2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Southern Pine Based Biorefinery Center

May 20 - 23, 2013
Bio-Oil Technology Area Review
Project WBS: 7.5.7.3

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Goal/Objective Statement

Leveraging kraft pulp mill infrastructure for biofuels and bio-based materials via pine wood, pine residues, and kraft cooking liquors.

- Develop novel woodchip extraction technology to recover hemi's 'lost' during pulping for cellulosic ethanol while providing excellent woodchips for pulp production
- Utilize acidic pulp mill pulp streams for DAP wood residues for cellulosic ethanol & identify cellulosic for novel biobased materials
- Catalytic thermal conversion of pine residues and kraft lignin to a pyrolysis oil that could be used as a feedstock for green diesel/gasoline or internal to a pulp mill for the thermal requirements of the lime kiln

Goal/Objective Statement

Leveraging kraft pulp mill infrastructure for biofuels and bio-based materials via pine wood, pine residues, and kraft cooking liquors.

- Microbiologically upgrading lignin fragments via oleaginous organisms to biodiesel;
- Developing an understanding of the role of cellulosic ethanol & pyrolysis oil constituents on metallic corrosion for typically used alloys in used in pulp mill & identify optimal materials

Project Quad Chart Overview

Timeline

- Project start date: 8/30/2010
- Project end date: 8/29/2013

Percent complete: 88%

Barriers

– Bt-C. Biomass Recalcitrance
– Bt-E. Pretreatment Costs
– Tt-E. Pyrolysis of Biomass

Budget

- Total project funding (DOE & cost share) = $1,258,798.27
- Funding received in FY 2011 (DOE & cost share): $0 (DOE) + $1324.17 (Cost Share) = $1,324.17
- Funding in FY 2012 (DOE & cost share): $ 0 (DOE) + $141.675.13 (Cost Share) = $141,675.13
- Funding for FY 2013 (DOE & cost share)>>> $0 (DOE) + $115,798.97 (Cost Share) = $115,798.9
- Years the project has been funded & average annual funding: $333,333.33 (DOE) + $86,266.09 (Cost Share) = $419,599.42

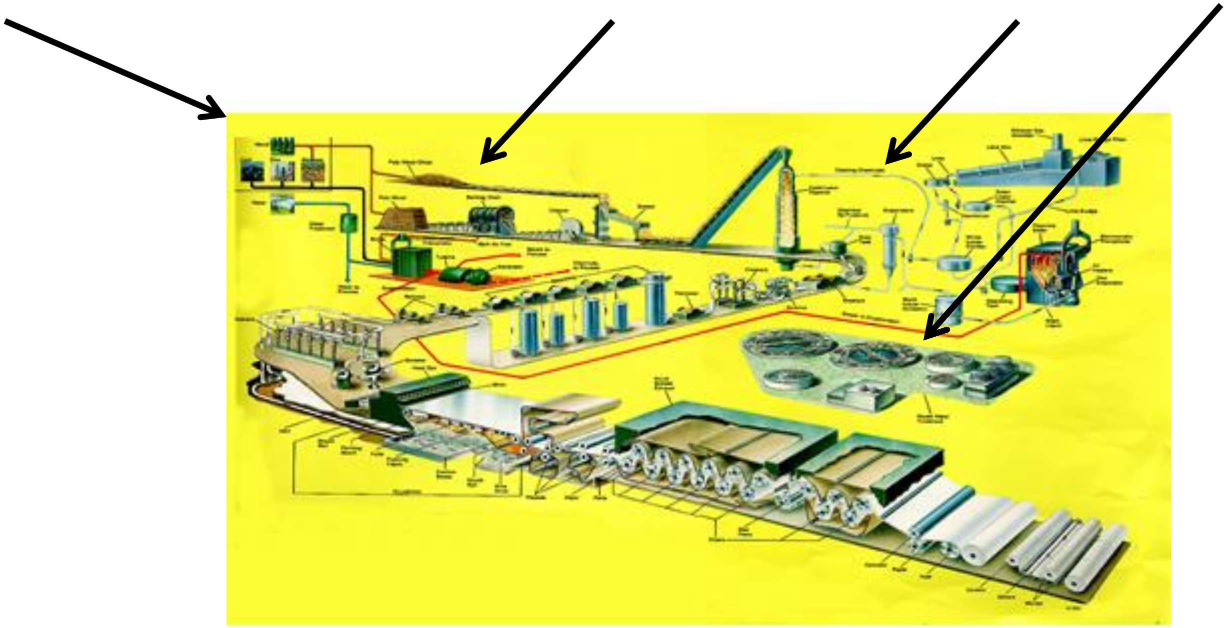
Partners & Roles

- Project managed by A.J. Ragauskas (PI) & P. Singh , Georgia Institute of Technology

Project Overview & Approach

Develop on the GA Tech campus an integrated southern pine wood to biofuels/biomaterials processing facility that will test advanced integrated wood processing exploratory technologies at the bench scale, including:

- Use of pine residues, bark, pine and kraft lignin
- Utilized for cellulosic ethanol, pyrolysis oil and biobased materials



Approach

– The efficient conversion of pine residues, bark and kraft cooking liquor into a green/bio-diesel.

- Deliverable: Pyrolysis yields/characterization at 350, 400, 500 & 550 °C
- Identify microbial organism/conditions viable on pyrolysis oil/lignin
- Go/No Go: Determine materials stable towards pyrolysis oil while minimizing cost

Technical Accomplishments/ Progress/Results

Pine residue and bark pyrolysis

-Basic chemical constituents info needed for all the studies

Component (% on o.d. wood sample)	Stem wood	Residue	Bark
Holocellulose	68.5	65.9	50.9
α-cellulose	45.4	42.1	29.3
Hemicellulose	20.1	16.2	15.2
Arabinose	1.4	1.3	1.1
Galactose	2.1	2.0	1.8
Xylose	7.0	5.3	5.1
Mannose	9.6	7.6	7.2
Lignin	28.0	26.7	33.7
Acid insoluble lignin (Klason lignin)	27.3	25.7	32.9
Acid soluble lignin	0.7	1.0	0.8
Dichloromethane (DCM) extractives	2.5	1.5	3.6
Tannins	-	3.7	11.6
Ash	0.3	0.8	0.9
Total mass	99.3	98.6	100.7

Stem wood

Residue

Bark

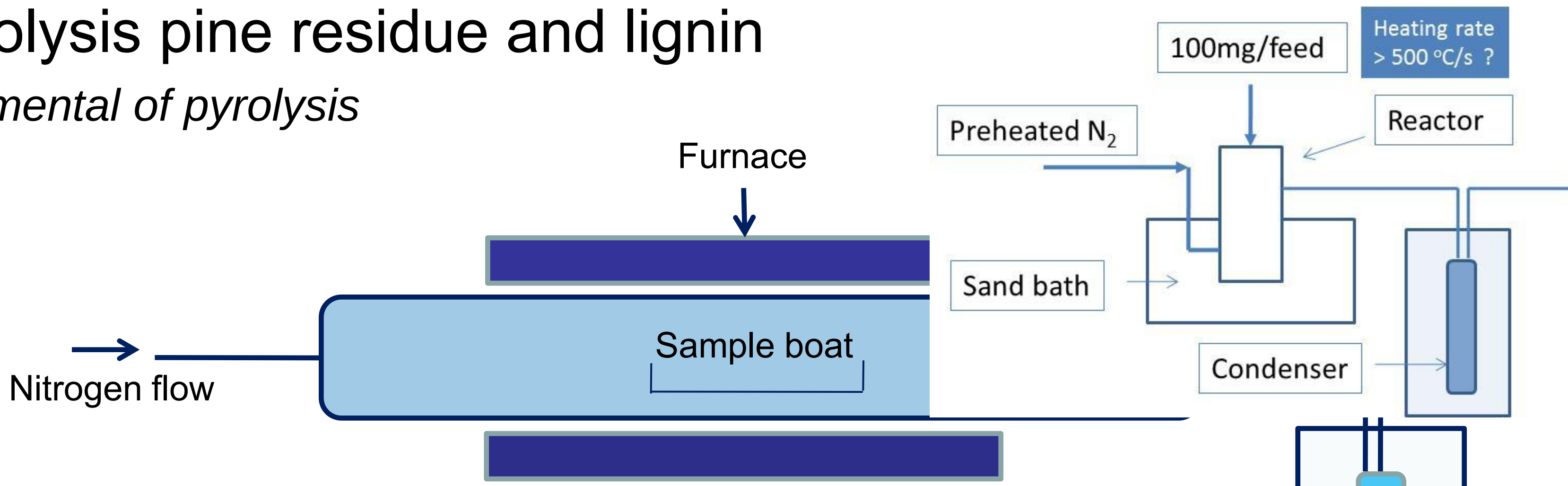
- Lignin, Tannin, Hemicellulose, Cellulose: Structure and DP determined/reported

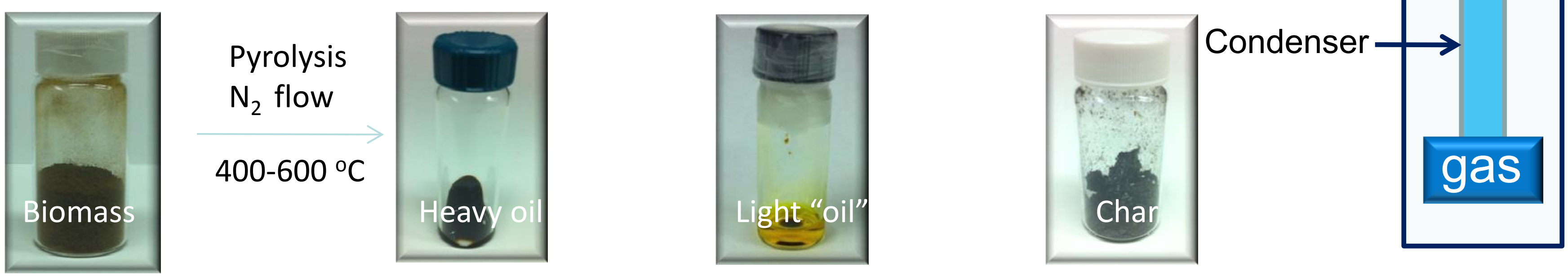
Journal of Agricultural and Food Chemistry (2011), 59(24), 12910
One of the first to report all components from same resource

Technical Accomplishments/ Progress/Results (cont'd)

