IEA Bioenergy
Task 34
Direct Thermochemical Liquefaction

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Proceedings of

Bio-oil and Bio-crude Characterization Workshop

December 1, 2017

CanmetENERGY-Ottawa, Ottawa, Canada

IEA Bioenergy
Task 34

Direct Thermochemical Liquefaction

Bio-oil and Bio-crude Characterization Workshop – December 1, 2017

CanmetENERGY-Ottawa, 1 Haanel Drive, Ottawa – Building #3

0900	**Introductions and Welcome**
0915	**Advancing Approaches for the Measurement and Description of Fast Pyrolysis Bio-Oils**
	Ben Bronson, Phil Bulsink, Fernando Preto,
	Dillon Mazerolle and Leslie Nguyen, CanmetENERGY-Ottawa
0945	**Chromatography of Oil from Fast Pyrolysis**
	Jorge Pimentel and Serge Genest, FPInnovations
1015	**Characterization Work at CanmetENERGY-Devon**
	Ajae Hall, Rafal Gieleciak, Nicole Heshka, Anton Alvarez-Majmutov,
	and Jinwen Chen, CanmetENERGY-Devon

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Advancing approaches for the measurement and description of fast pyrolysis bio-oils

Ben Bronson, Phil Bulsink, Fernando Preto, Dillon Mazerolle, Leslie Nguyen

CanmetENERGY-Ottawa, Natural Resources Canada

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About CanmetENERGY

- CanmetENERGY is a science and technology branch of Natural Resources Canada and operates three labs across Canada with over 450 scientists, engineers and technicians
- CanmetENERGY-Ottawa's mission is to lead the development of energy S&T solutions for the environmental and economic benefit of Canadians

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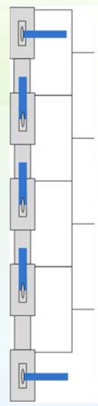
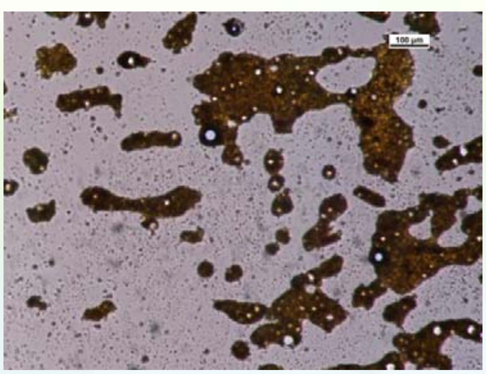
Uniformity Method Establishment

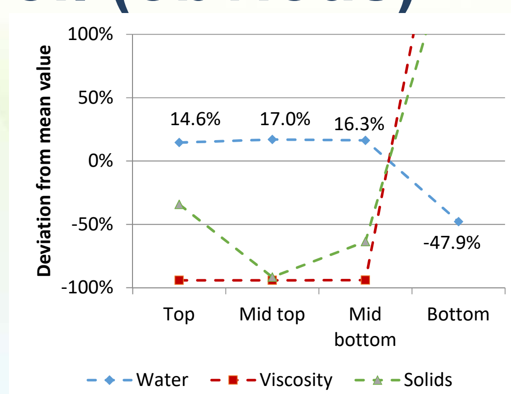
- Stand-alone pyrolysis burners, engines, and turbines all require a “uniform” liquid
- Explicitly mentioned in ASTM D7544-12 (3 month requirement)



- CanmetENERGY approach:
  - 500 mL settling column, 4 equal sections
  - 36” height (0.92 m) with seven day period
  - Water, viscosity and solids tracked

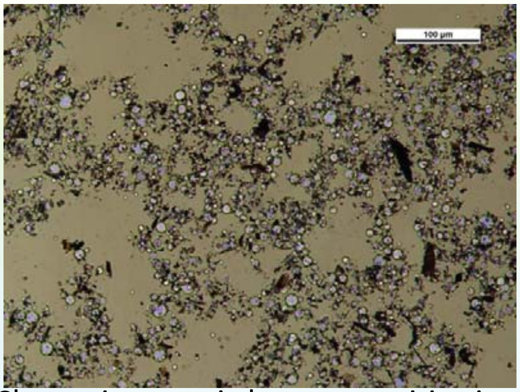
Non-uniform bio-oil (obvious)

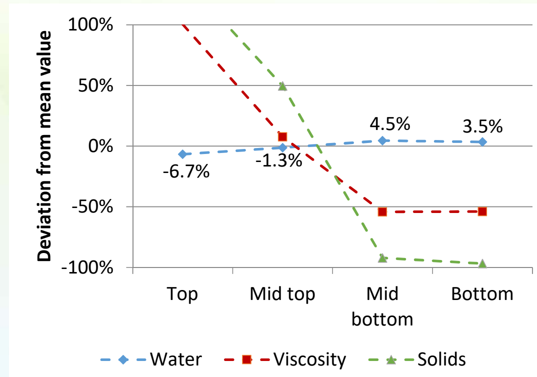




- Low water content, viscous phase sinks. Relatively constant properties in three upper stages where the aqueous phase was. Large water content deviation between mid-bottom and bottom stage

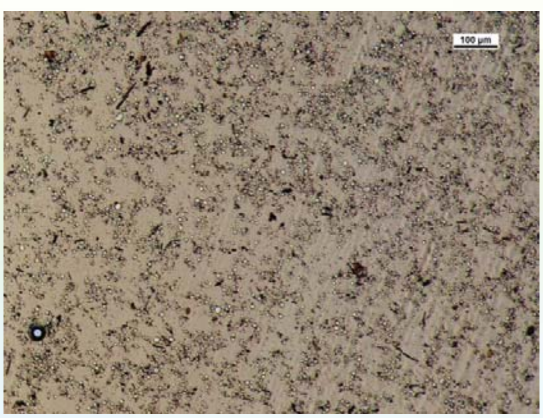
Non-uniform bio-oil? (non-obvious)

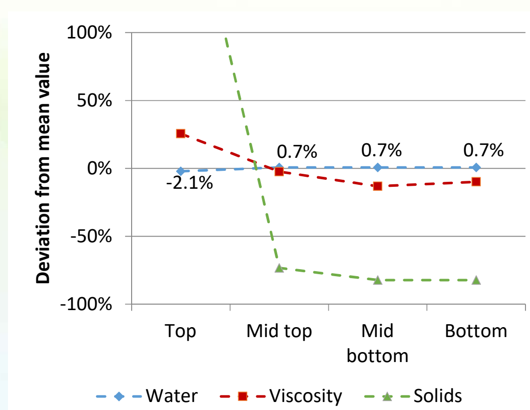




- Clear microscopic heterogeneities in sample, but macroscopically appeared uniform. Gradual variation in water content. Solids report to top ("sludge" layer observed at top)

Uniform bio-oil?





