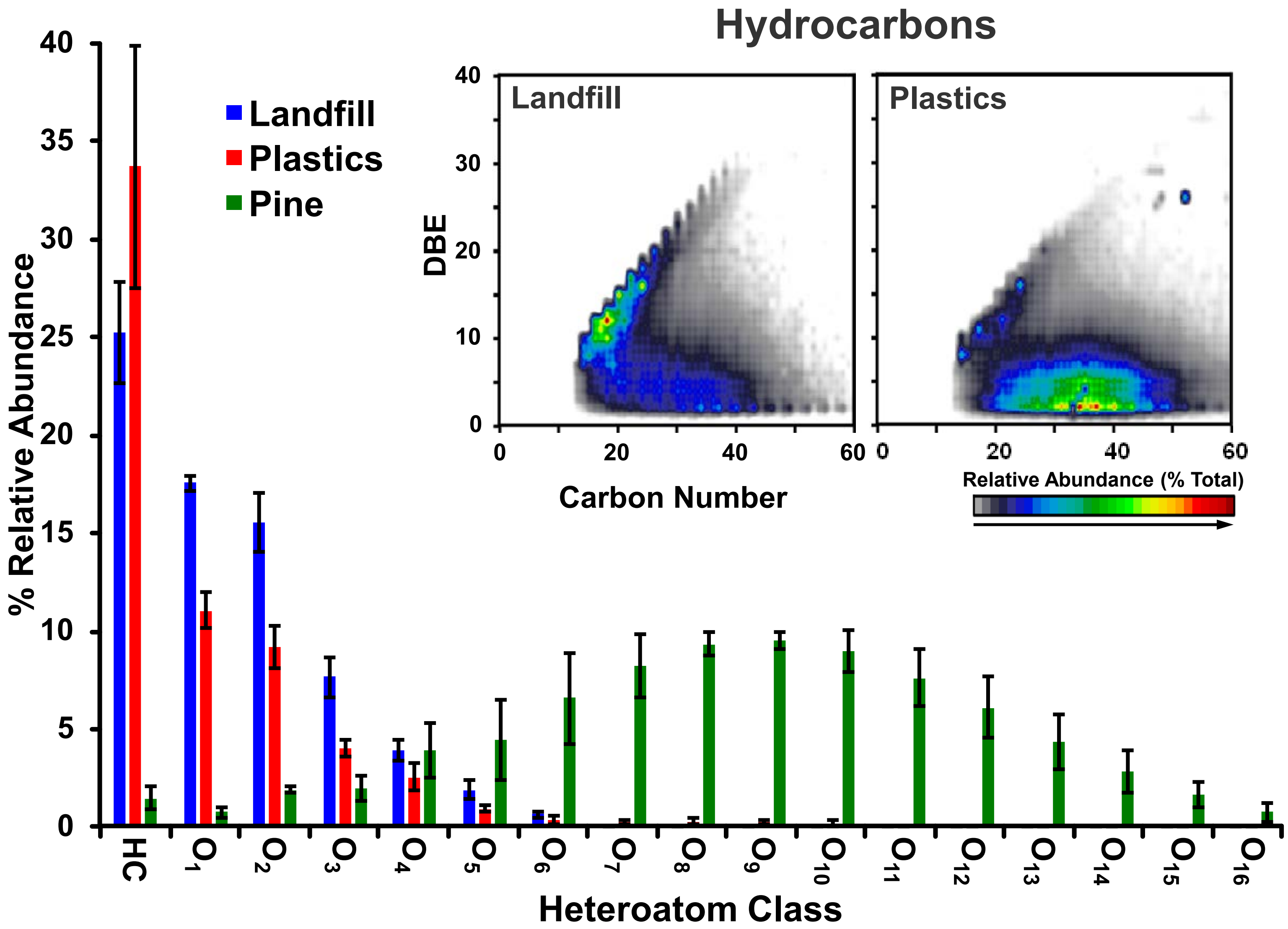


Ware, R. L., *et al.*, Energy Fuels 2017, 31, 8210−8216

Applications of FT-ICR MS

Influence of Feedstocks

- Comparison of oil from landfill, plastics, and pine feedstocks
- Landfill and plastics waste show similar distribution of oxygenates
- Provides insight into chemical composition for all analytes rather than average properties



Ware, R. L., *et al.*, Energy Fuels 2017, 31, 8210−8216

Summary

- Fast analysis time provides high sample throughput for statistical models
- Analysis without gas chromatography removes limitations on polarity and volatility
- Vapor analysis provides correlation to both product yield and quality
- High resolution and mass accuracy provides molecular-level characterization for a wide array of compounds for both vapor and liquid samples

Thank You

Acknowledgements

Daniel Carpenter
Calvin Mukarakate
Jordan Klinger
Anne Starace

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NREL/PR-5100-81472

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.