- Pyrolysis pine residue and lignin

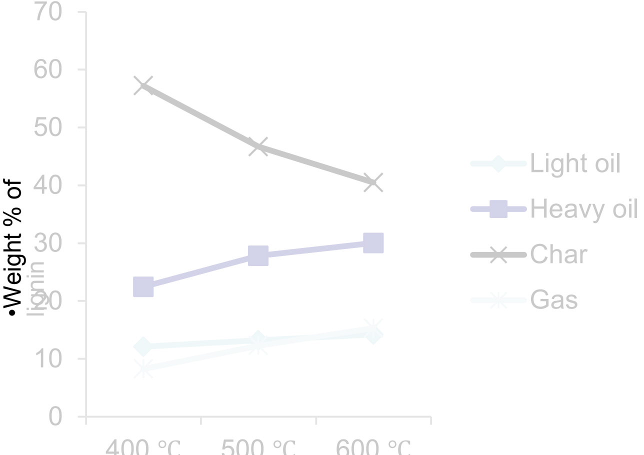
- Experimental of pyrolysis





•Precursor of bio-fuel and bio-chemical	•Contain >60 wt% water •Water soluble organic products •Ready to use bio-chemical	•Energy yields ~50% •HHVs (>31 MJ/kg) > coals (20-30 MJ/kg)	•Contain~50 mol% of CO & CO_2, ~25 mol% of H_2

Yields of pyrolysis products



Lignin(SW kraft)

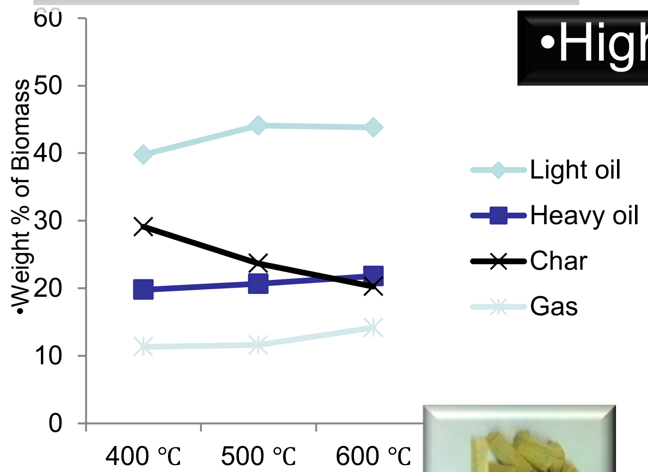
Cellulose

Tannin (pine bark)

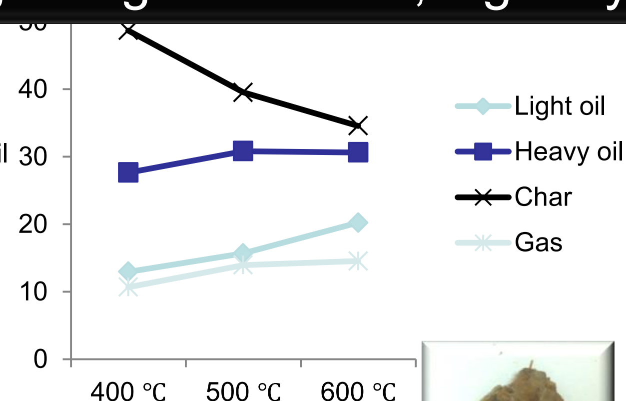
•Mostly heavy oil and

•Mostly light

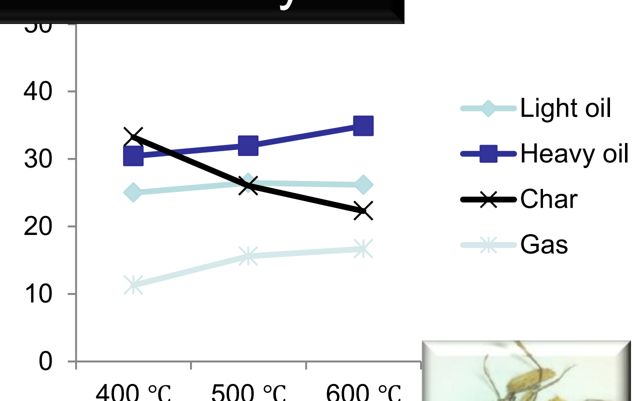
•Higher lignin content, higher yield of heavy oil



Pine wood

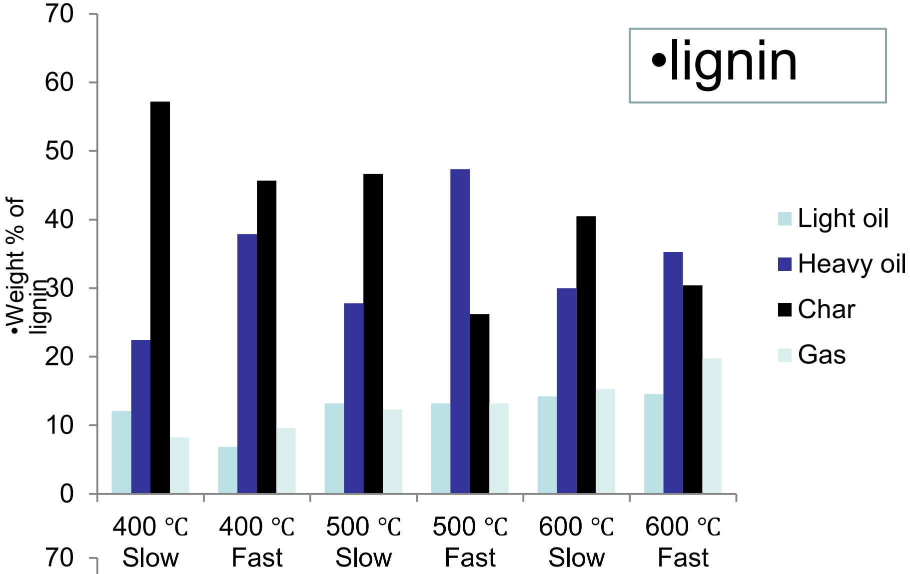


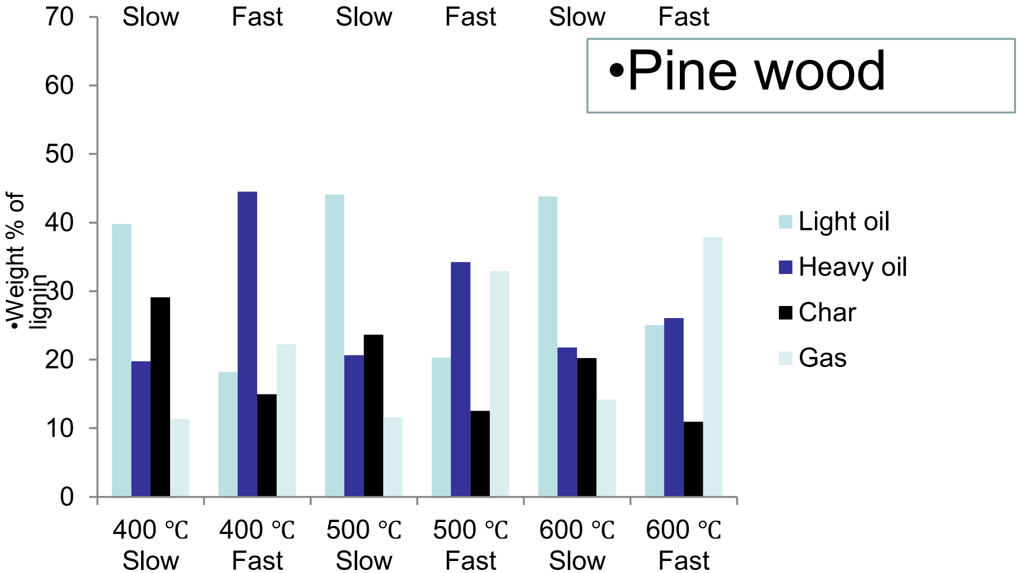
Pine bark



Pine residue

How to increase yields of liquid products?



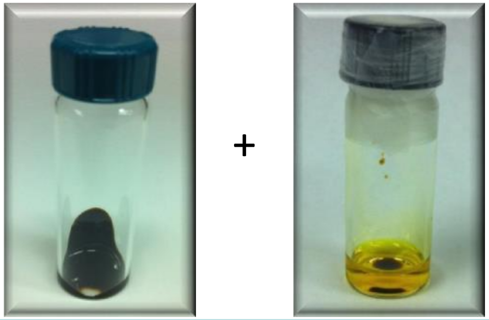


•Heavy oil

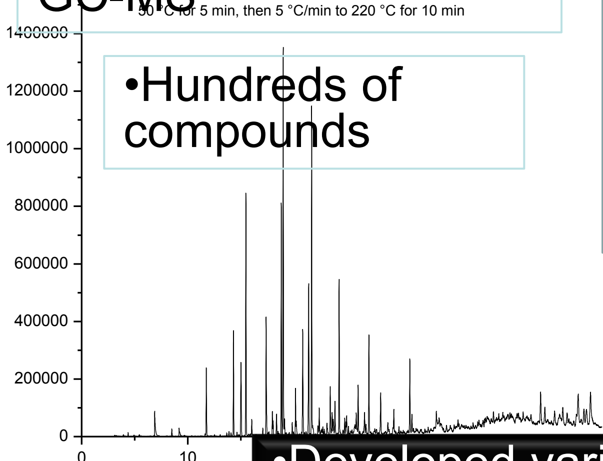
•Light oil

Higher lignin content
Higher heating rate
Produce more heavy oil

Higher carbohydrates contents
Lower heating rate
Produce more light oil

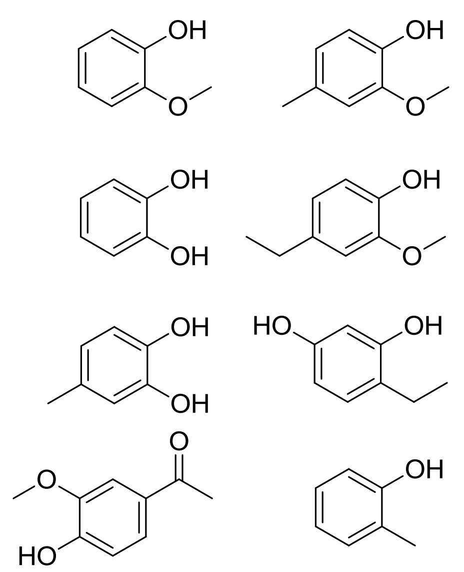


•Analysis mostly by GC-MS



•Hundreds of compounds

Major components



•Molecular weight < 200 g/mol detected by GC-MS vs.

