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DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

2.3.1.302 Bio-oil Quality Improvement and Catalytic Hydrotreating of Bio-oils - PNNL

March 24, 2015
Conversion R & D

PI: Alan Zacher
Presenter: Mariefel V. Olarte
Pacific Northwest National Laboratory

Problem Statement

Can liquid transportation fuel be produced sustainably and economically from biomass?

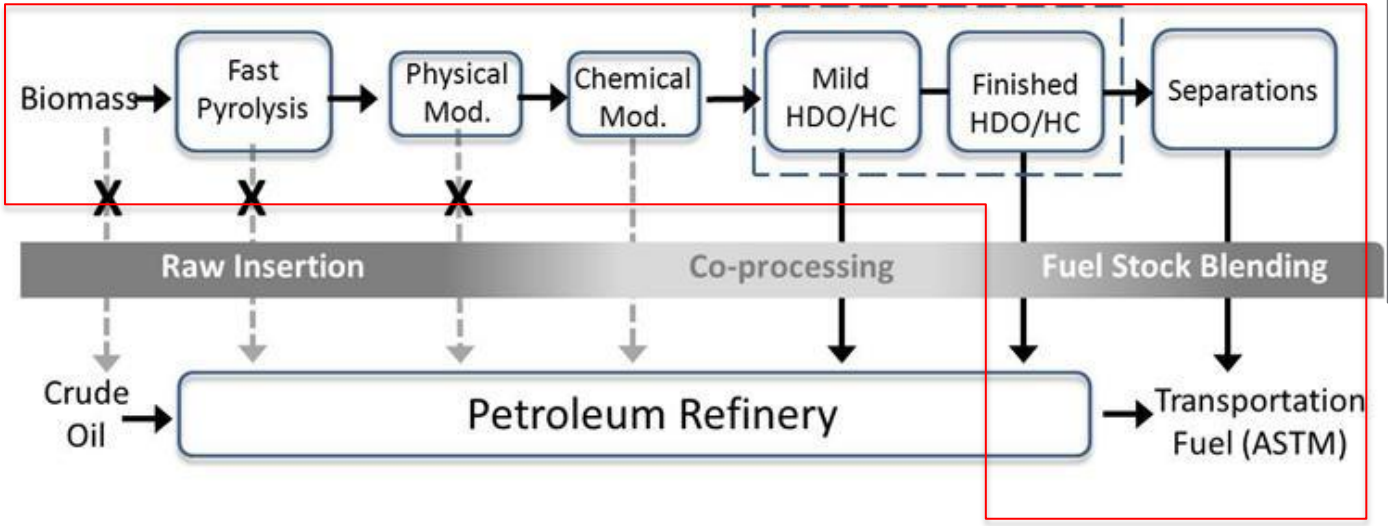
An infrastructure compatible fuel blend-stock can be made from biomass through **pyrolysis and catalytic upgrading**.

IF:

- Long catalyst and process life is demonstrated
- The process is economically competitive
- The product is of sufficient quality

Goal Statement

- Develop sustained improvements in catalyst lifetime
  - Define quality metric for oil feed and intermediate streams
  - Understand deactivation sources
  - Develop more robust catalysts
- Reduce cost drivers
  - Improve liquid yield
  - Develop more robust catalysts

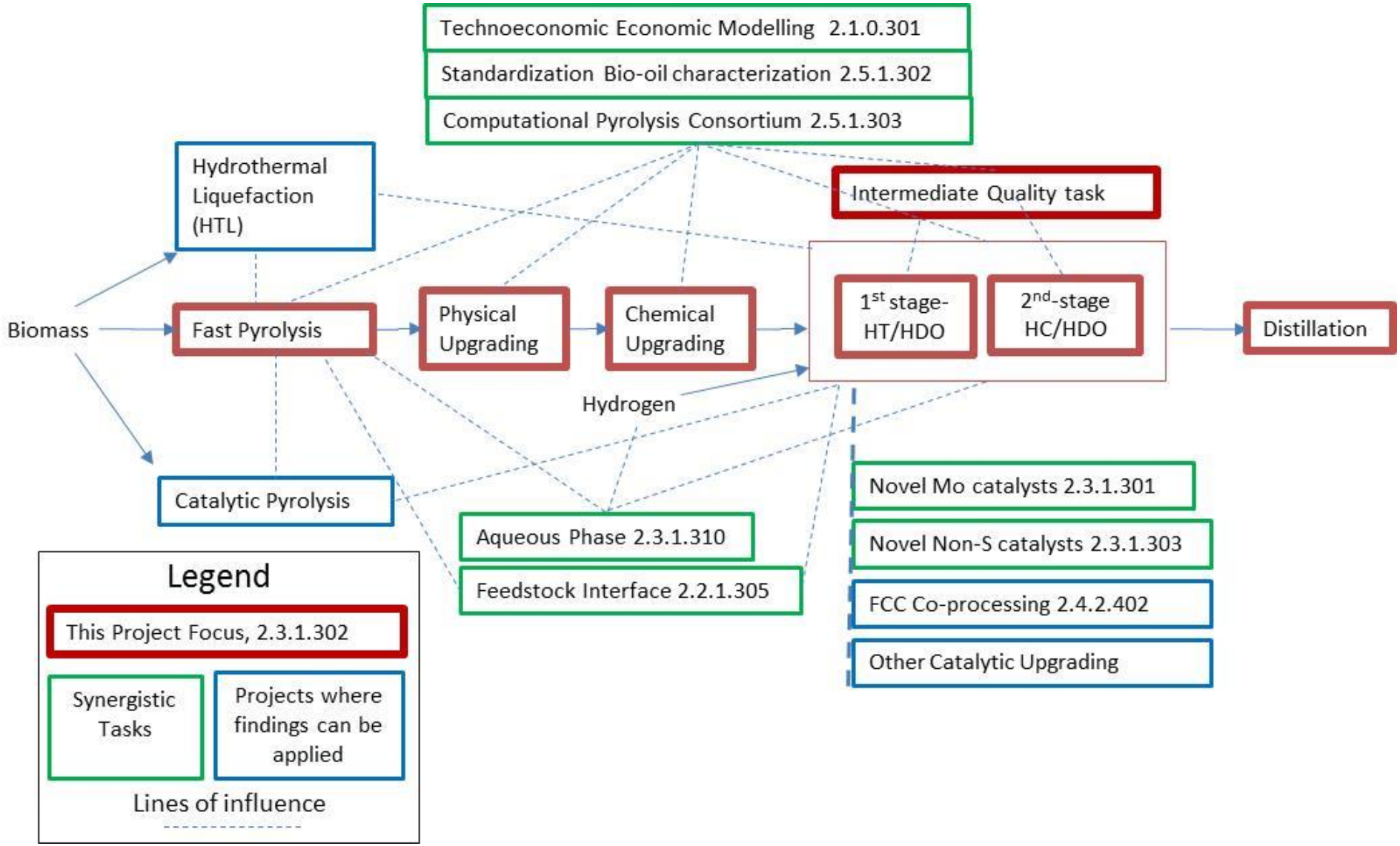


IMPACT:

- Contribute to US energy self-sufficiency
- Generate new technologies, markets, generate jobs and improve quality of life

Zacher AH, MV Olarte, DM Santosa, DC Elliott, and SB Jones. 2014. "A Review and Perspective of Recent Bio-Oil Hydrotreating Research ." *Green Chem., 16:491*

Context


Technoeconomic Economic Modelling 2.1.0.301
Standardization Bio-oil characterization 2.5.1.302
Computational Pyrolysis Consortium 2.5.1.303
Hydrothermal Liquefaction (HTL)
Intermediate Quality task
Biomass
Fast Pyrolysis
Physical Upgrading
Chemical Upgrading
1st stage-HT/HDO
2nd-stage HC/HDO
Distillation
Hydrogen
Catalytic Pyrolysis
Aqueous Phase 2.3.1.310
Feedstock Interface 2.2.1.305
Novel Mo catalysts 2.3.1.301
Novel Non-S catalysts 2.3.1.303
FCC Co-processing 2.4.2.402
Other Catalytic Upgrading
Legend
This Project Focus, 2.3.1.302
Synergistic Tasks
Projects where findings can be applied
Lines of influence