- Water content within 5% RD in all fractions. Solids still clearly segregate to top. Viscosity was also noticeably higher in top sections

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Sulfur in bio-oil

Method	ASTM D5453	Trace S/N cube	ASTM D1552	ASTM D4294
Instrument	MultiTek (2014) Antek S (2010)	Elementar	Leco	Contracted Out
Sample	mg/kg	mg/kg	mg/kg	mg/kg
2014-A	55	74	<100	357
2014-B	182	189	190	599
2010-A	972	1130	1200	1355
2010-B	114	134	121	298
2010-C	221	256	246	632
2010-D	338	440	440	536

Sulfur in bio-oil

- Participated in EN 16900 ILS run by Petrolab
  - 8 samples, 6 laboratories, ISO 20846 (UVF)
  - Not enough power to drop outliers, single extreme sample drove r, R calculation
- UVF vs. IR vs. XRF

Chlorine in bio-oil

- As lower quality residues are explored, Cl can start to become a concern for combustion applications
  - Deposition and corrosion
  - Organochloride emissions

Cl example results

Feedstock	Cl in Feedstock	Cl determined by NAA	Cl determined by bomb IC
	ppm	ppm	ppm
Hardwood Sawdust (Type I)	24	18	19
Clean Softwood Sawdust (Domtar)	155	88	84
Interior Hog	770	150	145
Coastal Residue*	460	250	235
Hardwood Sawdust (Type I)**	24**	1000	960
* This was a very high ash version of "coastal residue"			
**1000 ppm of Cl was added into this bio-oil sample using KCl			

Quantification of chemicals

- Identification of extraction opportunities
- Health and safety (ex: volatile aldehydes including formaldehyde)
- Understanding root causes of bio-oil consistency or changes (between operating conditions or suppliers)
- Bio-oil description for modelling

Quantification - history

- 2002 round robin [1]: different labs were given freedom to use the method of their choosing to quantify the chemical composition of bio-oil. Order of magnitude differences reported, especially for carbonyls and acids

Selected Results from IEA-EU Round Robin[1]

Lab Type	Dynamotive				Pyrovac				Ensyn				BTG			
Lab No.	9	12	3	5	9	12	3	5	9	12	3	5	9	12	3	5
Formaldehyde	0.84	8.92		3.3	0.51	2.6		1	0.25	5.23		1.4	1.15	9.37		4
Acetaldehyde	0.14	1.88			0.004	1.1			0.01	1.34			0.17	1.67		
Glycoladehyde		3.32	6.42	7.7		1.09	3.18	3.2		1.81	3.34	2.9		6.89	8.2	11
Glyoxal		0.24		2.4		0.33		1.5		0.67		1		0.91		2
Acetol		2.07	7.82	7.1		0.84	3.17	1.8		1.48	3.65	1.8		3.28	7.1	7

- 2016 study [2]: 5 labs given the same standard and provided with the same instructions for the method, 21 of 31 compounds with <20% RSD.

[1] Oasmaa, A and Meier, D "Pyrolysis Liquids Analyses The Results of IEA-EU Round Robin" pg. 41-58 in Bridgwater (Ed.), "Fast Pyrolysis of Biomass: A Handbook Volume 2." IEA Bioenergy, 2002
[2] J. R. Ferrell, M. V. Olarte, E. D. Christensen, A. B. Padmaperuma, R. M. Connatser, F. Stankovikj, D. Meier and V. Paasikallio, "Standardization of chemical analytical techniques for pyrolysis bio-oil: history, challenges and current status of methods." Biofuels Bioproducts & Biorefining, 2016

Quantification - history

- Early results echoed some of the literature results: large variability between labs and duplicated bio-oil samples
- Subsequent refinement of the method has led to less variability
- Question remained: were the methods narrowing in on the **correct** values?

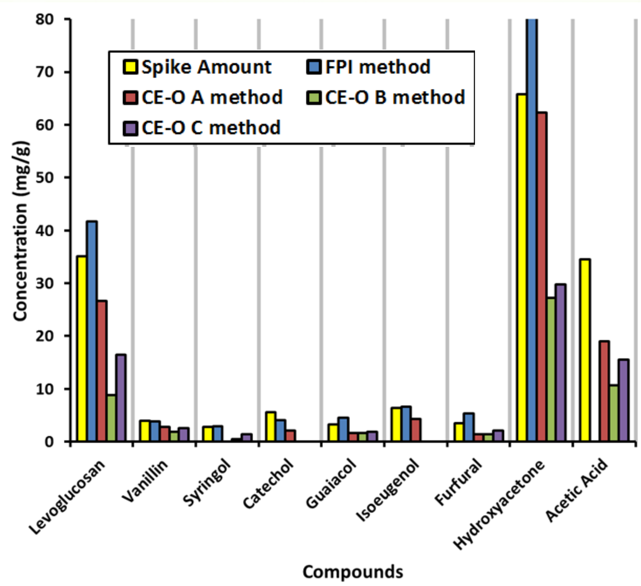
Before method refinement – repeated hardwood sawdust trials, 2 labs (mg/g)

Trial	26	36	26	36
Method	CE-O	CE-O	FPI	FPI
Acetic Acid	60.4	84.7	69.3	
Glycoaldehyde	5.3		11.4	36.8
Hydroxyacetone	14.9	30.9	14.2	27.5
Furfural	5	4	3.5	0.2
Guaiacol	3.7	2.9	3.9	4.2
Syringol	2.4	6.9	7.9	
Isoeugenol			6.3	3.4
Vanillin	6.5	2.3		1.3
Levoglucosan	28.3	74.9	320.6	33.9

CE-O - Characterization Laboratory at CanmetENERGY-Ottawa
FPI - FPInnovations

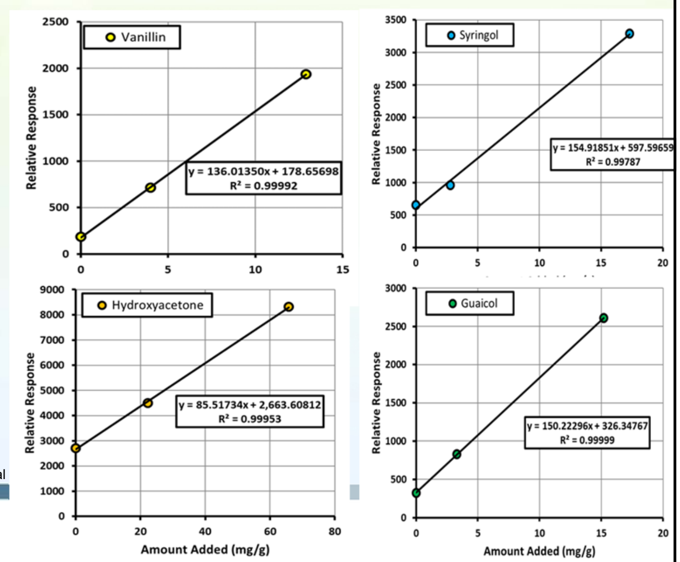
Method assessment with spiking

- Comparison of actual and estimated excess amounts from various GC-MS methods for one level of spiking
- Qualitative agreement between actual and measured excess concentration due to spike
- Still some considerable variability between methods