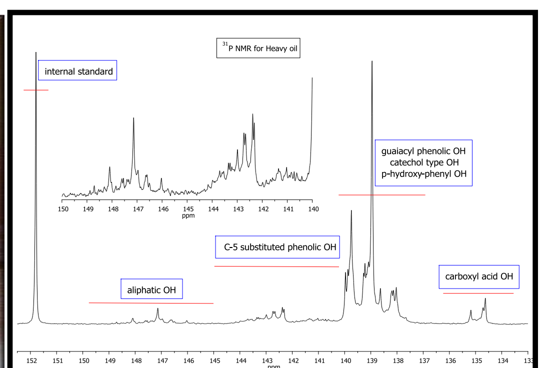
•Average molecular weight ~300-1300 g/mol detected by GPC

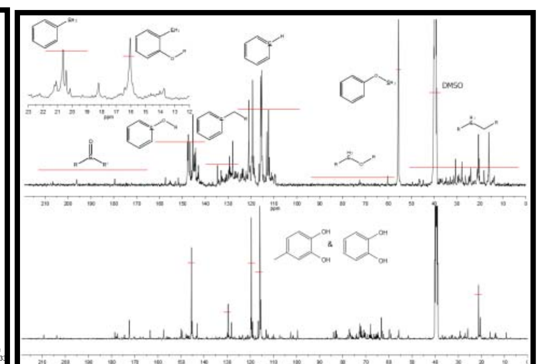
•Pyrolysis oil contains ~20 mass% water, ~40 mass% GC-detectable compounds, ~ 15 mass% non-volatile HPLC detectable compounds and ~15 mass% high molar mass non-detectable compounds.

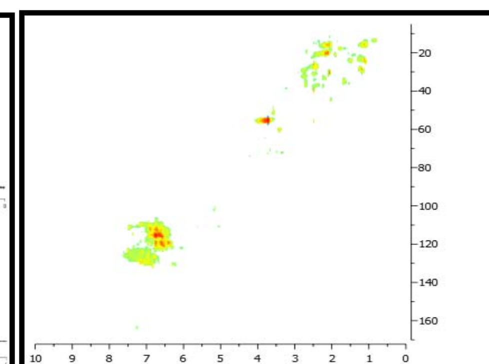
•*Biomass and Bioenergy, 2007, 31, 222-242*.

•How to analyze such complex pyrolysis mixtures?

•Developed various NMR methods to analyze whole portion of pyrolysis oil

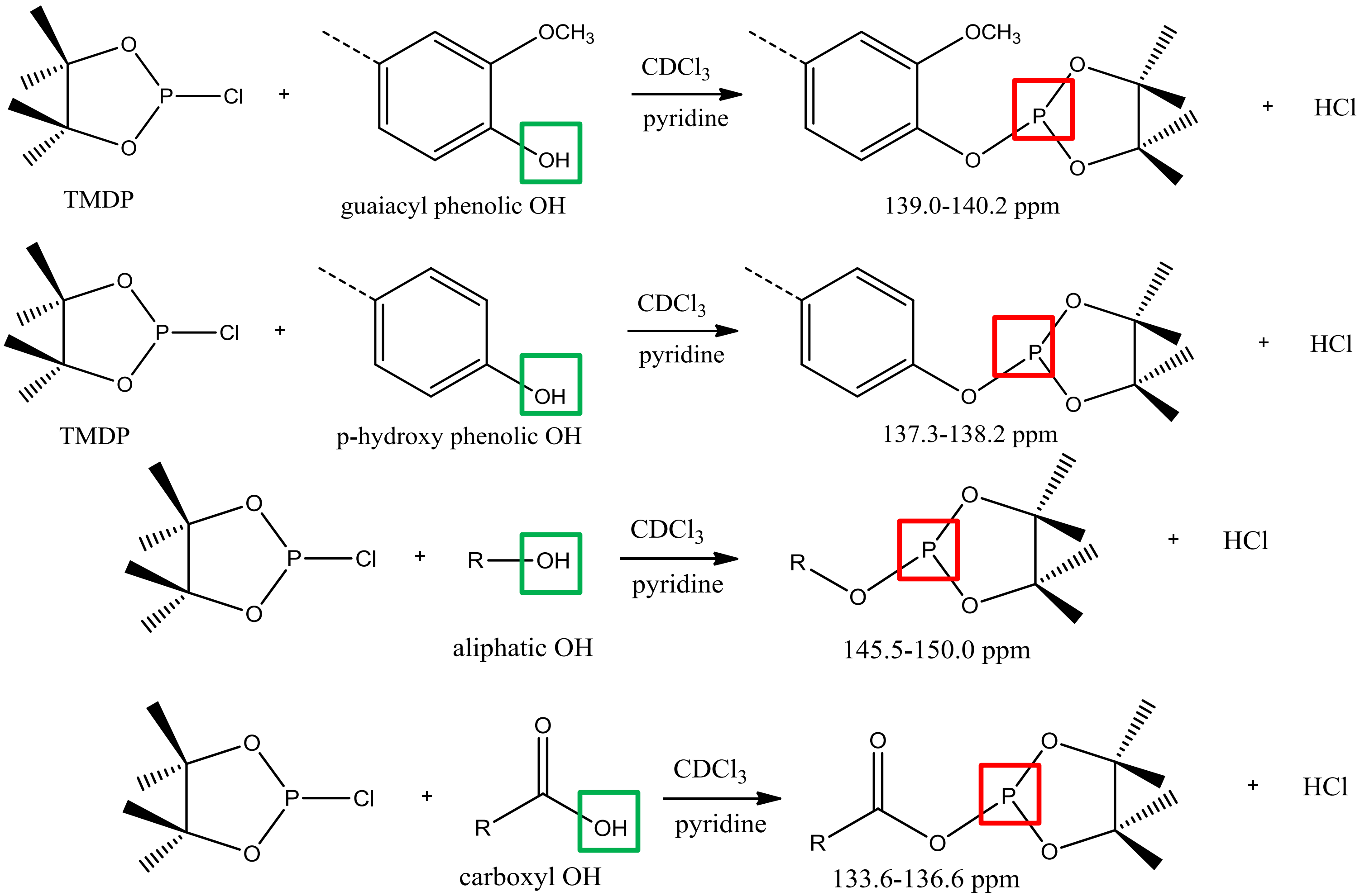






The first reported effort to analyze pyrolysis oils by HSQC

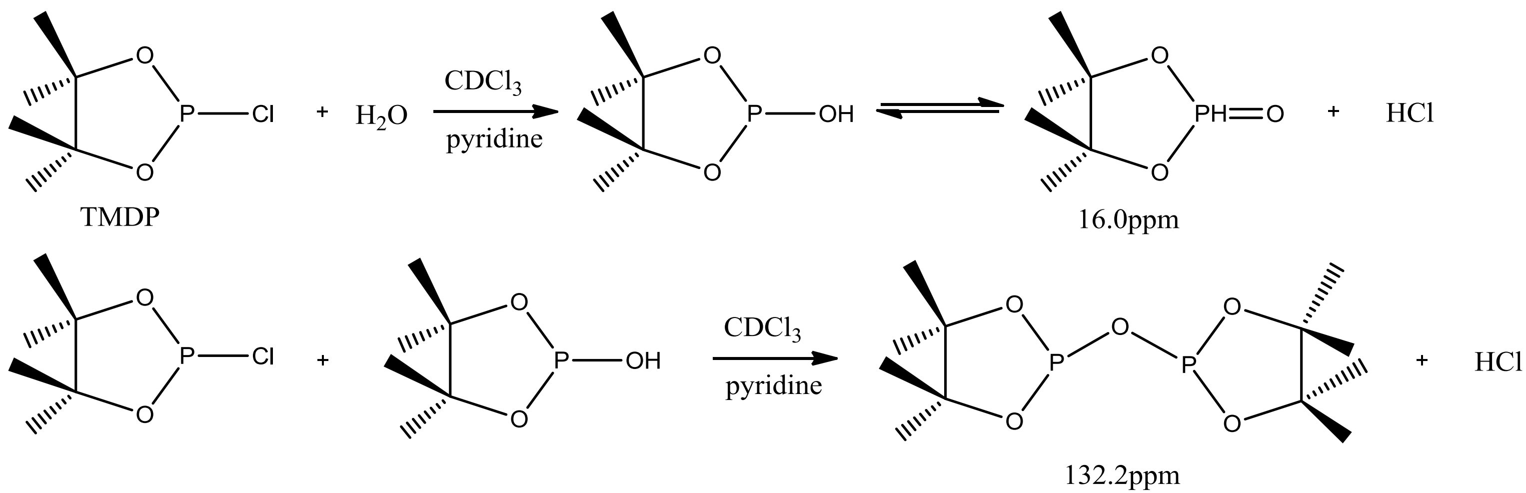
Quantitatively determine hydroxyl functional groups by ^{31}P NMR



•Reactions of the phosphorous reagent (TMDP) with hydroxyl functional groups and the ^{31}P NMR assignment of phosphitylated compounds

•Pu, Y.; Cao, S.; Ragauskas, A. J., *Energ. Environ. Sci. 2011, 4, (9), 3154-3166.*