Quad Chart Overview

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Timeline

- Start: October 2006
- End: December 2017
- 70% Complete

Barriers

- Barriers addressed
  - Tt-F Biomass Deconstruction to Bio-oil
  - Tt-H Bio-oil stabilization
  - Tt-J Catalytic upgrading to fuel
  - Tt-K Product Finishing
  - Tt-L Process Knowledge gaps
  - Tt-O Separations Efficiency
  - Tt-R Process Integration

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	0	0	$975,216	$5,684,784.00

Partners

- Partners
  - NREL
  - ORNL
  - INL
- Technical Research Centre of Finland (VTT)
- CanmetENERGY, Natural Resources Canada
- International Energy Agency, and country members
- Computational Pyrolysis Consortium

1 - Project Overview

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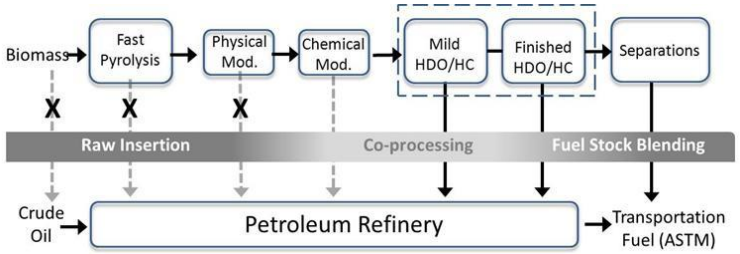
Need: Sustainable, economical, infrastructure compatible bio-fuels from biomass



This project aims to address pyrolysis/catalytic upgrading key technical challenges

- Process fouling due to bio-oil instability
- Catalyst lifetime
- "Quality" of bio-oil derived intermediates, fuels, and chemicals
- Hydrogen utilization
- Market confidence in pyrolysis and upgrading

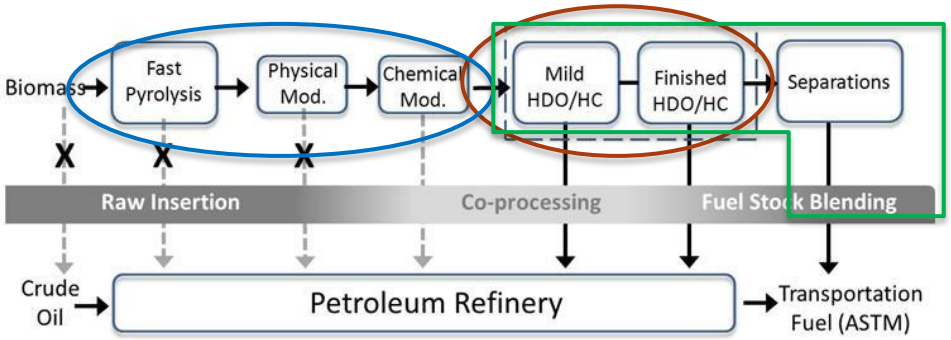
This challenge is bigger than any one laboratory, university, or industry.

National labs are in a unique position to lead a variety of domestic and international stakeholders to overcome barriers to this technology.

PNNL is an international leader in developing this upgrading technology.

2 – Approach (Technical)

- Research Focus Areas
  - Pyrolysis research
  - Advanced analytical
  - Catalyst and process improvement
  - Novel catalyst development
  - Scale-up



- Approach
  - Research is targeted by the techno-economic model
  - Focus is on largest barriers: **Process and catalyst lifetime,** process efficiency
  - Applied research: **real bio-oils in continuous systems**, but consider model approach if it can directly solve applied challenges
  - Formal/Informal collaborations with other National Labs with unique strengths and international and domestic stakeholders in pyrolysis and catalysis
- Primary Metric
  - Modelled cost of lignocellulosic gasoline, diesel, jet range hydrocarbons
  - Largest drivers: Catalyst/process lifetime, hydrogen efficiency, product yield
  - Develop “solution based approaches,” rather than an “approach based solution”

2 – Approach (Management)

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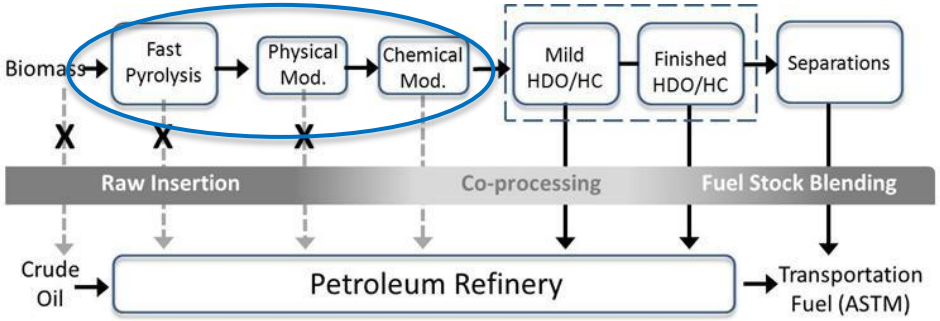
- **Approach Structure**
  - **Project Management Plan** (PMP) guiding scope, budget and schedule
  - **Annual Operating Plans** (AOP) prepared prior to each fiscal year
  - **Quarterly reporting** to BETO
- **Critical Success Factors:**
  - Achieve modelled cost targets for cellulosic gasoline, diesel, jet range fuels
  - Demonstrate process/catalyst reliability
  - Demonstrate product suitability for its intended purpose
- **Potential challenges**
  - **Researcher proximity**: active communication (calls and data exchanges) with partners for collaborative work
  - **Catalyst/process lifetime**
  - **Integration of unit operations**
  - **Market**

3 – Progress: Pyrolysis Research

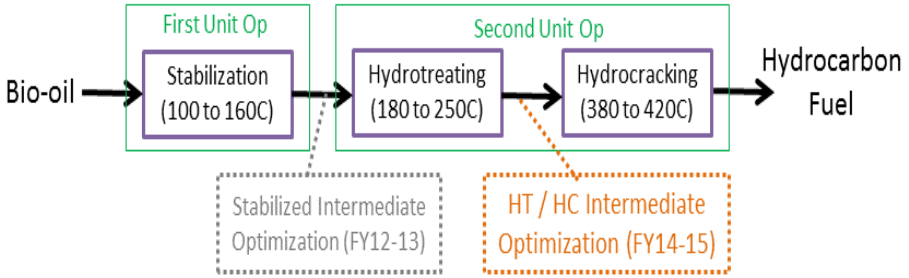
- Objectives:
  - Improve biomass pyrolysis knowledge
  - Be involved in relevant oil production
    - *"bio-oil is an intermediate"*

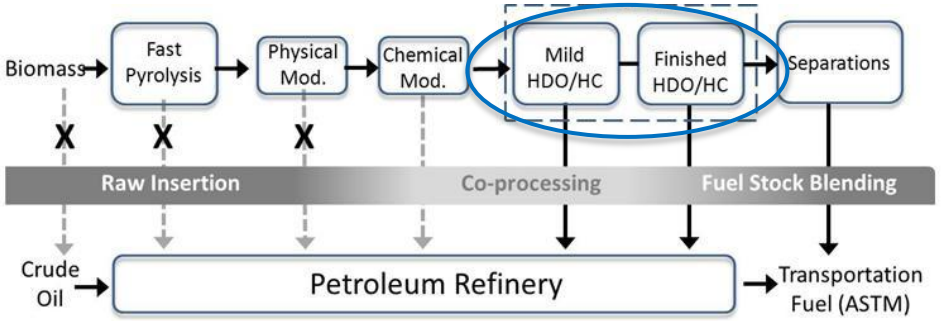


- Accomplishments:
  - Participation in IEA mixed feed pyrolysis round-robin
    - Gives context for international pyrolysis research
  - Working with pilot scale oils from VTT and Canmet
  - Developed correlation between bench scale pyrolysis and py-GCMS research
  - With NREL, demonstrated that hot vapor filtration (HVF) aids bio-oil upgrading
    - HVF removes inorganics in pyrolysis oil during formation/collection
    - More easily upgraded in short term testing