Standard Addition Calibration

- Using the data from method described in [2]
- Raw analytical response produced from GC-MS analyses correlated linearly with excess amounts (R^2 >0.99 for 8 of 9 compounds, R^2>0.95 for last one)
-



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Continuing GC-MS Development

- Successful implementation of PNNL method for oxygenates in pyrolysis oils [1]
  - Excellent comparison to previously developed in-house methods
- Extension to upgraded oils (biojet fuels) ongoing:
  - Liquid/Liquid extraction (not dilution)
  - Modified ISTD choices,

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[1] Christensen, E.; Ferrell, J. Quantification of Semi-Volatile Oxygenated Components of Pyrolysis Bio-Oil by Gas Chromatography/ Mass Spectrometry (GC–MS) Laboratory Analytical Procedure (LAP); NREL

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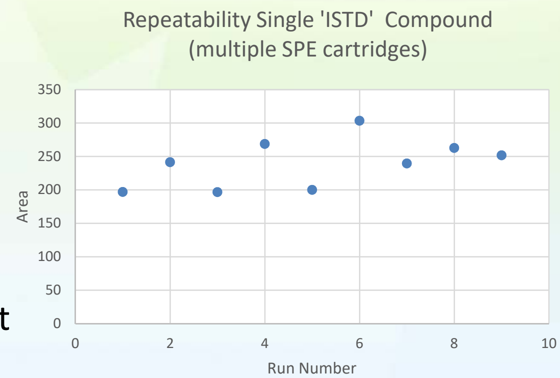
HPLC Methods

- Volatile Acids
  - Issues with DMSO ISTD, put aside
  - Will attempt HILIC in future
- Carbonyls with DNPH by HPLC
  - Repeatability of cartridges
  - Availability of DNPH outside of cartridges
  - Attempting (PFBHA) with/without extraction [1,2]



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[1] Jakober, C. et.al. *Anal. Chem.* **2006**, *78*, 5086-5093
[2] Yu, J. et.al. *Environ. Sci. Technol.* **1995**, *29*, 1923-1932

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Future Priorities

- Establishing capabilities to complete Carbonyl titration method
- Improving heteroatom (S, Cl, N, etc...) and inorganic (Na, K, Ca, Mg, Fe, P, etc...) composition
- Explore innovative approaches for speciated carbonyl quantification by GC
- Work on speciated acid quantification. By HPLC?

Are these the highest priorities? Where else does the group believe characterization gaps exist?

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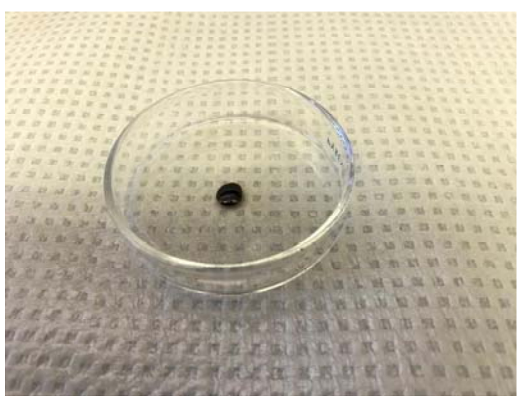
Chromatography of Oil from Fast Pyrolysis

Jorge Pimentel & Serge Genest

December 1, 2017

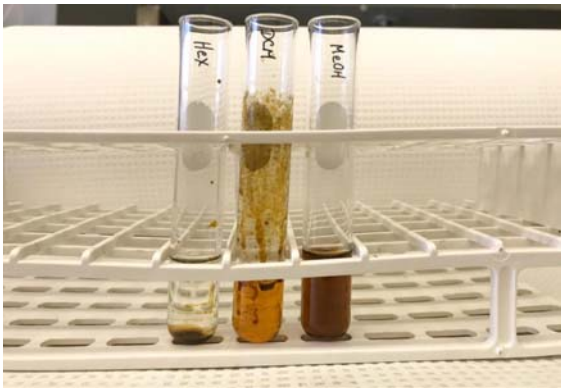
Oil from Fast Pyrolysis



- Very strong smoky scent
- Dark in colour

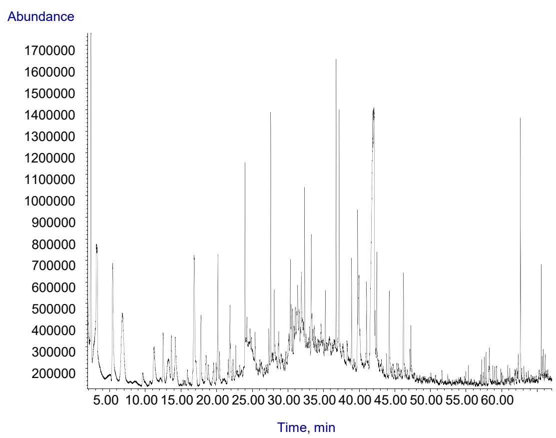
Solvent for Oil from Fast Pyrolysis for Chromatography (GC-MS)

- Not a typical oil



Solvent	Polarity Index
Hexane	**0**
Trichloroethylene	1
Toluene	2.4
Methyl-t-Butyl Ether	2.5
Benzene	2.7
Ethyl Ether(Di-)	2.8
Dichloromethane	**3.5**
Propanol(iso-)	3.9
Tetrahydrofuran	4
Propanol(n-)	4
Chloroform	4.1
Methanol	**5.1**
Acetone	5.1
Ethanol	5.2
Acetonitrile	5.8
Acetic Acid	6.2
Dimethyl Sulfoxide	7.2
Water	9

Chromatogram of Oil from Fast Pyrolysis (GC-MS)



- Rich in compounds (>200)

Components in Oil from Fast Pyrolysis (GC-MS)

- Many of components
  - Initial work identified 154
  - Settled for components present >0.01% (w/w)
  - Components grouped into classes
    - Acids, Ketones and Aldehydes, Alkyl Benzenes, Hydrocarbons, Guaiacols and Syringols, Alcohols, Furans, Phenolics, Sugars
  - Quantified using RRF approach with representative compounds (e.g. phenol for all phenolic type compounds)

Components in Fast Pyrolysis Oil (GC-MS)

- Later, focused more on marketable components
  - Hydroxyacetone
  - Furfural
  - Guaiacol (Phenol, 2-methoxy-)
  - Catechol (1,2-Benzenediol)
  - Syringol (Phenol, 2,6-dimethoxy-)
  - Isoeugenol (Phenol, 2-methoxy-4-(1-propenyl)-)
  - Vanillin
  - 1,6-Anhydro-β-D-glucopyranose (levoglucosan)
- Quantified using internal standard and RRF of each compound above

Components in Oil from Fast Pyrolysis (HPLC)

- Analysed for Saccharinic Acids (LMW water soluble acids)
  - Glycolic
  - Formic
  - Lactic
  - Acetic
  - Fumaric
  - Propionic
  - Levulinic
  - Butyric

Analysis of Oil from Fast Pyrolysis

- Can chromatographically accounts for about 30-35% (w/w) of sample composition
- Headspace GC-MS?
- GC X GC (2 dimensional GC)?
- New separation technologies ?