Quantitatively determine water content by ^{31}P NMR

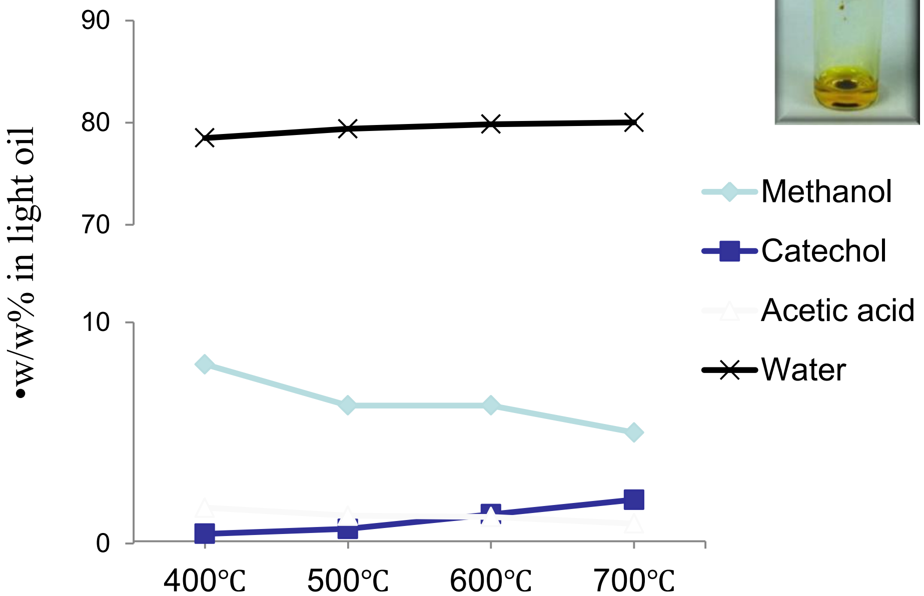


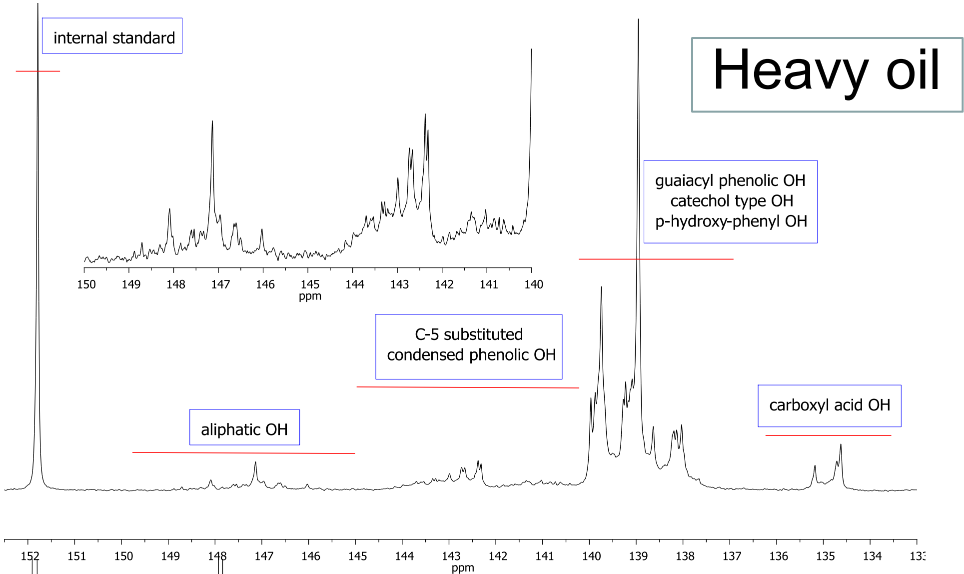
•Very simple one step measurement, takes ~3-30 min.

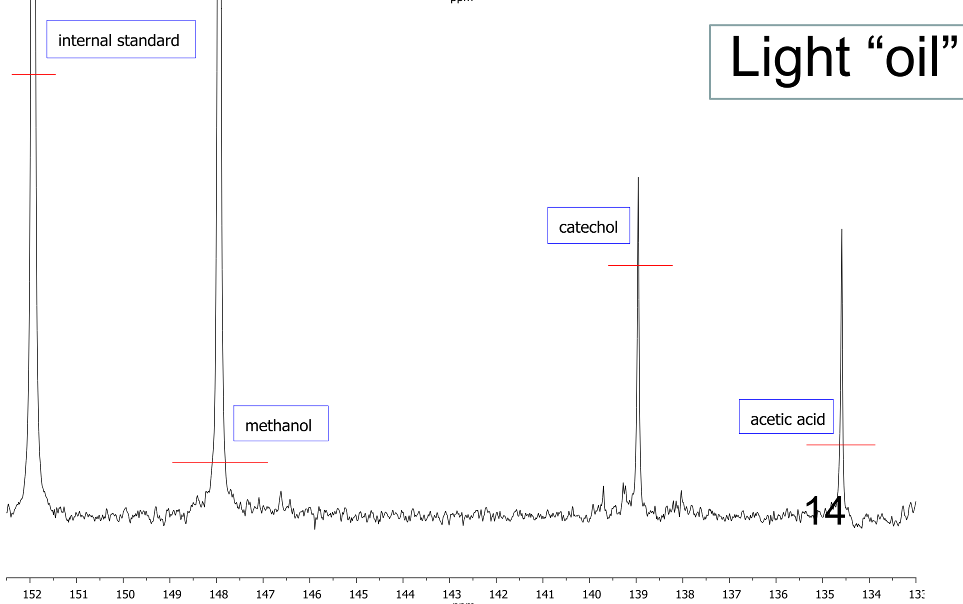
Reactions of the phosphorous reagent (TMDP) with water and the ^{31}P NMR assignment of phosphitylated compounds

^{31}P NMR analysis of pyrolysis oils

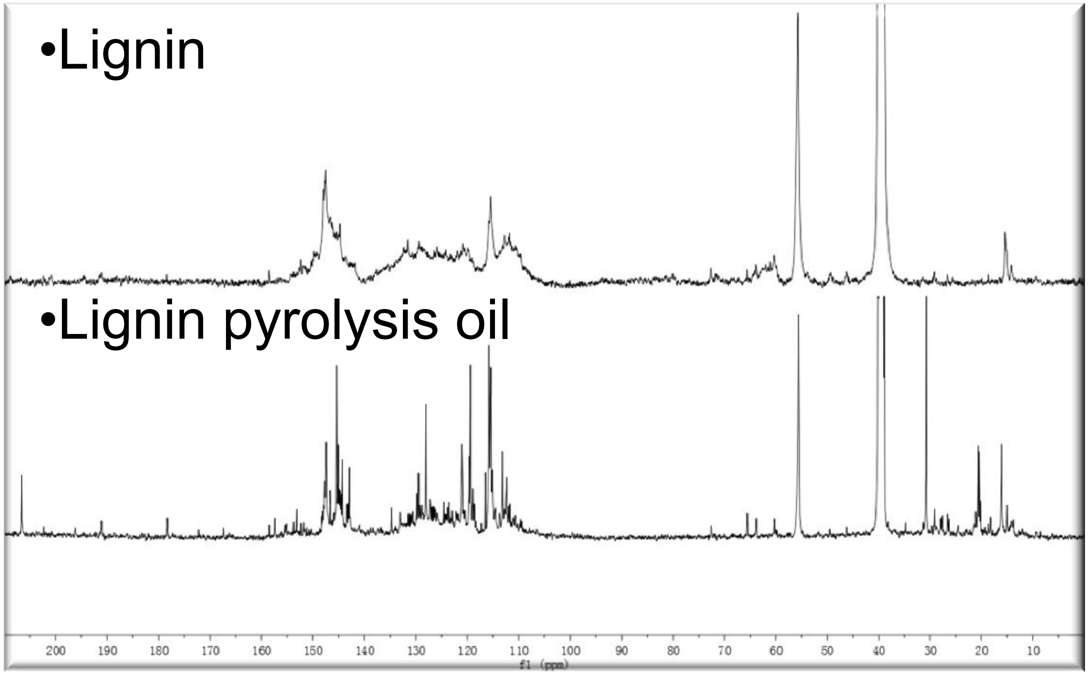
•Light oils







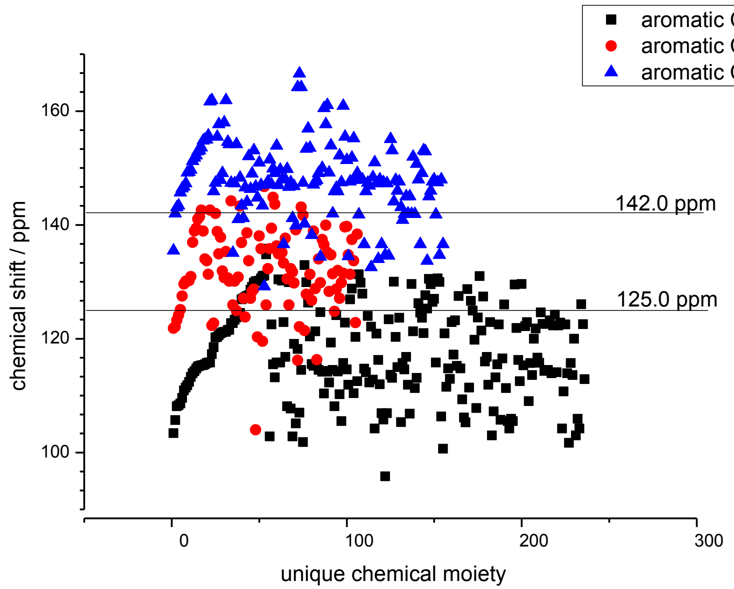
How to analyze the pyrolysis oil by ^{13}C NMR?

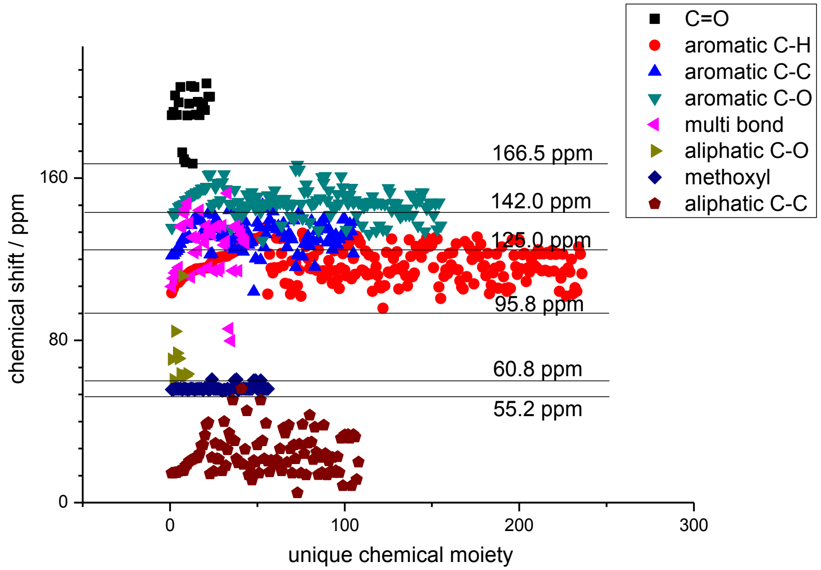


Traditional chemical shift assignment ranges could not provide precise integration results for pyrolysis oils

We need new chemical shift assignment ranges based on?