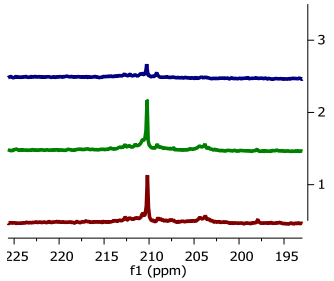
Elliott, DC, Wang, H, French, R, Deutch, S and Iisa, K. 2014. "Hydrocarbon Liquid Production from Biomass via Hot-Vapor-filtered Fast Pyrolysis and Catalytic Hydroprocessing of the Bio-oil". *Energ. Fuel.* 28:5909-5917.

3 – Progress: Intermediate Quality

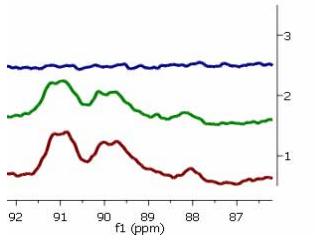




- Objective: Define "quality" indicators for bio-oil intermediates
- Relevance: Improve integration of operating process, enable commoditization of bio-oil
- Accomplishments:
  - Identified important functional groups that define stabilized oil
    - Decrease/loss in carbonyl content
    - Loss of carbohydrate fragments
  - Comparison between pyrolysis oil vs. HTL oil
    - Use 2D-NMR to compare bio-oil and bio-crude
    - Identify possible reason for thermal instability of pyrolysis oil



carbonyl



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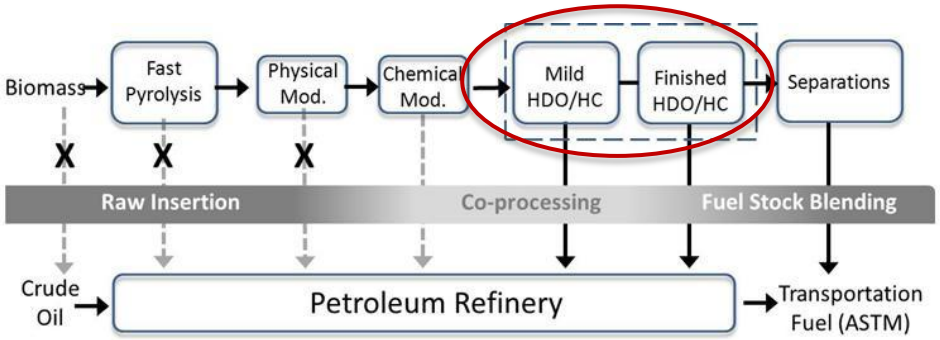
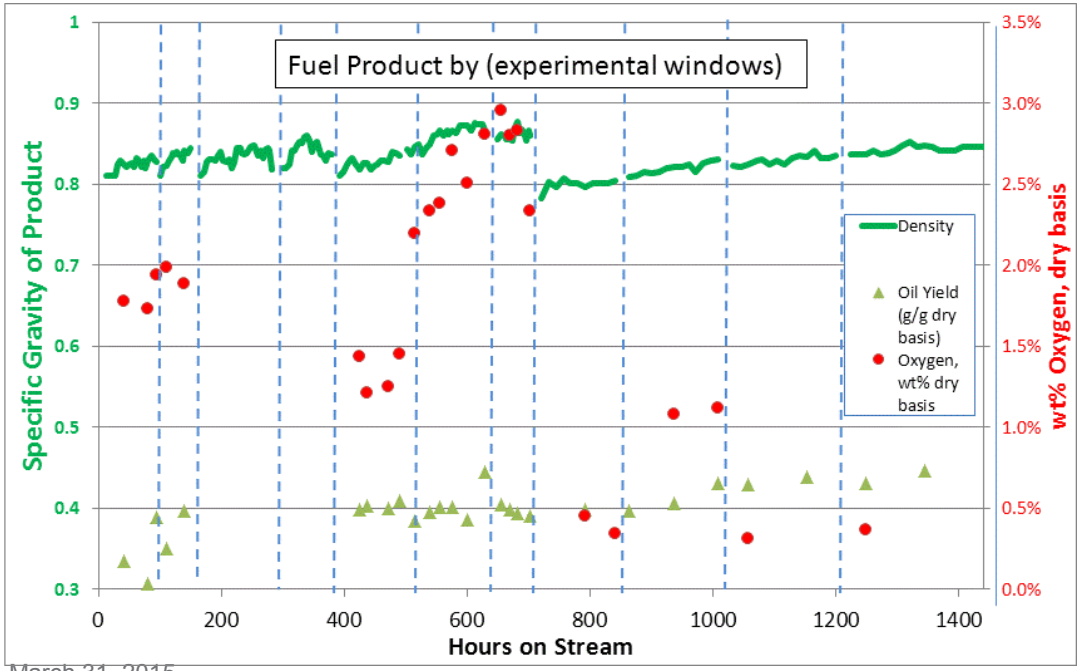
3 – Progress: Catalyst and Process Improvement by Bio-oil Stabilization

- Objective:
  - Identify robust process/catalysts that have longer lifetimes
- Relevance:
  - directly addresses the key challenge of the technology
- Accomplishment:
  - Achievement of 60-day on stream on a single batch of deep HT catalyst

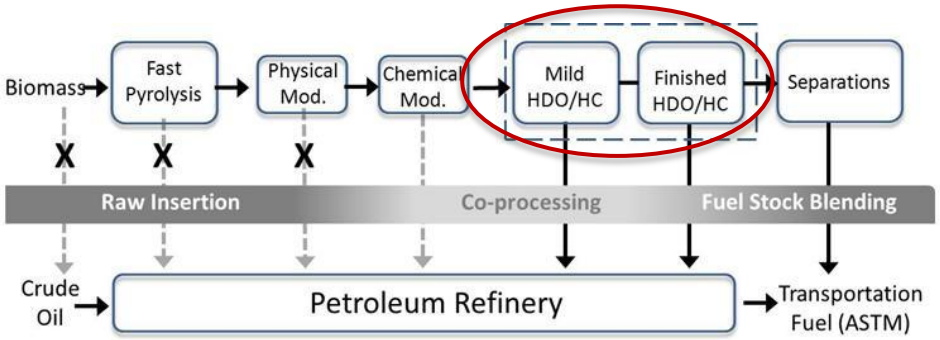




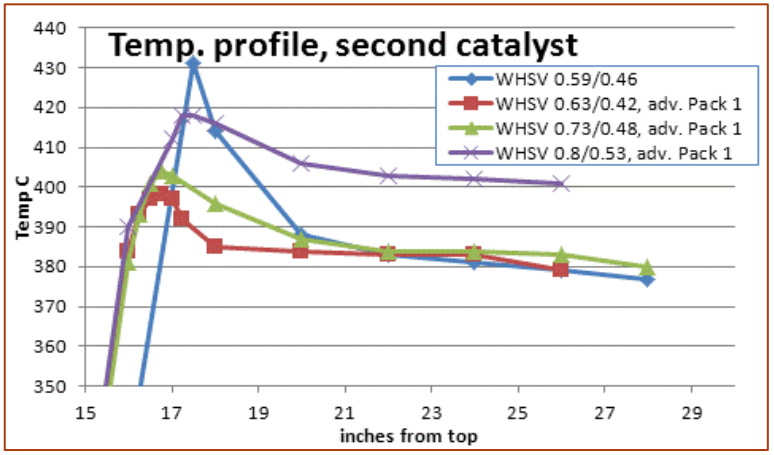
- Historical single batch catalyst lifetime was about 5.8 days
- Enabled by:
  - Feed pre-hydrogenation
  - Use of industrial catalysts
- Identified challenges/opportunities:
  - Catalyst deactivation
  - Exotherm management leading to decreased feed flowrates