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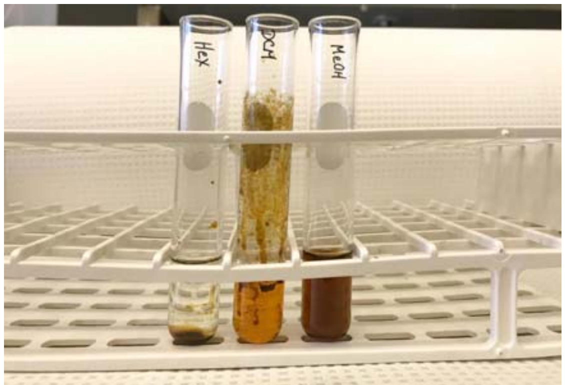
Headspace Analysis of Oil from Fast Pyrolysis (GC-MS)

- What was in the headspace of those vials?



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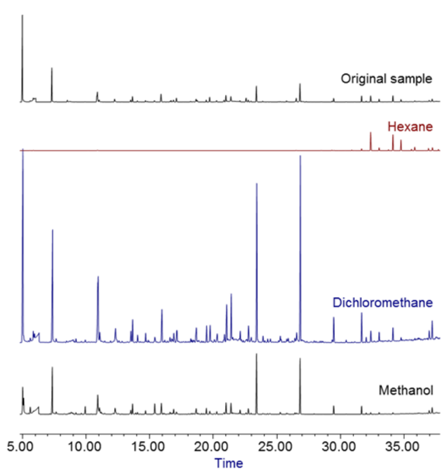
Headspace Analysis of Oil from Fast Pyrolysis (GC-MS)



Solvent Polarity Chart

Relative Polarity	Compound Formula	Group	Representative Solvent Compounds
Nonpolar	R - H	Alkanes	Petroleum ethers, ligroin, hexanes
	Ar - H	Aromatics	Toluene, benzene
	R - O - R	Ethers	Diethyl ether
	R - X	Alkyl halides	Tetrachloromethane, chloroform
	R - COOR	Esters	Ethyl acetate
	R - CO - R	Aldehydes and ketones	Acetone, methyl ethyl ketone
	$R - NH_2$	Amines	Pyridine, triethylamine
	R - OH	Alcohols	Methanol, ethanol, isopropanol, butanol
	$R - COHN_2$	Amides	Dimethylformamide
	R - COOH	Carboxylic acids	Ethanoic acid
Polar	H - OH	Water	Water

Increasing Polarity

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Analysis of Oil from Fast Pyrolysis

- Can chromatographically accounts for about 30-35% (w/w) of sample composition
- How to analyze the other 65-70% of the sample

Merci

Pour plus d'information, contactez :

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Bio-oil and Biofuel Characterization CanmetENERGY-Devon

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Introduction to CanmetENERGY Devon

- CanmetENERGY Devon is one of the three CanmetENERGY research labs.
- Primarily focused on oil sands and petroleum research in areas of extraction, upgrading and environmental impacts.
- Standard and advanced analytical groups reside within Hydrocarbon Conversion (Upgrading), and are focused on providing data for pilot plants and creating new analytical methods.
- Biomass related work is primarily hydrotreating, co-processing and fuels characterization.

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Highlighted Research Projects on Advanced Characterization of Biocrudes and Biofuels

- Evaluation of Forestry Residues as Feedstocks for Hydrocarbon Replacement Liquids (Innotech Alberta)
- Quantification and Speciation of Hydrocarbon Types in Low-Carbon Fuel Products (CRC)
- Identification and Quantification of FAMES in Biodiesel and Biodiesel Blend Products (CARB)
- Standardization and Evaluation of Analytical Methods for Biooil Characterization (PNNL)
- Advanced Combustion of Biodiesel Fuels (FACE)
- Fitting HTL Biocrude into petroleum refineries. (CFS-FIP)

Advanced Analytical Capabilities

Gas Chromatography

- Multiple instruments with varied detection
  - Flame ionization,
  - sulphur chemiluminescence,
  - nitrogen Chemiluminescence
  - Mass Spectrometry
  - Vacuum Ultraviolet
  - One- and two-dimensional separations

Pyrolysis

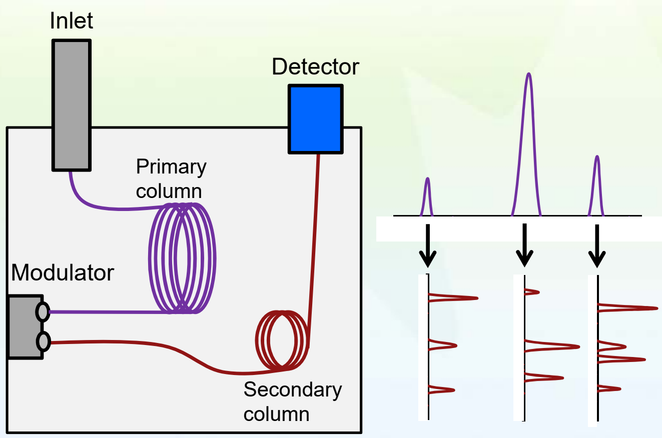
- Combust samples prior to GC analysis
- Can use pressure
- Can load catalyst