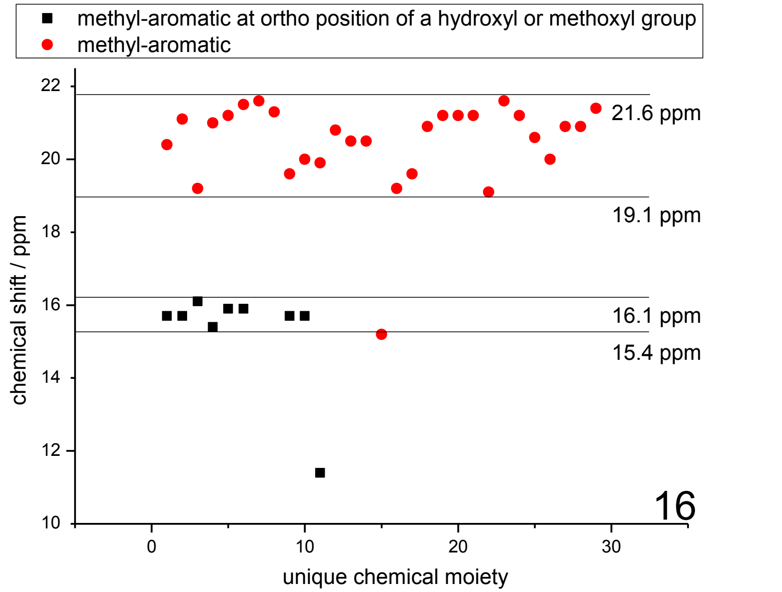
Detailed chemical shift analysis of pyrolysis oil model compounds





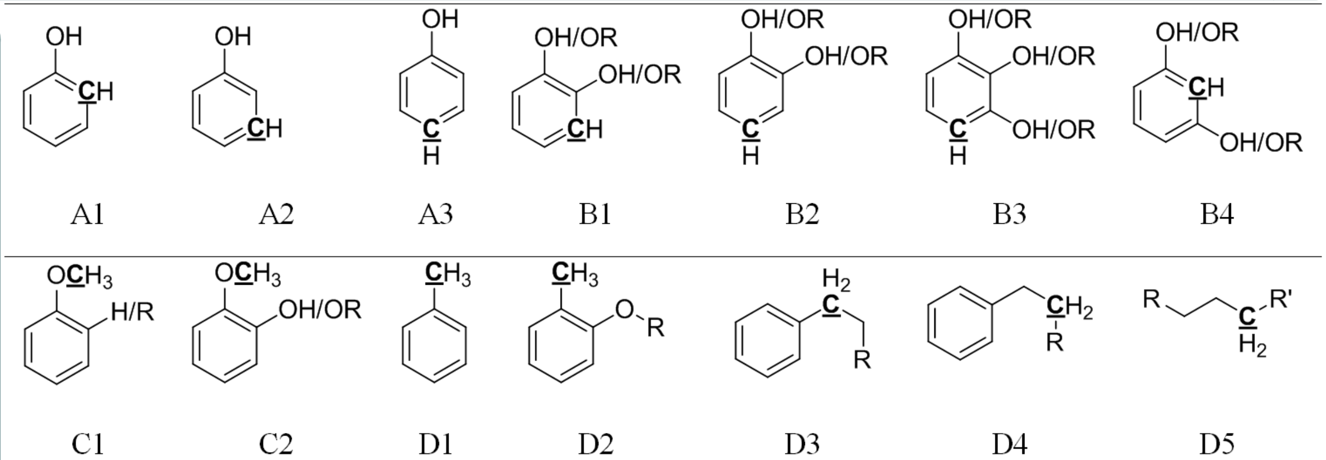
Plot >1000 chemical shifts for each carbon of the reported components in the pyrolysis oil

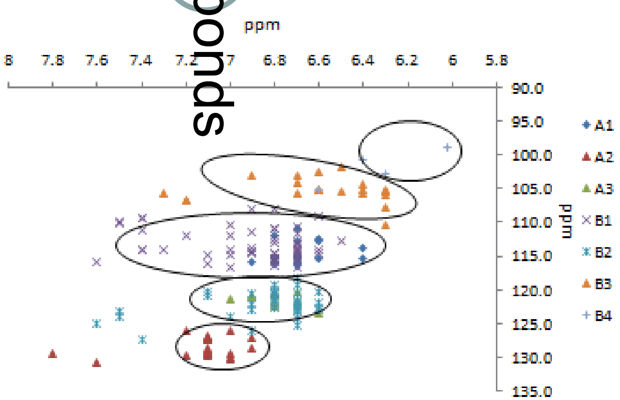
The new chemical shift assignment ranges for nine different carbons have been proposed

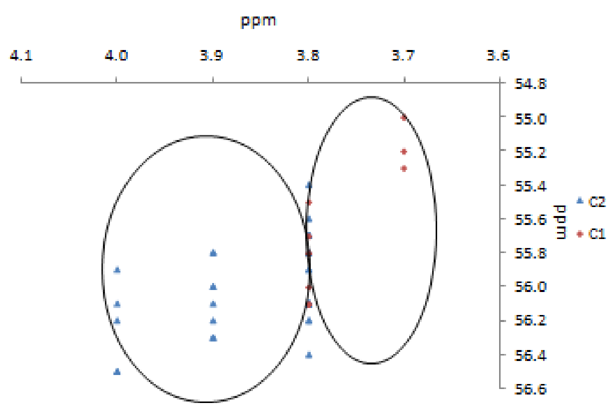


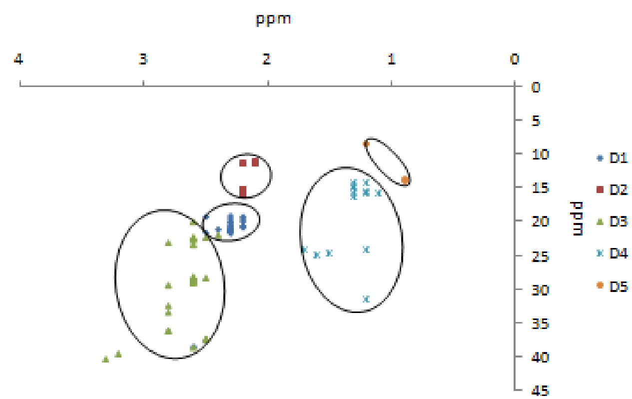
HSQC-NMR fingerprint analysis of pyrolysis oil model compounds

- ~30 different C-H bonds

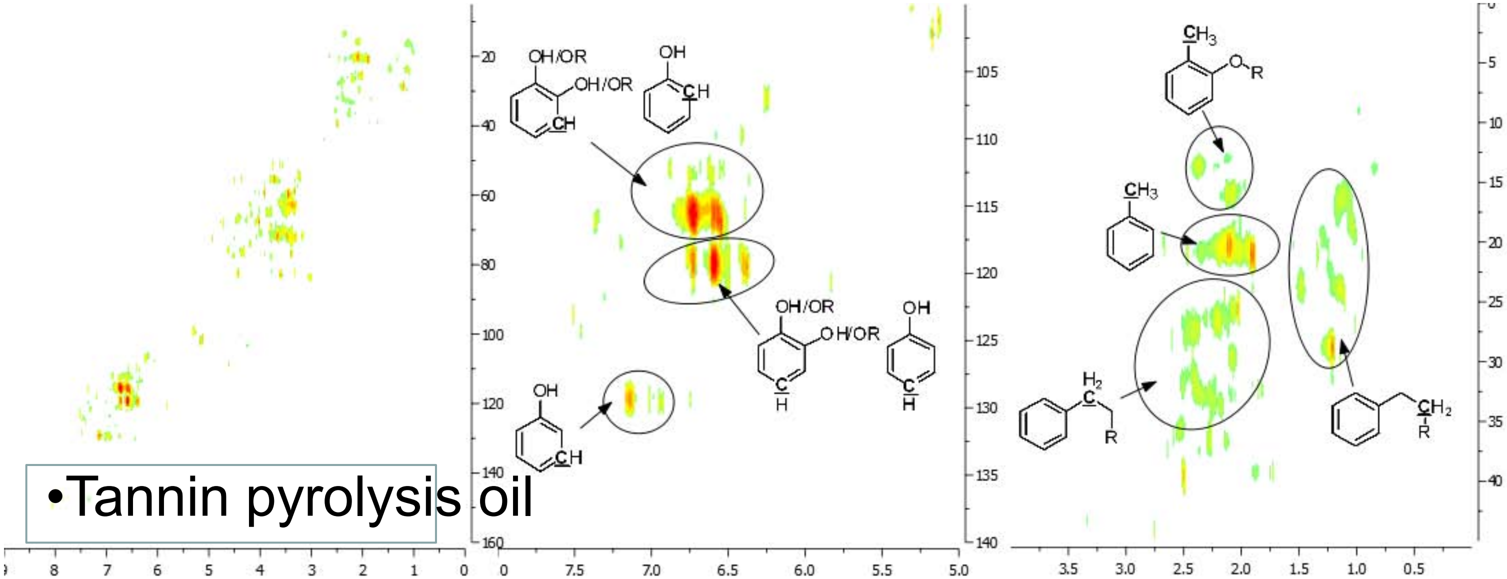




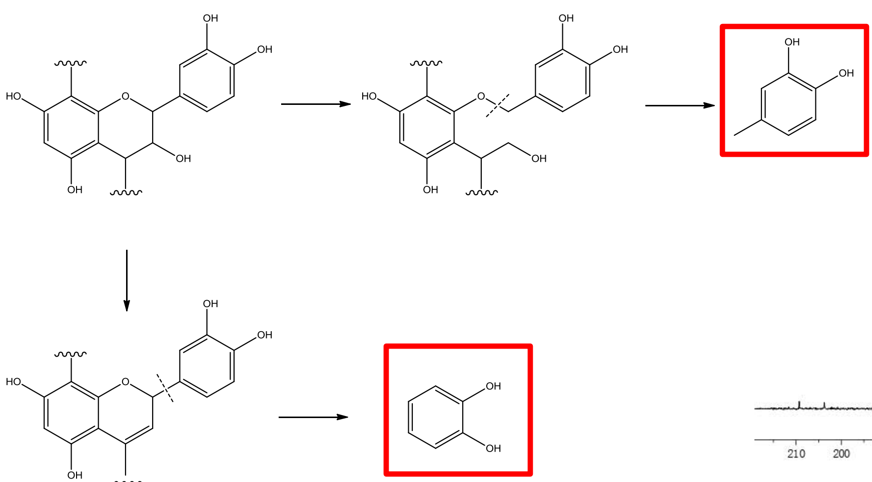


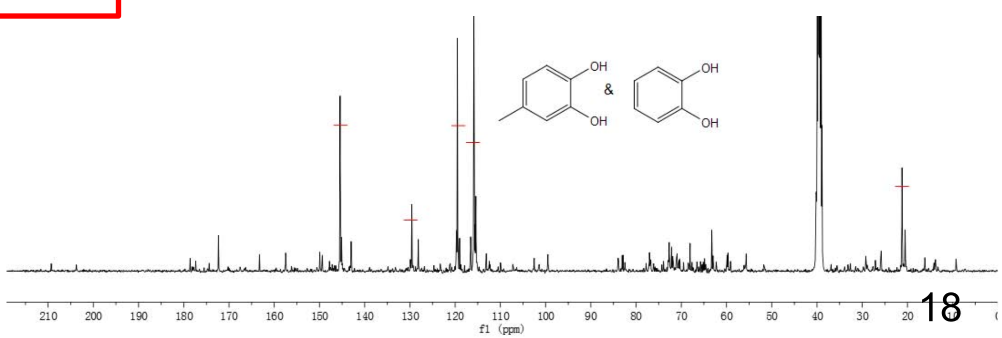


What happens during pyrolysis process?