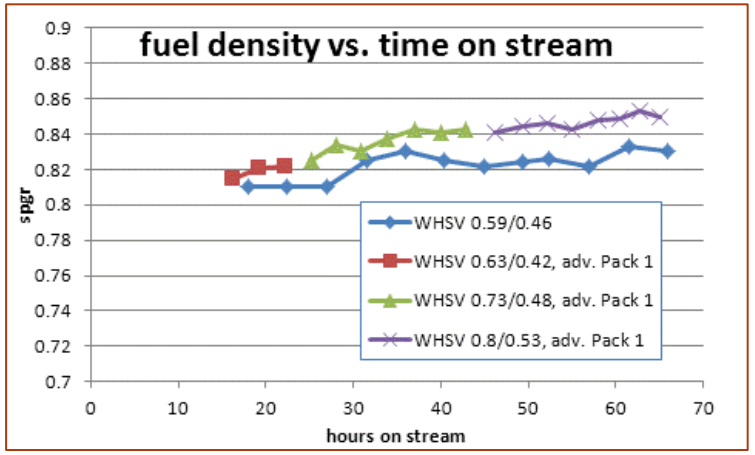
3 – Progress: Catalyst and Process Improvement, Increasing WHSV

- Objective:
  - Improve liquid throughput
- Relevance:
  - directly addresses one of the key challenges of the technology



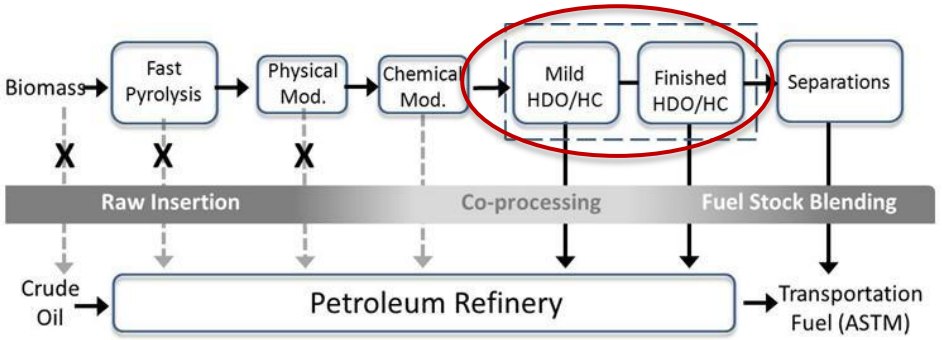
- Accomplishment:
  - Increased process WHSV by improving mass and heat transfer
    - Process has been throughput limited
    - Achieved 2014 SOT target by implementing hybrid support and packing
    - Resulted in an overall decrease in catalyst cost due and equipment size





3 – Progress: Catalyst/process Improvement by Reactor Design

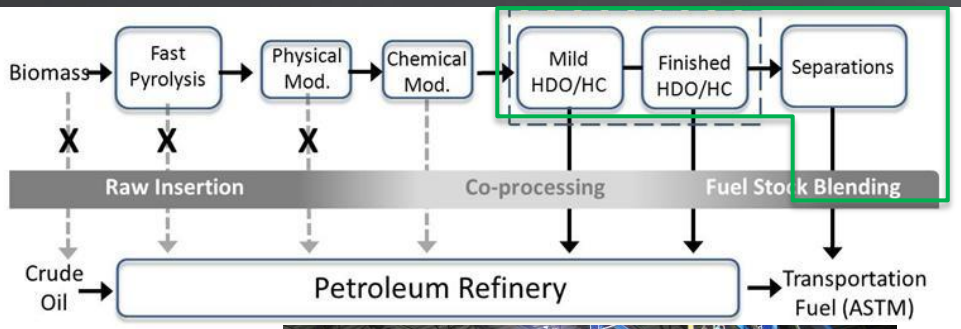
- Objective:
  - Enable high-throughput screening with bio-oil compatible multichannel system
  - Evaluate novel reactor systems

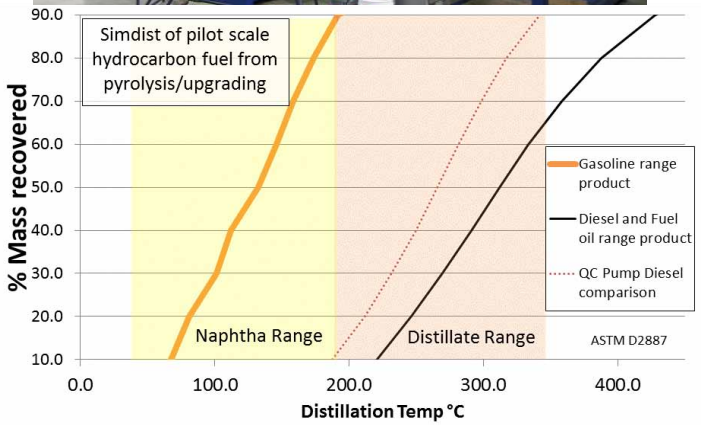


- Accomplishment:
  - Developed multichannel hydrotreater testing compatible with bio-oils
    - Historical research required pilot (400ml) or bench (40ml) scale screening due to complexity of bio-oil and chemistry
    - Existing multichannel not compatible bio-oil (complex chemistry, phase transitions, physical properties)
    - Enable high throughput catalyst research in 2015
  - Evaluation of other reactor configurations now underway
    - Developing novel configurations to deal with the uniqueness of bio-oil rather than forcing bio-oil into existing petroleum technologies

3 – Progress: Scale-up

- Objective:
  - Produce upgraded oil and fractionated blendstock in large scale
- Relevance:
  - Engine testing and industrial interest requires relevant amounts of hydrocarbon fuel blendstocks
  - Reduce technical risk in industrial-scale applications
- Accomplishment:
  - Startup and routine operations completed for scaled-up distillation
    - Multi-gallon quantities of gasoline and diesel range fuel from upgraded bio-oil demonstrated.
    - Distillation procedures being tuned to address the complex suite of compounds in upgraded bio-oils
  - Hydrotreater start-up in progress





4 – Relevance

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"By 2017, validate the R&D performance goal of $2.50/GGE nth plant (BETO performance goal of $3/GGE MFSP) via a thermochemical pathway." -- BETO MYPP, Nov 2014, p2-72

- Solving the barriers to catalyst/process life and efficiency will…
  - Drive modeled conversion costs to the MYPP goal of $2.5/GGE
  - Encourage private investment to optimize the technology for market
  - Reduce technical risk for bio-oil pioneer plants needed for the basis of a bioeconomy
- Broader Application of expected results:
  - Defining intermediate "quality" indicators will enable more meaningful correlation between laboratory and university research
  - Developed catalysts will have broad applications in upgrading of other liquefied biomass processes to chemicals and fuels. (HTL, catalytic pyrolysis, etc.)
  - Bio-oil handling and process improvements will have application for other processes that use bio-oil or liquefied biomass for bio-power, bio-chemical conversion, and refinery co-processing of modified bio-oils