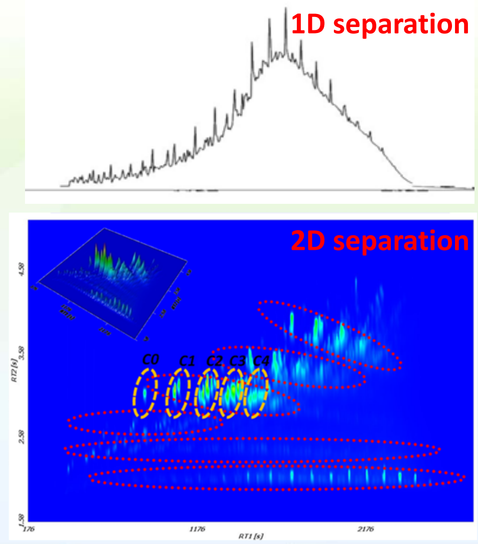
NMR

- 1H and 13C spectra
- 1D and 2D possible
- 15N and 31P possible

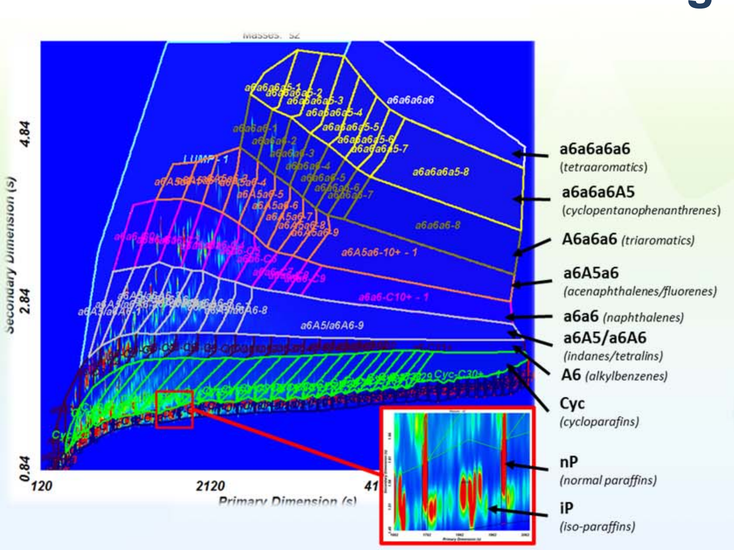
GCxGC - how it works

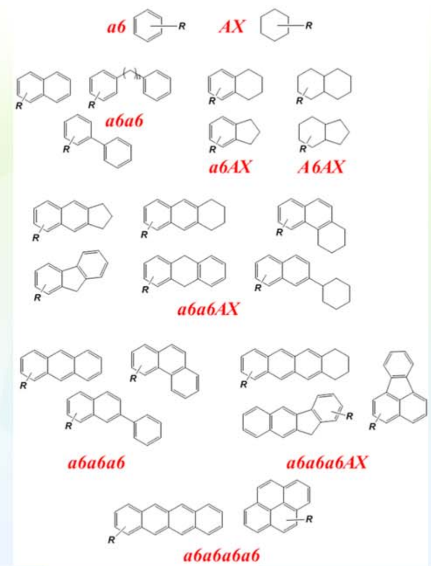
Separate on two columns – double the power





GCxGC – Structured chromatogram of finished fuel





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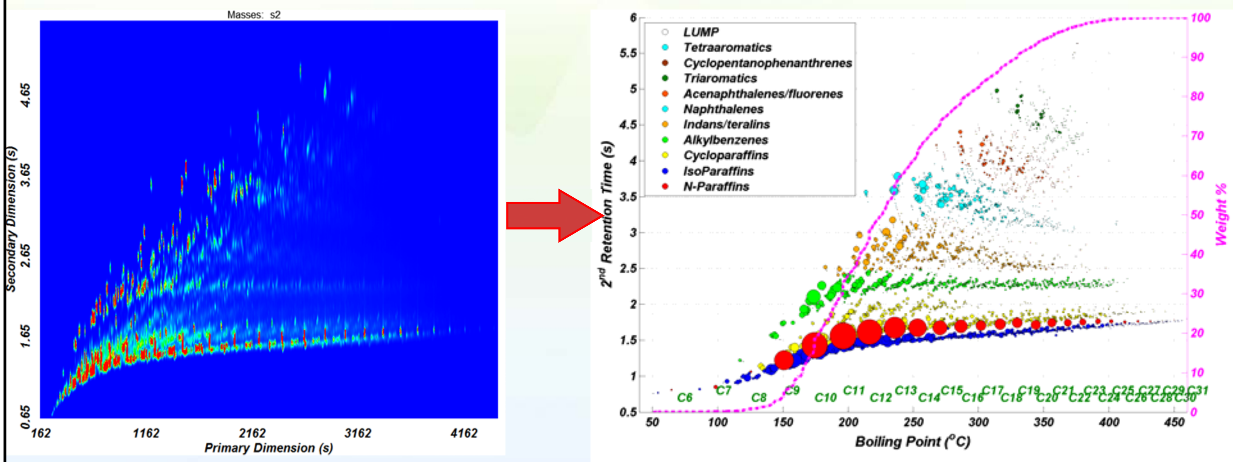
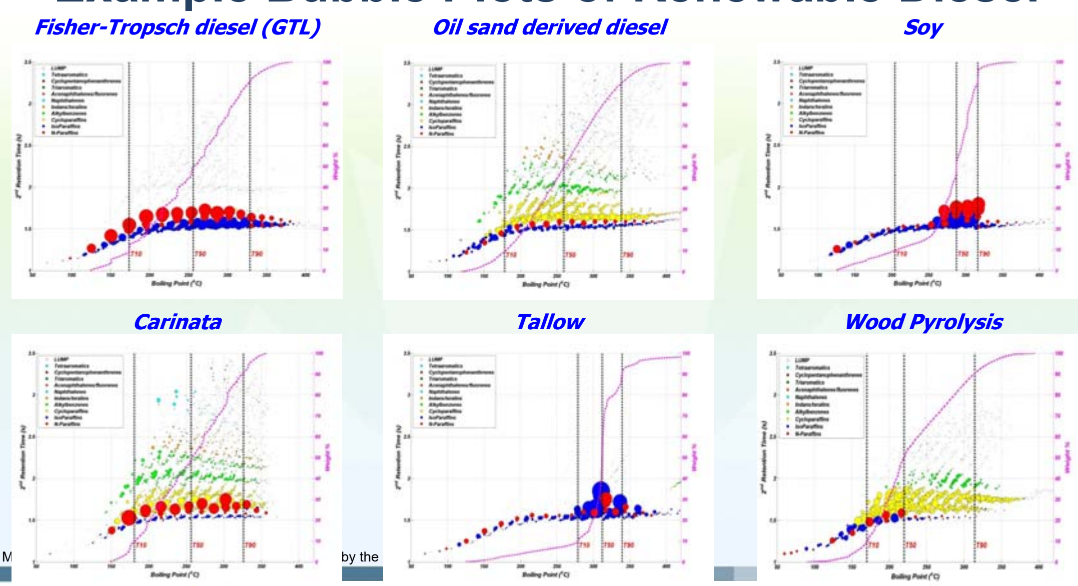
Bubble plot and GCxGC profiles