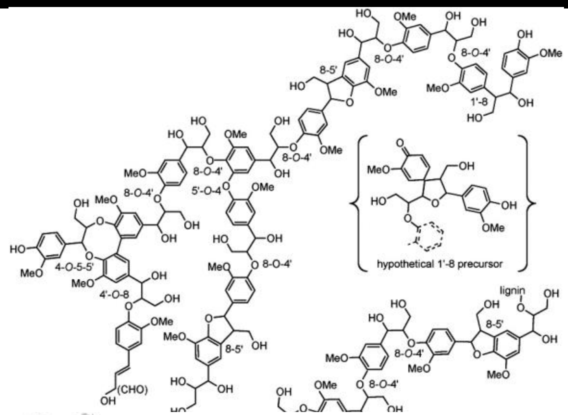


•Tannin pyrolysis oil



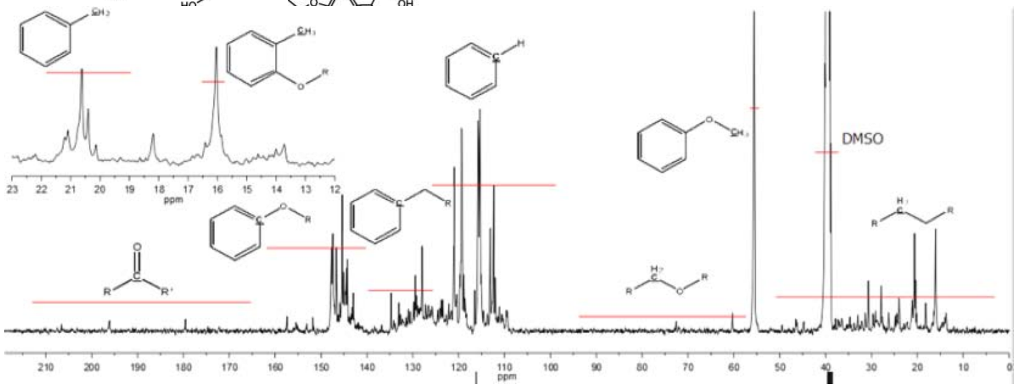


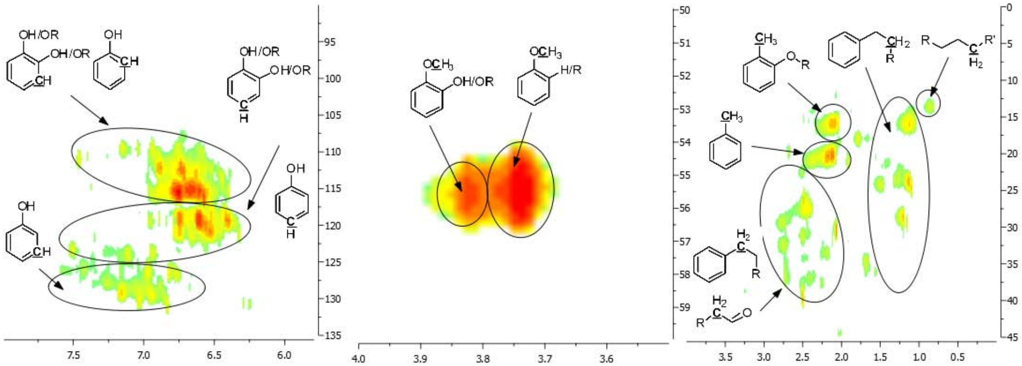
What happens during pyrolysis process?

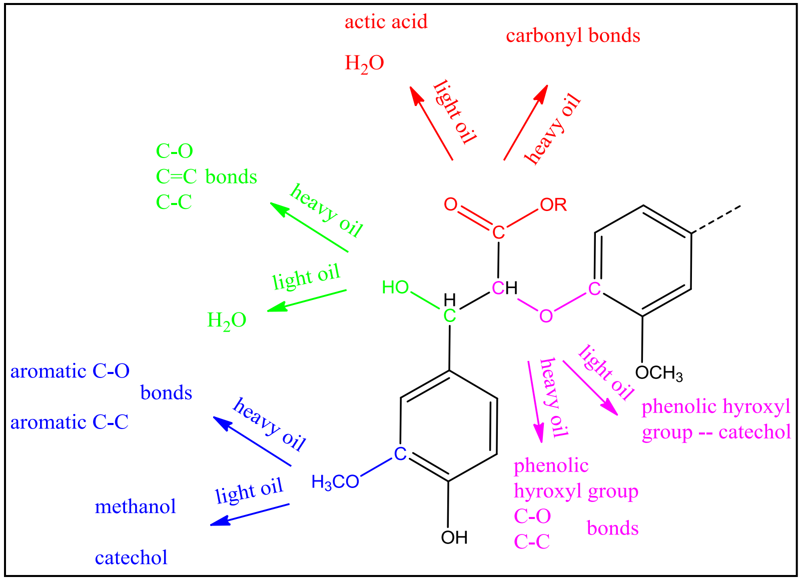


- Pyrolysis
- N_2 flow
- 400-600 ^oC

•+





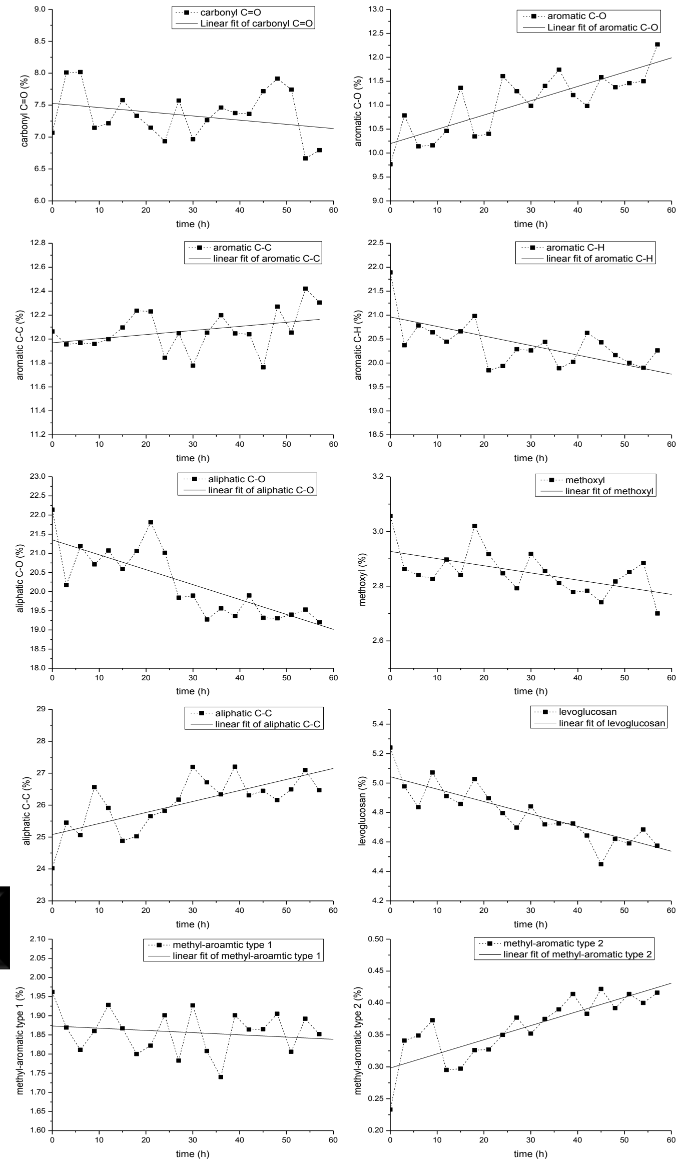


Negative properties of pyrolysis oils

- High oxygen content – 20-30 wt%; 0 wt% for gasoline and <0.6 wt% for diesel
- High acidity – 0.3 mmol/g-1.5 mmol/g of pyrolysis oil is acid-OH; <0.002 mmol/g of diesel
- High molecular weight – 300-1300 g/mol; 120 g/mol for gasoline and 230 g/mol for diesel
- **Aging** – molecular weight and acidity increase during storage.
-

•http://www.ufa.com

Aging process of pyrolysis oils



In situ NMR characterization of pine residue pyrolysis oils
• during the accelerated aging process at 80 °C for 60h

Aging process of pyrolysis oils

Type of protons	Lignin		Cellulose		Poplar wood			Pine wood		
	Fresh	1 y @ RT	Fresh	1 y @ RT	Fresh	30 h @ 80 °C	60 h @ 80 °C	Fresh	60 h @ 80 °C	1 y @ RT
-C**H**O, -COO**H**	5.0	5.2	0.3	0.7	0.4	0.6	0.6	0.2	0.4	0.8
Ar**H**, **H**C=C-	29.2	27.1	2.3	1.5	11.2	10.5	10.0	12.0	11.2	10.8
-C**H**$_n$-O-, C**H**$_3$-O-	34.3	22.8	66.1	63.0	43.4	36.6	35.9	45.7	43.2	39.2
-C**H**$_3$, -C**H**$_n$-	31.5	44.9	31.3	34.8	45.0	52.3	53.5	42.1	45.2	49.2

- More carbonyl and carboxyl protons – higher acidity
- Less aromatic protons – higher substituted aromatics
- Less C-O bonds – improved dehydration reaction, cleavage of methoxyl group and ether bonds
- More aliphatic protons – methyl-aromatic bonds, condensation products
- Lignin pyrolysis oil has a much higher aging rate than the cellulose pyrolysis oil
- The hardwood pyrolysis oil has a higher aging rate than the softwood pyrolysis oil
- Methoxyl group is one of the major target functional groups during the aging