5 – Future Work

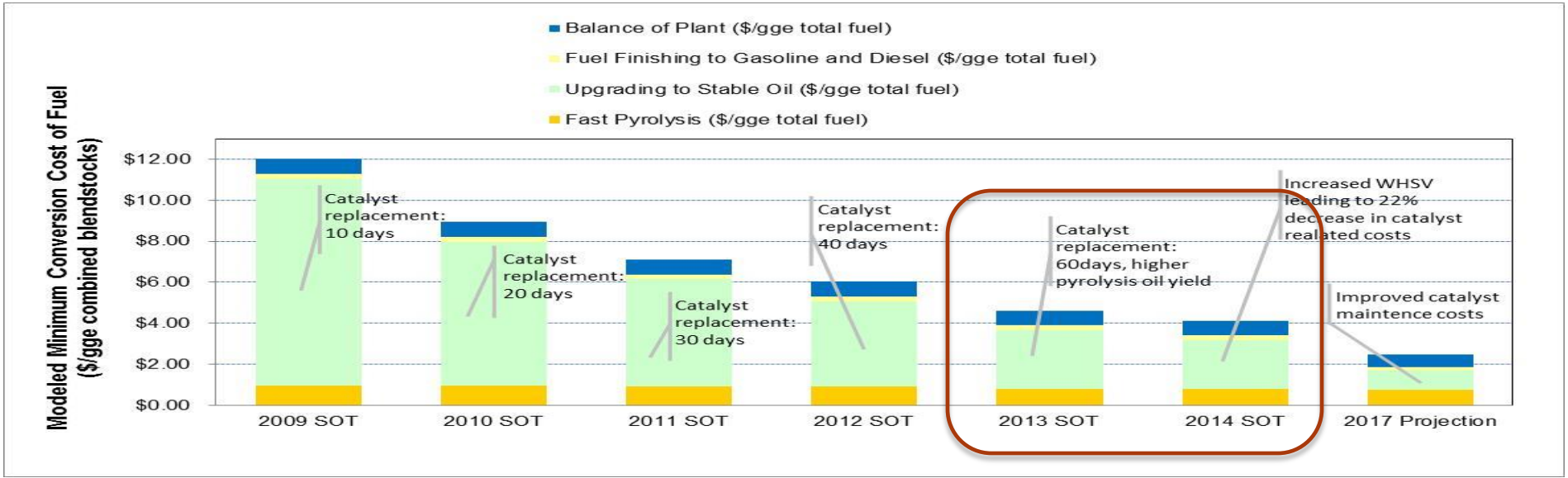
- Catalyst development and lifetime improvement
  - Extend lifetime through modified conditions, improved bio-oils, or enhanced catalysts
  - Develop novel catalyst to reduce processing costs: less expensive, poison tolerant, easily regenerable, higher activity, or more stable
- Quality evaluation of intermediates and products
  - Develop bio-oil intermediate indicators for catalysts and processes improvements tuning
  - Evaluate upgraded oil distillate cuts fuel suitability
- Novel process concept development
  - Examine novel processes and systems that can address the current challenges of bio-oil
- Scale-up
  - Generate scale-up data reduce technical risk for piloting
  - Produce gallon quantity samples for end-use evaluation
  - Prepare for 2017 demonstration of technology

Summary

PNNL and other national laboratories are leading the effort to develop sustainable and competitive liquid transportation fuel from biomass

This project is addressing the barriers of catalyst and process lifetime, catalyst efficiency, and product/intermediate quality to de-risk the technology for broader application

If successful, efforts in this project have broader application to other processes that upgrade, catalytically convert, or process bio-oil produced from fast pyrolysis of biomass.



Additional Slides

Responses to Previous Reviewers' Comments

"A valuable attempt to stabilize and characterize bio-oils. However, heteroatoms can have huge impacts on catalyst, corrosion, and sour water contaminants. There is more to insertion than getting a group of molecules in the right boiling range."

- We are cognizant of the implications and potential pitfalls that new heteroatom containing species, even at low concentrations, may have on industrial application of the process as stated. **An important thrust of the research is in fuel product characterization and speciation to proactively identify challenges and potential barriers earlier in the research phase.**

"The project is looking at highly relevant issues related to upgrading liquid bio-oil. The work is a very good example of the ways the labs can team and perform high-quality research that advances the stage of the art in an area, as well as show how the core research can be a valuable and effective part of the DOE portfolio."

"This is solid work at the interface between science and practical application—much more relevant that purely scientific work, but not likely to keep pace with industry in terms of commercial implementation. The work would be far more valuable in collaboration with industry, as well as universities and other labs."

"This project appears to be a relatively good use of the national lab assets. It supports other national lab projects and informs other pyrolysis researchers in universities and corporations, and fills a basic, core research gap that should advance the state of technology."

- We agree there is a unique role that national laboratories provide for the benefit for public progress. We also agree that to stay relevant with industrial implementation there is an increased need to continue and **expand quality collaboration with industry and university partners as well as sister laboratories** and we are working to broaden the current collaborations and industrial oversight.

Publications, Patents, Presentations, Awards, and Commercialization

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- Zacher AH, DC Elliott, MV Olarte, DM Santosa, F Preto, and K Iisa. 2014 “Pyrolysis of Woody Residue Feedstocks: Upgrading of Bio-Oils from Pine Beetle Killed Trees and Hog Fuel . *Energ. Fuel.,* 28:7510-7516. PNNL-SA-104767, Pacific Northwest National Laboratory, Richland, WA
- Elliott, DC, Wang, H, French, R, Deutch, S and Iisa, K. 2014. “Hydrocarbon Liquid Production from Biomass via Hot-Vapor-filtered Fast Pyrolysis and Catalytic Hydroprocessing of the Bio-oil”. *Energ. Fuel.* 28:5909-5917.
- Olarte MV, DC Elliott, GG Neuenschwander, LJ Rotness, Jr, JR Cort, SD Burton, AB Padmaperuma, C Drennan, and AH Zacher. "Bio-oil streams in the current fast pyrolysis – catalytic upgrading route of producing renewable liquid fuel from biomass." . AIChE Fall Meeting, Atlanta, GA, Nov. 19, 2014. PNNL-SA-102711. Pacific Northwest National Laboratory, Richland, WA.
- Olarte MV, AH Zacher, SB Jones, LJ Snowden-Swan, PA Meyer, AB Padmaperuma, LJ Rotness, Jr, GG Neuenschwander, DC Elliott, and C Drennan. 2014. "Current State of the Technology (SOT) of the Fast Pyrolysis-Hydrotreating Pathway." Biomass 2014, Washington DC, DC, July 29, 2014. PNNL-SA-104180.
- Zacher AH, MV Olarte, DM Santosa, DC Elliott, and SB Jones. 2014. "A Review and Perspective of Recent Bio-Oil Hydrotreating Research ." *Green Chem., 16:491.* PNNL-SA-96894, Pacific Northwest National Laboratory, Richland, WA.
- Olarte MV, DC Elliott, GG Neuenschwander, LJ Rotness, Jr, SD Burton, B Schwenzer, AB Padmaperuma, and AH Zacher. 2013. "Towards long-term fast pyrolysis oil catalytic upgrading." Presented by Mariefel V. Olarte at 2013 ACS Fall National Meeting , Indianapolis, IN on April 9, 2013. PNNL-SA-94898.
- Zacher AH, MV Olarte, and DC Elliott. 2013. "Enabling Extended Catalyst Lifetime in Fixed Bed Hydrotreating of Bio-Oil ." Presented by Alan Zacher (Invited Speaker) at TCBiomass 2013, Chicago, IL on September 6, 2013. PNNL-SA-97972.
- Holladay JE, H Wang, AH Zacher, DC Elliott, AJ Schmidt, MV Olarte, Z Abdullah, GSJ Lee, and SB Jones. 2013. "Biomass to Jet Fuel via Thermochemical Conversion." Presented by John Holladay (Invited Speaker) at SAE 2013 Aerospace Alternative Fuels Symposium, Brussels, Belgium on June 13, 2013. PNNL-SA-96337.
- Olarte MV, DC Elliott, GG Neuenschwander, LJ Rotness, Jr, SD Burton, B Schwenzer, AB Padmaperuma, JL Male, and AH Zacher. 2013. "Enabling long-term catalytic upgrading of fast pyrolysis oil ." Presented by Mariefel V. Olarte at SEDP Presentation of Technical Posters, Richland, Washington, WA on May 22, 2013. PNNL-SA-95556.