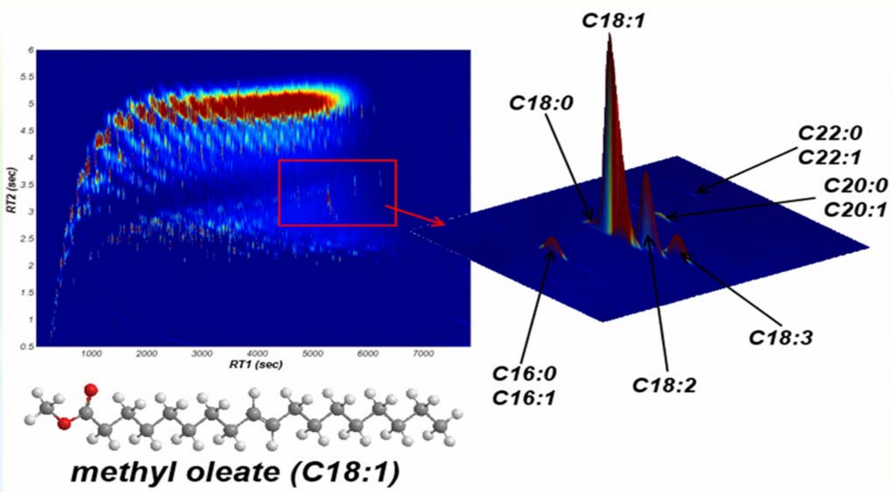


Example Bubble Plots of Renewable Diesel

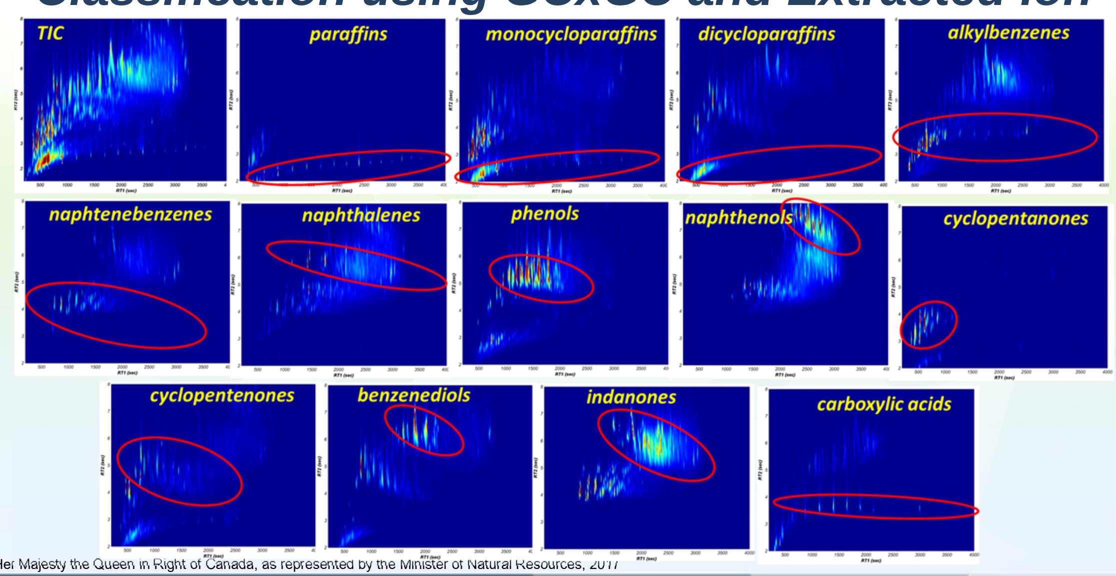


- IsoParaffins
- N-Paraffins
- Alkylbenzenes
- Cycloparaffins
- Naphthalenes
- Indans/teralins
- Triaromatics
- Acenaphthalenes

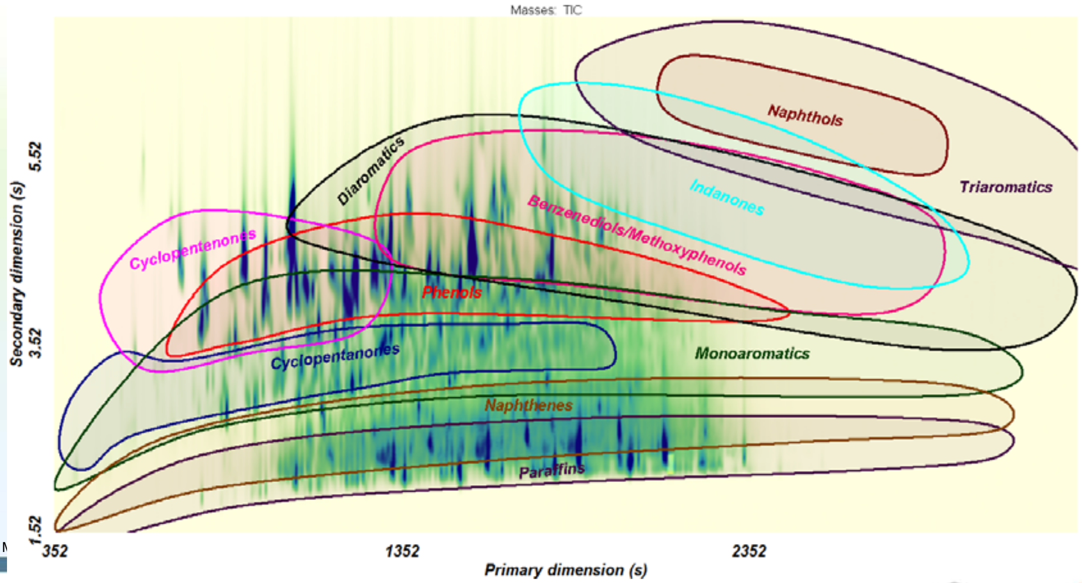
Analysis of Biodiesel/Diesel blends



Classification using GCxGC and Extracted Ion



Classification Map



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High Pressure Pyrolysis with Reactor

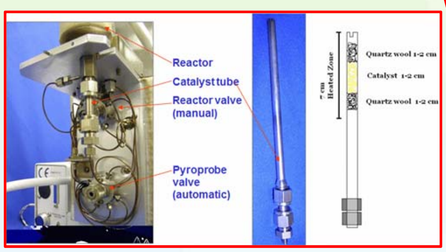
Interface (250°C)