Upgrade of pyrolysis oils

- Upgrade pyrolysis oil during the pyrolysis process–pyrolysis of biomass with metal salts and zeolites.
- Upgrade pyrolysis oil after the pyrolysis process–hydrogenation and deoxygenation of pyrolysis oils.
- Pyrolysis with $NiCl_2$ and CaO produced "upgraded" pyrolysis oils have more methoxyl groups and ether bonds, and higher molecular weight.
- The metal salts always involved in pyrolysis reactions.
- $$NiCl_2 + 2H_2O \longrightarrow NiO + 2HCl$$

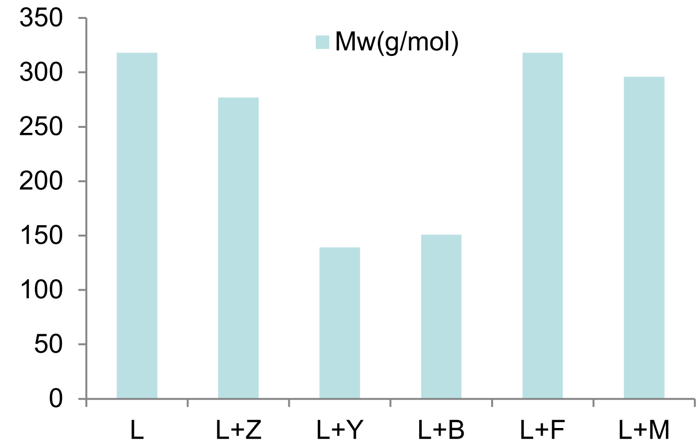
$$CaO + H_2S \longrightarrow CaS + H_2O$$

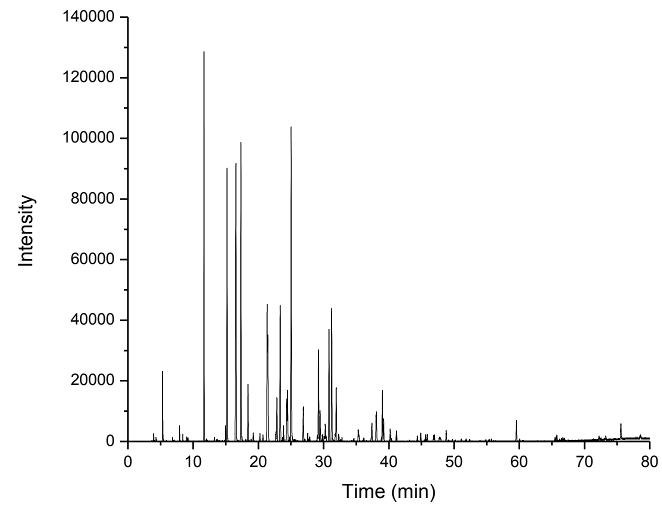
$$CaO + CO_2 \longrightarrow CaCO_3$$

•Guan, R.; Li, W.; Li, B., *Fuel 2003, 82, (15-17), 1961-1966.*

•Zou, X.; Yao, J.; Yang, X.; Song, W.; Lin, W., *Energy Fuels 2007, 21, 619-624.*

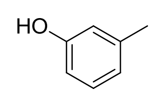
One step thermal conversion of lignin to the gasoline molecular range liquid products by using zeolites as additives



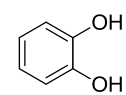


•The molecular weight of Y and B zeolites upgraded pyrolysis oils decreased to the gasoline range (80-120 g/mol)

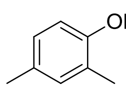
•Major components detected by GC-MS



Phenol, 3-methyl-



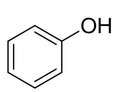
1,2-Benzenediol



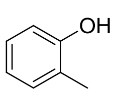
Phenol, 2,4-dimethyl-

•The aliphatic hydroxyl groups completely decomposed

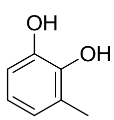
•The content of carboxylic acid decreased by 50%



Phenol



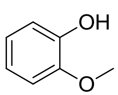
Phenol, 2-methyl-



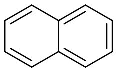
1,2-Benzenediol, 3-methyl-

•Methoxy groups decreased by 80%

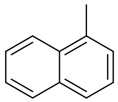
•Almost all the oxygen belonged to phenolic hydroxyl groups



Phenol, 2-methoxy-



Naphthalene

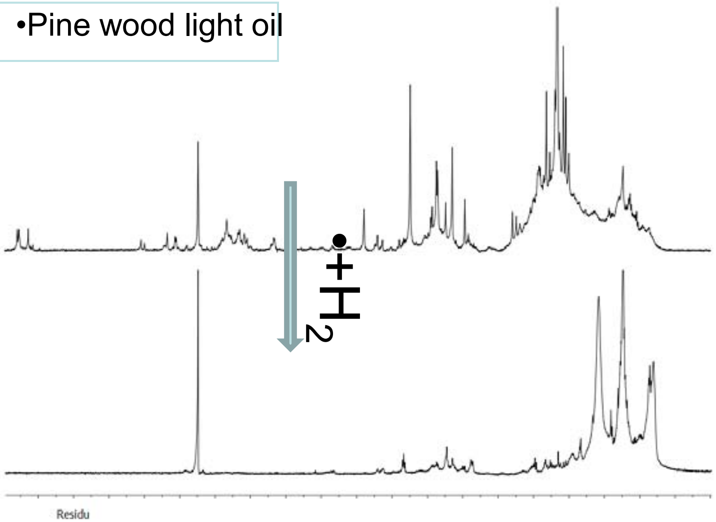


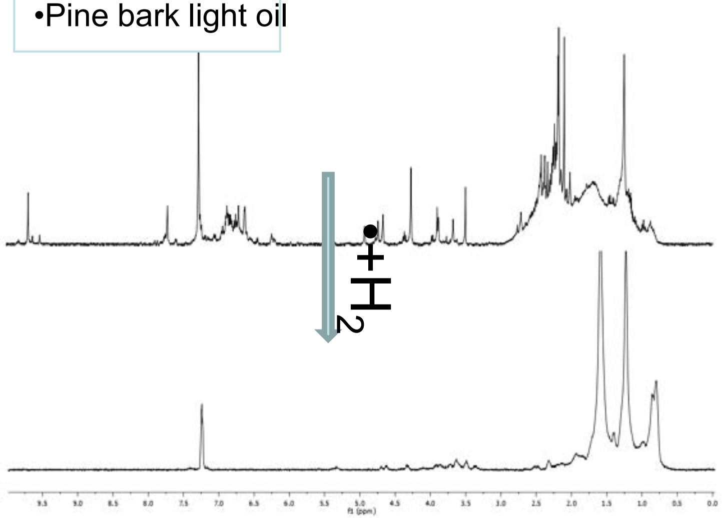
Naphthalene, 1-methyl-

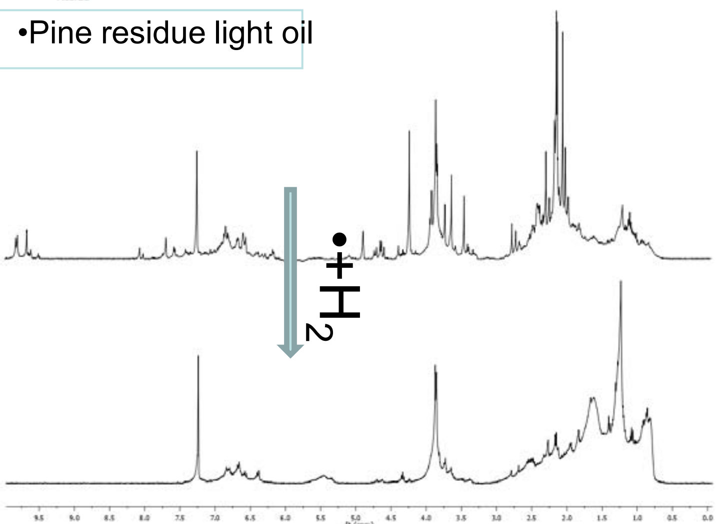
Pour point—lowest temperature to flow decreased from 9 to -21°C

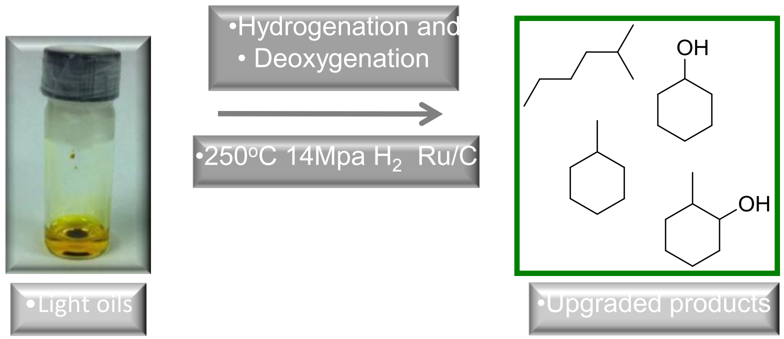
Possible precursor of gasoline and substitution of petrochemicals