Publications, Patents, Presentations, Awards, and Commercialization

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- Zacher AH, and K Iisa. 2013. "Pyrolysis Core R&D, Stabilized Oil Upgrading, 2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review." Presented by Alan Zacher (Invited Speaker) at 2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review, Washington DC, DC on May 21, 2013. PNNL-SA-95399.
- Elliott DC, AH Zacher, and AJ Schmidt. 2012. "Catalytic Upgrading of Biomass to Infrastructure Compatible Liquid Fuels ." Presented by Douglas C. Elliott at Biomass Thermochemical Conversion Symposium, Raleigh, NC on October 24, 2012. PNNL-SA-91460.
- Westover T, M Phanphanich, M Clark, S Rossberg, S Egan, C Wright, R Boardman, AH Zacher, and DM Santosa. 2012. "Impact of thermal pretreatment on the fast pyrolysis conversion of southern pine." PNNL-SA-91542, Pacific Northwest National Laboratory, Richland, WA.
- Bu Q, H Lei, AH Zacher, L Wang, S Ren, J Liang, Y wei, L Yupeng, J Tang, Q Zhang, and R Ruan. 2012. "A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis ." PNNL-SA-90300, Pacific Northwest National Laboratory, Richland, WA.
- Elliott DC, TR Hart, GG Neuenschwander, LJ Rotness, Jr, MV Olarte, AH Zacher, and Y Solantausta. 2012. "Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil from Pine Sawdust." Energy and Fuels 26(6):3891-3896. doi:10.1021/ef3004587
- Olarte MV, AH Zacher, DC Elliott, DM Santosa, GG Neuenschwander, TR Hart, and LJ Rotness, Jr. 2011. "Bio-Oil Upgrading and Stabilization at PNNL." Presented by Mariefel V. Olarte (Invited Speaker) at Harvesting Clean Energy Conference 2011 , Boise on October 23, 2011. PNNL-SA-83598.
- Olarte MV, AH Zacher, DC Elliott, DM Santosa, GG Neuenschwander, TR Hart, and LJ Rotness, Jr. 2011. "Bio-Oil Upgrading and Stabilization at PNNL." Presented by Mariefel V. Olarte (Invited Speaker) at WSU Graduate Seminar, Richland, WA on October 28, 2011. PNNL-SA-83729.
- Zacher AH. 2011. "Catalysis of Pyrolysis Oil." Presented by Alan Zacher (Invited Speaker) at WSU Tricities Class ChE581, Richland, WA on October 12, 2011. PNNL-SA-83389.
- Elliott DC, GG Neuenschwander, TR Hart, LJ Rotness, Jr, and MV Olarte. 2011. "Bio-oil upgrading by catalytic hydroprocessing in a fixed-bed reactor." Presented by Douglas C. Elliott at TCBiomass 2011, Chicago, IL on September 27, 2011. PNNL-SA-82778.

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- Zacher AH, DM Santosa, and DC Elliott. 2011. "Mild Catalytic Fast Pyrolysis of Biomass and Catalytic Hydrotreating to Liquid Transportation Fuels Plus Development of a Ebullated Bed Reactor." Presented by Alan Zacher at TCBiomass 2011 , Chicago, IL on September 30, 2011. PNNL-SA-82908.
- Brown C, D Beckman, AH Zacher, and DC Elliott. 2011. "Development of an Ebullated Bed Reactor for Bio-oil Upgrading." Presented by David Beckman at TCBIOMASS2011, Chicago, IL on September 27, 2011. PNNL-SA-82977.
- Male JL, DC Elliott, AH Zacher, and DM Santosa. 2011. "Pyrolysis of Biomass" Presented by Jonathan Male (Invited Speaker) at EBI and JBEI Joint Workshop: Lignin - Characterization, Extraction & Adding Value, Emeryville, CA on July 19, 2011.
- Elliott DC. 2011. ""Process Routes for Biomass Pyrolysis to Produce Hydrocarbon Fuels—Comparisons and Recent Results"." Presented by Douglas C. Elliott (Invited Speaker) at 7th International Conference on Renewable Resources and Biorefineries, Brugge, Belgium on June 9, 2011.
- Zacher, A.H. and DC Elliott "Bio-Oil Upgrading and Stabilization" Presented by AH Zacher (invited speaker) to The Kansas State University Bioenergy Symposium, April 27, 2011.
- Elliott DC. 2011. "Process Development for Biomass Conversion to Fuels by Thermochemical Methods." Presented by Douglas C. Elliott (Invited Speaker) at visit to KTI, Karlsruhe, Germany on April 5, 2011.
- Elliott DC. 2011. "Process Routes for Biomass Pyrolysis to Produce Hydrocarbon Fuels – Comparisons and Recent Results." Presented by Douglas C. Elliott (Invited Speaker) at KiOR visit, Houston, TX on March 9, 2011.
- Elliott DC. 2011. "Hydrothermal Processing." Chapter 7 in Thermochemical Processing of Biomass:Conversion into Fuels, Chemicals and Power, ed. Robert C. Brown, pp. 200-231. Wiley-Blackwell, Oxford, United Kingdom.
- "Stability of Bio-Oil and Its Impact on Hydrotreating." Presented by DC Elliott (Keynote Speaker) to Pacifichem 2010, Honolulu, Hawaii, December 19, 2010.
- Oasmaa A.; Elliott, D.C.; Korhonen, J. "Acidity of biomass fast pyrolysis bio-oils." *Energy & Fuel.* **24** (12), 6548-6554, 2010.

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- Santosa DM, AH Zacher, and DC Elliott. "Catalytic Hydroprocessing of Bio-Oil Derived From Catalytic Fast Pyrolysis of Biomass to Produce Hydrocarbon Products." AIChE 2010 Annual Meeting in Salt Lake City, UT on November 9, 2010.
- "Advancement of Bio-Oil Utilization for Refinery Feedstock." Presented by DC Elliott (Invited Speaker) to Washington State Bioenergy Research Symposium, Seattle, Washington, November 8, 2010.
- Elliott, D.C. "Status of Process Development for Pyrolysis of Biomass for Liquid Fuels and Chemicals Production." *International Sustainable Energy Review*, 4 (2), 56-57. June 2010.
- Nowakowski, DJ; Bridgwater, AV; Elliott, DC; Meier, D; de Wild, P; 2010 "Lignin fast pyrolysis: Results from an international collaboration." *Journal of Analytical and Applied Pyrolysis,* **88** (2010) 53-72.
- Zacher, AH; Pacific Northwest National Laboratory, IEA Bioenergy Task 34--Pyrolysis newsletter (PyNe), Issue 26, pp. 10-11, December, 2009.
- Zacher, A.H.; Elliott, D.C.; Santosa, M.D.; Rotness, L.J.: 2009 "Fast Pyrolysis for the Production of Bio-Oil from Biomass," presented by AH Zacher at the 2009 Annual meeting of the American Institute of Chemical Engineers, Nashville, November 11th.
- Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G.; Rotness, L.J.; Zacher, A.H.; 2009. "Catalytic Hydroprocessing of Biomass Fast Pyrolysis Bio-oil to Produce Hydrocarbon Products." *Environmental Progress and Sustainable Energy* **28** (3) 441-449. The paper was presented by DC Elliott at the International Conference of Thermochemical Biomass Conversion Science, Chicago, September 18th.
- Oasmaa, A.;.Elliott, D.C.; Müller, S. 2009. "Quality Control in Fast Pyrolysis Bio-Oil Production and Use." *Environmental Progress and Sustainable Energy* **28** (3) 404-409. The paper was presented by A Oasmaa, the Task 34 national team lead from Finland, at the International Conference of Thermochemical Biomass Conversion Science, Chicago, September 18th.
- Elliott, D.C.; Hart, T.R. 2009. "Catalytic Hydroprocessing of Chemical Models for Bio-oil." *Energy & Fuels*, **23**, 631-637 web publication, December 12, 2008.
- DC Elliott "Overview of Liquid Fuels from Biomass by Thermochemical Conversion." invited seminar presented at the Forest Bioproducts Research Institute, University of Maine, Orono, November 17, 2008.