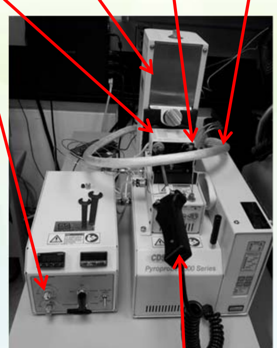
Reactor

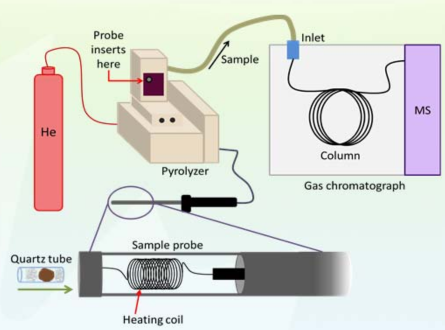
Trap

Transfer Line (300C)

The Pressure controller







Pyroprobe (250°C (1s)– 750°C(1s) @ 20°C/ms)

Pyroprobe 5200 High Pressure Reactor w/Built-in Trap

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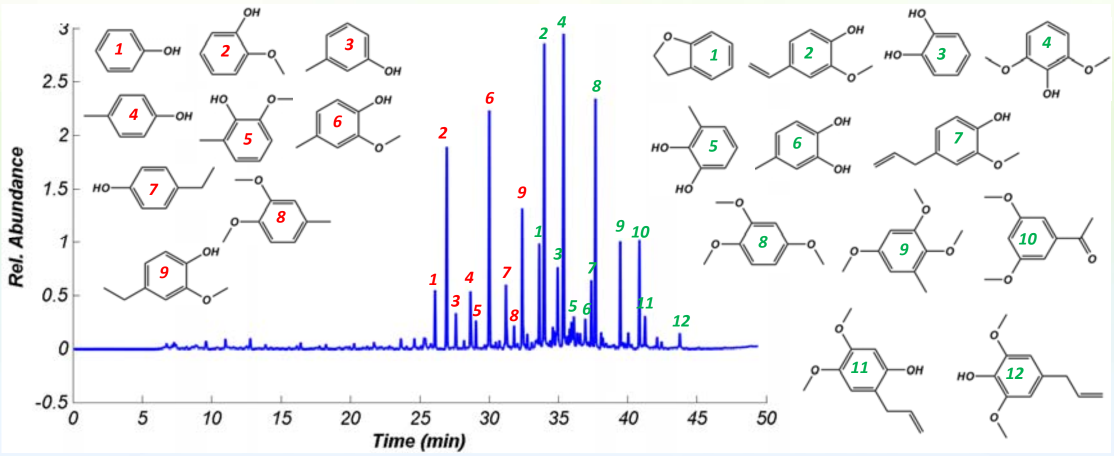
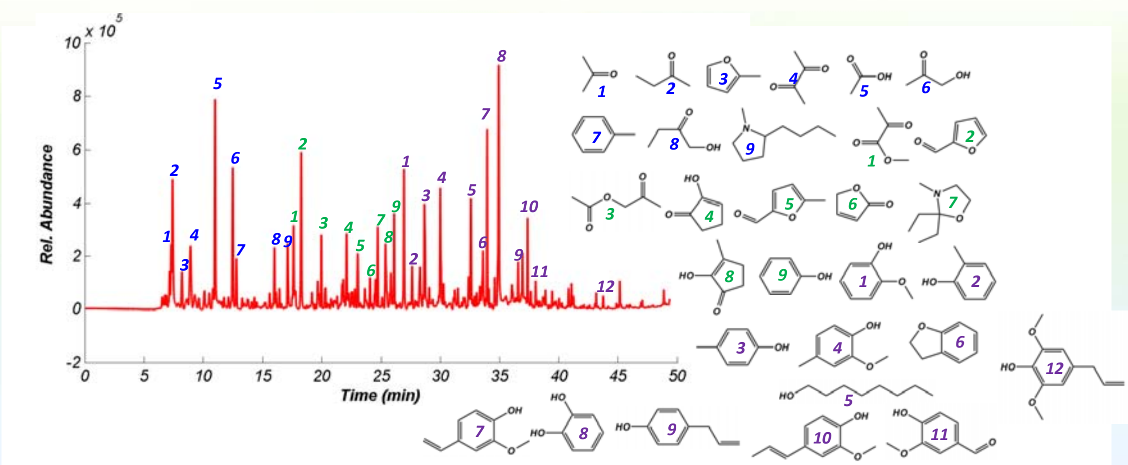
Pyro-GCMS: Lignin

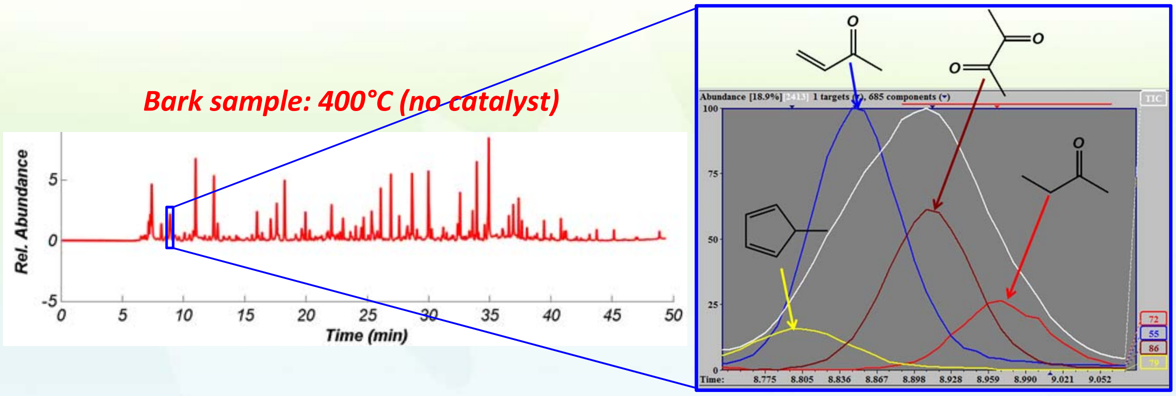


Pyro-GCMS: Bark

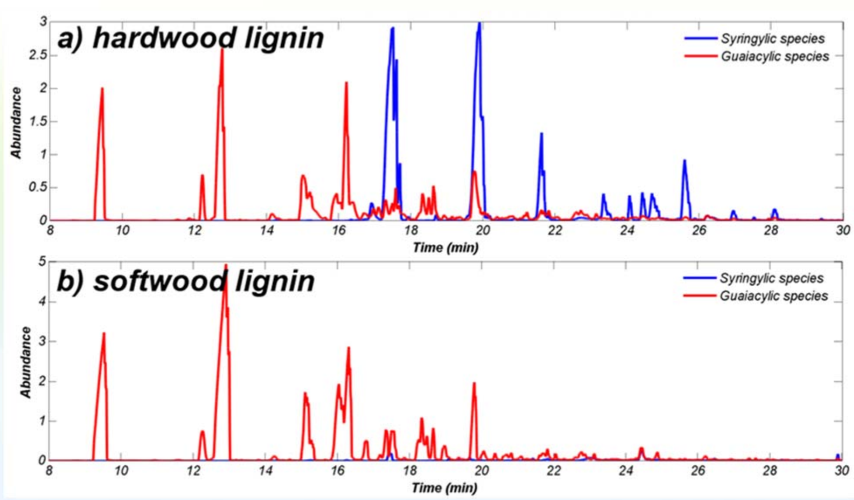


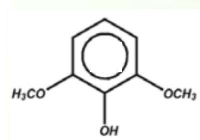
Peak deconvolution

Bark sample: 400°C (no catalyst)