One step upgrade light oils to the total aliphatic products









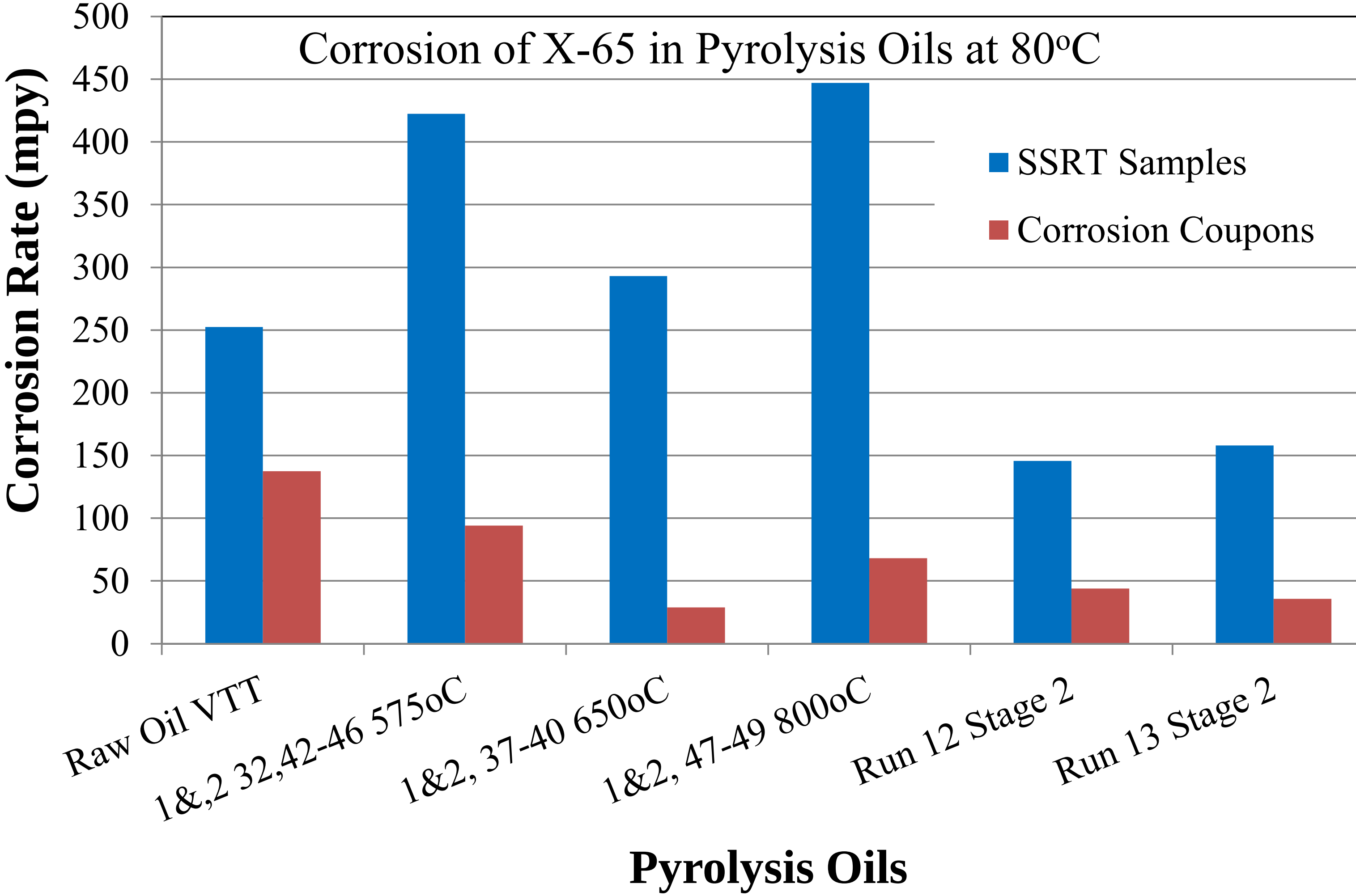
Light oils could be upgraded to the total aliphatic products by one step HDO process

•Why incomplete hydrogenation of whole biomass pyrolysis oils?

Technical Accomplishments/ Progress/Results

- Task C.4 Corrosion science of pine pyrolysis oil

-*Deformation induced corrosion acceleration*



Technical Accomplishments/ Progress/Results

- Corrosion science of pine pyrolysis oil

-*General conclusions*

- **Carbon steel had significant general corrosion in tested pyrolysis oils, pine based pyrolysis oil**
- **Al alloy (1100) showed some signs of localized attack at the 2nd phase particles, causing pit initiation along with some general corrosion.**
- **Stainless steels, 316L, 2205 and 2101 had very low corrosion rates in both pyrolysis oils tested.**
- **Brass and Cu samples had some tarnish at the surface and showed localized corrosion in the form of small pits, which do not seem to be active. This may be due to dissolution of some active phase, leaving noble Cu based matrix unattacked.**

Technical Accomplishments/ Progress/Results

- Corrosion science of pine pyrolysis oil

-*Lessons Learned and Path Forward*

- **Results form this study has provided information on the type of corrosion issues related to different process streams of pine based biorefinary**
- **Strategies to mitigate corrosion in different process streams of biorefianary can now be based on the results from this study.**
- **Design of new plants or equipment to handle tested environments can be based on the knowledge developed in this project**
- **Testing protocols are in place to test any specific environmental changes in specific biorefinary stream**
- **We will work with companies to provide information on corrosion and material performance to design and operate pine-based biorefineries**

Summary

Future Work:
- Examine fundamentals of oleaginous organisms biochemistry
- Improve catalytic upgrading of pyrolysis oil
- Tailoring sections of these studies for industrial sponsorship

Success Factors and Challenges:
- All deliverables will be accomplished with NCE

Technology Transfer
- 16 peer reviewed publications, 3 additional under review and~ 6 more to be submitted
- 10 technical presentations to industry and research community
- Select fundamentals hosted on web at http://ipst.gatech.edu/faculty/ragauskas_art/bio_ragauskas_art.html
- Students hired in bioenergy/biorefining field
- 1 Student currently at Chalmers University/Sweden

Additional Slides

Publications and Presentations

Publications

•Improving the Mechanical and Thermal Properties of Gelatin Hydrogels Cross-Linked by Cellulose Nanowhiskers. Dash, R.; Ragauskas, A.J., Carbohydrate Polymers (2013), 91, 638-645.

•Production of renewable gasoline from aqueous phase hydrogenation of lignin pyrolysis oil. Ben, H.; Mu, W.; Deng, Y.; Ragauskas, A.J., Fuel, (2013) 103, 1148-1153.

•Influence of Si/Al ratio of ZSM-5 zeolite on the properties of lignin pyrolysis products. Ben, H.; Ragauskas, A.J., ACS Sustainable Chemistry & Engineering (2013), 1(3), 316-324.

•One step thermal conversion of lignin to the gasoline range liquid products by using zeolites as additives. Ben, H; Ragauskas, A.J. RSC Advances (2012), 2 (33), 12892 – 12898.

•Biotechnological opportunities with the β-ketoadipate pathway. Wells, T.; Ragauskas, A.J., Trends in Biotechnology, (2012), 30(12), 627-637.

•Grafting of model primary amine compounds to cellulose nanowhiskers through periodate oxidation. Dash, R.; Elder, T.; Ragauskas, A.J. Cellulose (2012), 19(6), 2069-2079.

•In Situ NMR Characterization of Pyrolysis Oil during Accelerated Aging. Ben, H; Ragauskas, A.J., ChemSusChem (2012), 5(9), 1687-1693.

•Chemical Characterization and Water Content Determination of Bio-oils Obtained from Various Biomass Species using ^{31}P-NMR Spectroscopy. Biofuels, David, K.; Ben, H.; Muzzy, J.; Feik, C.; Lisa, K.; Ragauskas, A.J. Biofuels (2012), 3(2), 123-128.

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•Cellulose Nanowhisker Foams by Freeze Casting, Carbohydrate Polymers, Dash, R.; Li, Y.; Ragauskas, A.J., (2012), 88(2), 789-792.

Publications and Presentations

Publications

•Bioconversion of Lignin Model Compounds with Oleaginous *Rhodococci,* Applied Microbiology and Biotechnology, Kosa, M.; Ragauskas, A.J. Applied Microbiology and Biotechnology (2012), 93(2), 891-900.

•Dilute H_2SO_4 and SO_2 Pretreatments of Loblolly Pine Wood Residue for Bioethanol Production. Huang, F.; Ragauskas, A.J. Industrial Biotechnology (2012), (2012), 8(1), 22-30.

•Heteronuclear Single-Quantum Correlation-Nuclear Magnetic Resonance (HSQC-NMR) Fingerprint Analysis of Pyrolysis Oils. Ben, H.; Ragauskas, A. J. Energy & Fuels (2011), 25(12), 5791-5801.

•Pyrolysis of Kraft Lignin with Additives. Ben, H.; Ragauskas, A.J., Energy & Fuels (2011), 25(10), 4662-4668.

•Characterization of Milled Wood Lignin (MWL) in Loblolly Pine Stem Wood, Residue, and Bark Full. Huang, F.; Singh, P.M.; Ragauskas, A.J. Journal of Agricultural and Food Chemistry (2011), 59(24), 12910-12916.

•NMR Characterization of Pyrolysis Oils from Kraft Lignin. Ben, H.; Ragauskas, A.J. Energy & Fuels (2011), 25(5), 2322-2332.

Book title:

•Chemical Pretreatment Techniques for Biofuels and Biorefineries from Softwood. Huang, F.; Ragauskas, A.J., *In* Pretreatment Techniques for Biofuels and Biorefineries. Ed. Fang, Z. (2013) 8, 151-182.

Publications and Presentations

Presentations

INVITED SPEAKER

- ContrBiorefining: How to Make a Difference Today – Tomorrow , IPST Members Meeting (April, 2013).
- (i) Introduction to Biorefining Session (ii) Biorefining, Expanding the Envelope for Green Forest Manufacturing, IPST Members Meeting (April, 2012).
- Biorefineries and Bioconversions: Current and Future Challenges. GA Tech Fall 2011 Transformational Energy Speaker Series.
- A Fresh Look at the Biorefinery Concept: What Works and What Doesn't. Ragauskas, A.J., Wood Science and Engineering, Oregon State University (April 2011).
- Creating Sustainable Chemical Solutions Essential to Converting Lignocellulosic Biomass resources to BioMaterials, BioFuels, BioChemicals and BioPower for People Everywhere. Ragauskas, A.J., Department of Energy, Washington, DC (April 2011).

Contributed Participation

- 34th Symposium on Biotechnology for Fuels and Chemicals. New Orleans, (May 2012).
- Pyrolysis of biomass to biofuels. Ben, H.; Ragauskas, A.J., 243rd ACS National Meeting & Exposition, San Diego, CA, (March, 2012).
- Corrosion Susceptibility of Different Alloys in Pyrolysis Oils. Singh P. M., Ragauskas A. J., Mahmood J., Keiser J. R CORROSION 2012, NACE International, Orlando, Fl, March 2012.
- Corrosion and Stress Corrosion Cracking in Biofuels, P. M. Singh, Gordon Research Conference on Aqueous Corrosion, Colby-Sawyer College, New London, New Hampshire. July 8-13th, 2012.
- Lignin to Lipid Bioconversion by Rhodococci Bacteria. Kosa, M.; Ragauskas, A.J. 242nd ACS National Meeting & Exposition, Denver, CO (August, 2011).

Technical Accomplishments/ Progress/Results

Corrosion science of pine pyrolysis oil

-SSRT - X-65 C-Steel in “VTT raw pyrolysis oil” at 50^{o}C