Exotherm difference between 60-mL and 400 mL reactors

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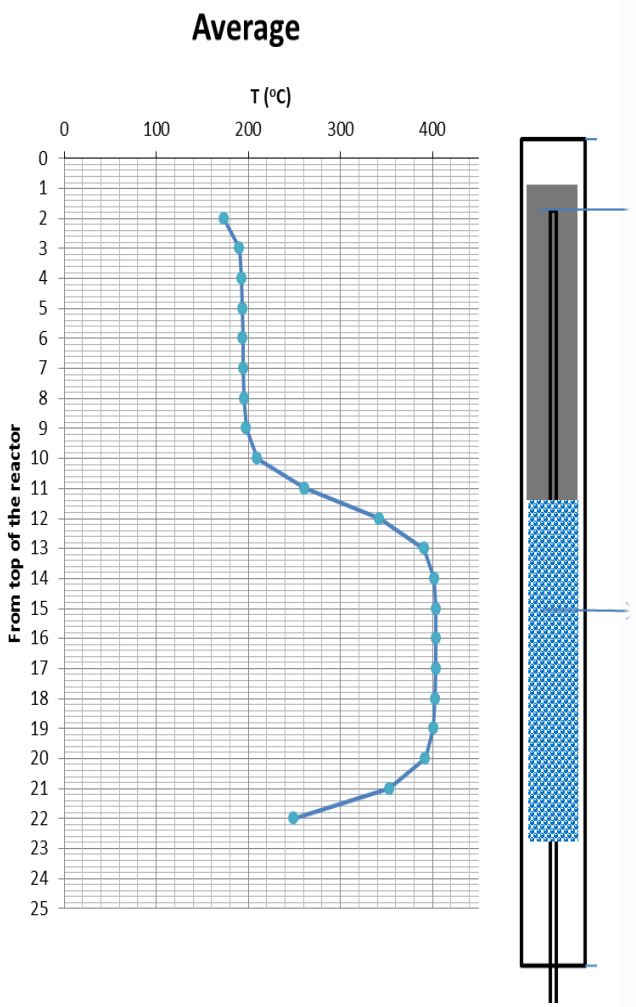
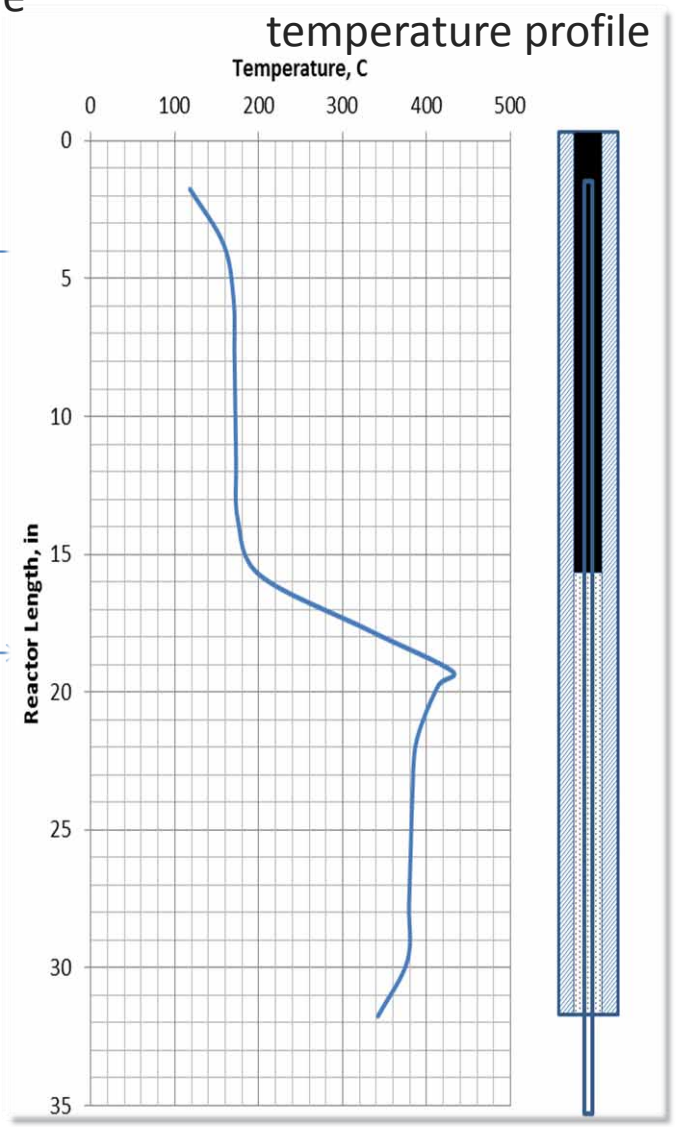
Typical 60-mL temperature profile