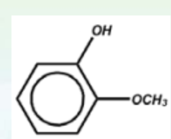


Pyro-GCMS: hardwood vs softwood lignin



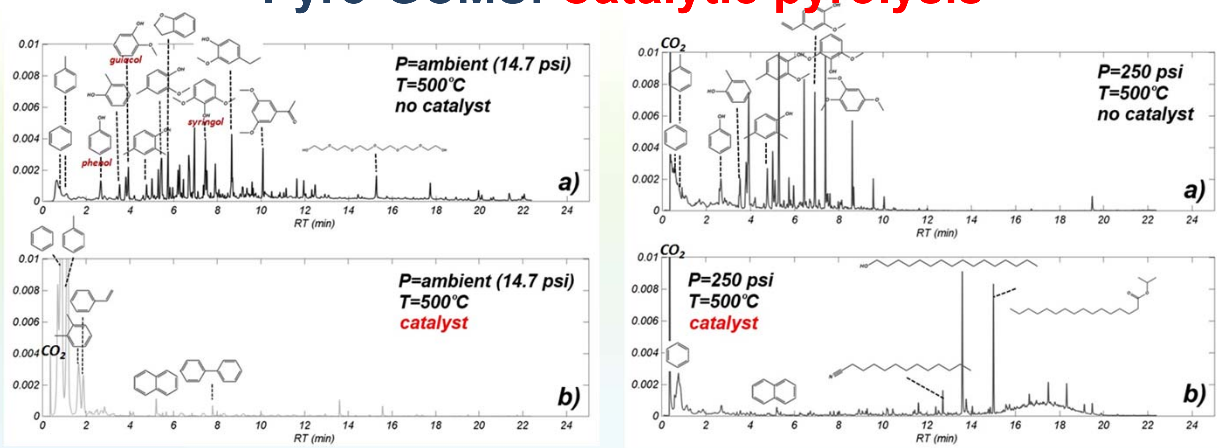


syringol



guaiacol

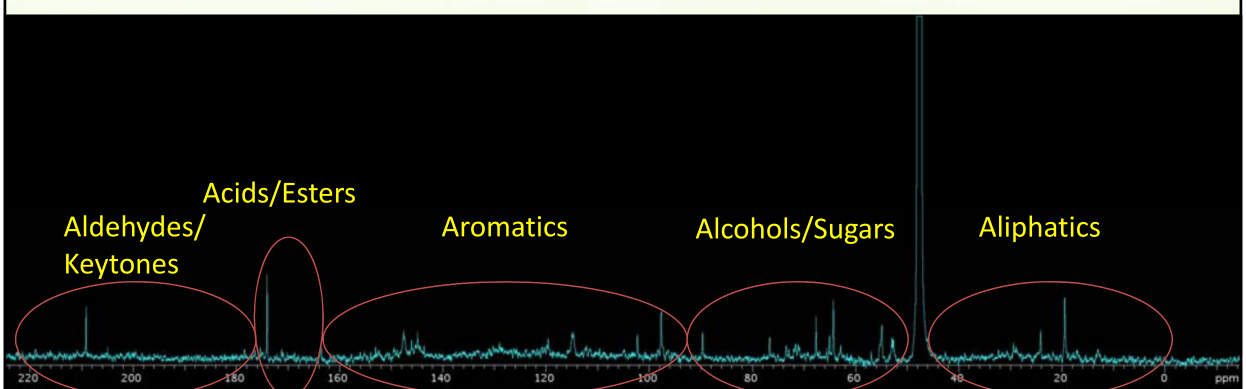
Pyro-GCMS: Catalytic pyrolysis



Pyrograms of softwood lignin pyrolysis products
(a) without catalyst, and
(b) with catalyst, pyrolyzed at ambient pressure.

Pyrograms of softwood lignin pyrolysis products
(a) without catalyst, and
(b) with catalyst pyrolyzed at high pressure (250 psi)

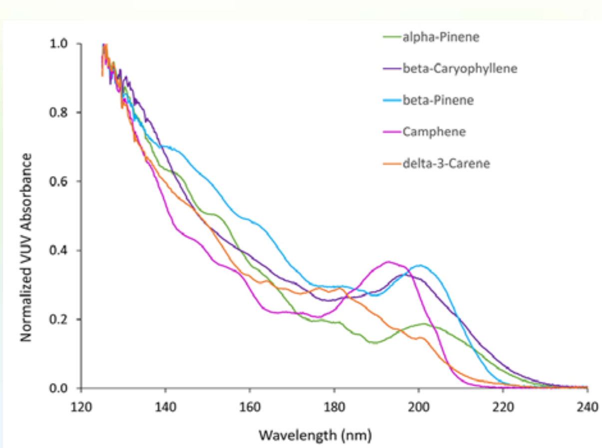
13C NMR: BioOil

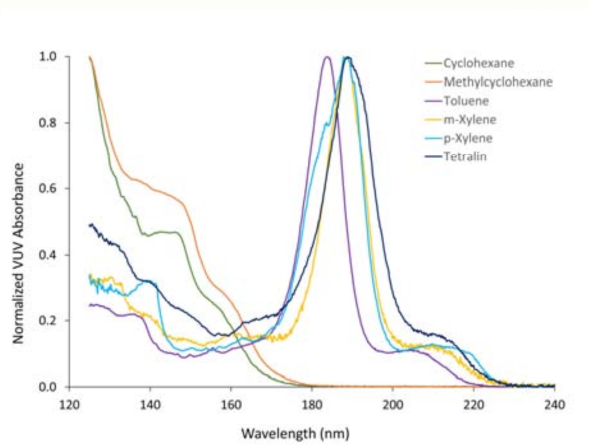


Future Possibilities

- Raman and FTIR spectroscopy (Carbonyl Content)
- HPLC (Class Separation)
- Open column liquid chromatography (Pre separation for GC)
- ICP-MS (Dissolved metals content)
- Physical properties (Distillation, Thermal Conductivity, Rheology, etc)
- GC-VUV (Oxygenate speciation, library building)

Vacuum Ultraviolet Detector





Spectra from https://vuvanalytics.com/

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Our Collaborators, Partners and Clients

Thank you!

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