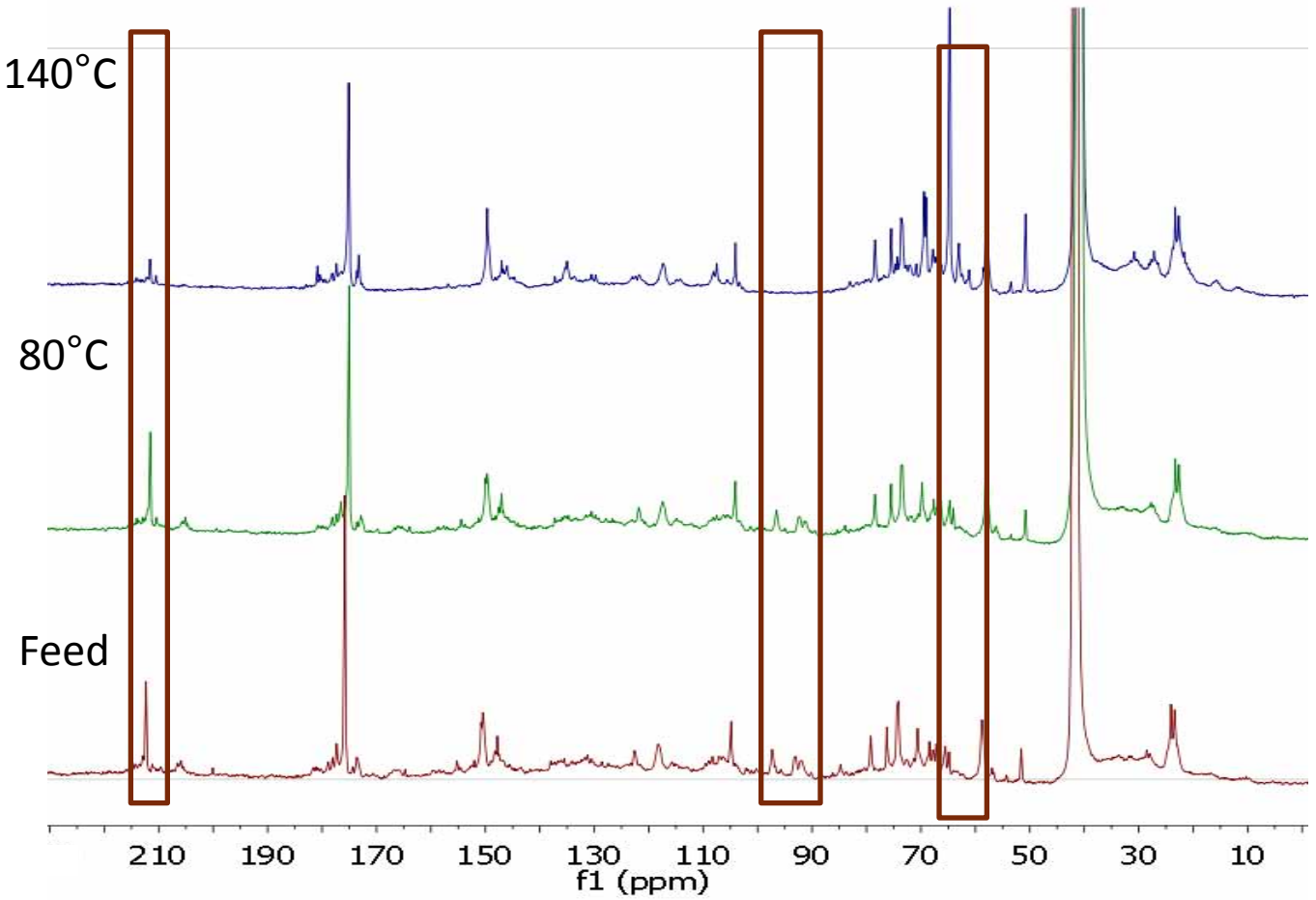


Representative 400-mL temperature profile



Exotherm is typically not seen in the smaller 60-mL reactor, but is readily apparent in the 400-mL at similar LHSVs

Pre-treated oil: ^{13}C NMR analysis



Changes in functional groups in the 140°C product oil are apparent.

Functional groups affected by pre-treatment

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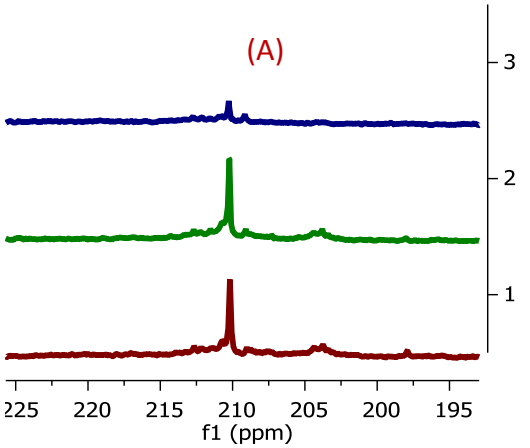
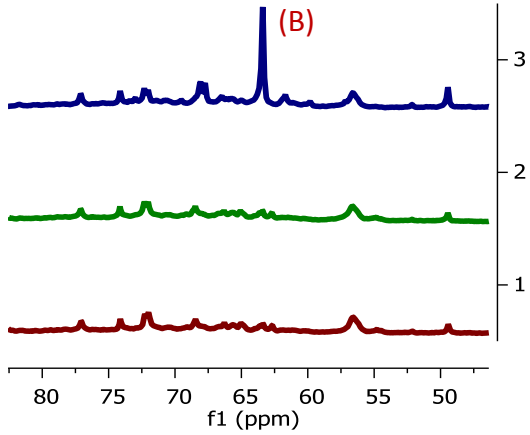
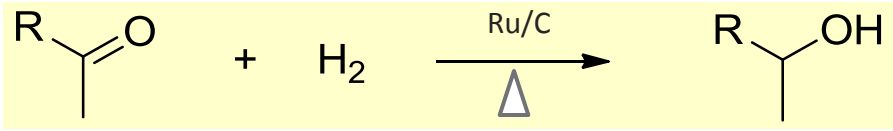
Carbonyl region:



Alcohol/ether region:

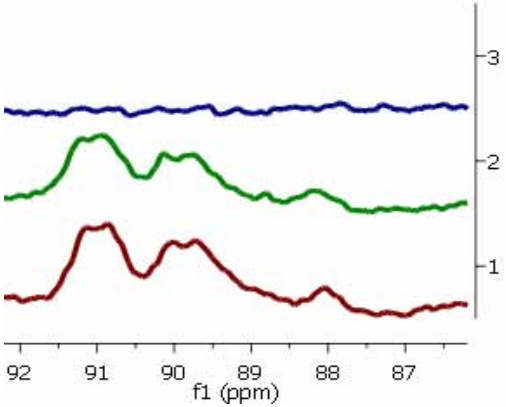


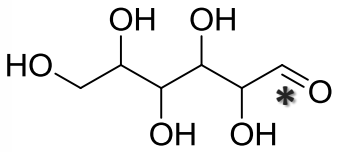
In the presence of **high pressure H_2** and **noble metal catalyst** (Ru/C), <u>decrease in the carbonyl</u> region and <u>increase in the alcohol/ether</u> region suggests **hydrogenation** of the carbonyls



(A) (B)

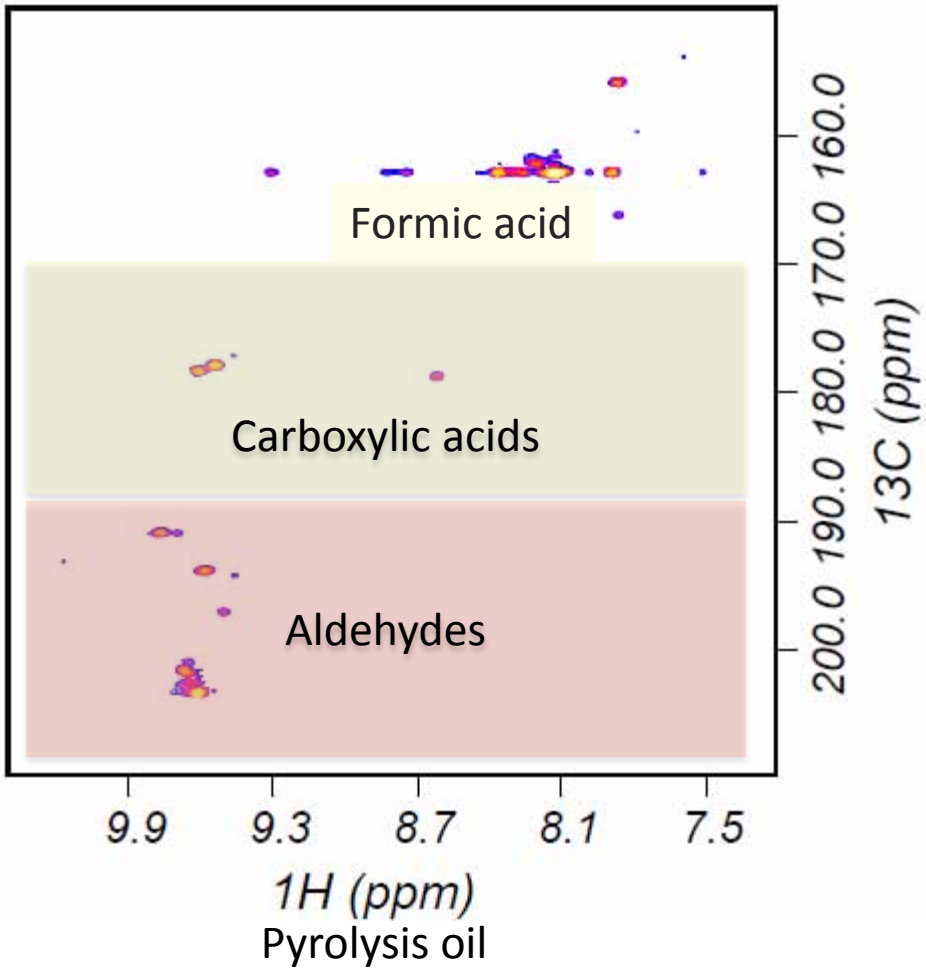
Region typically associated with anomeric C in carbohydrates:



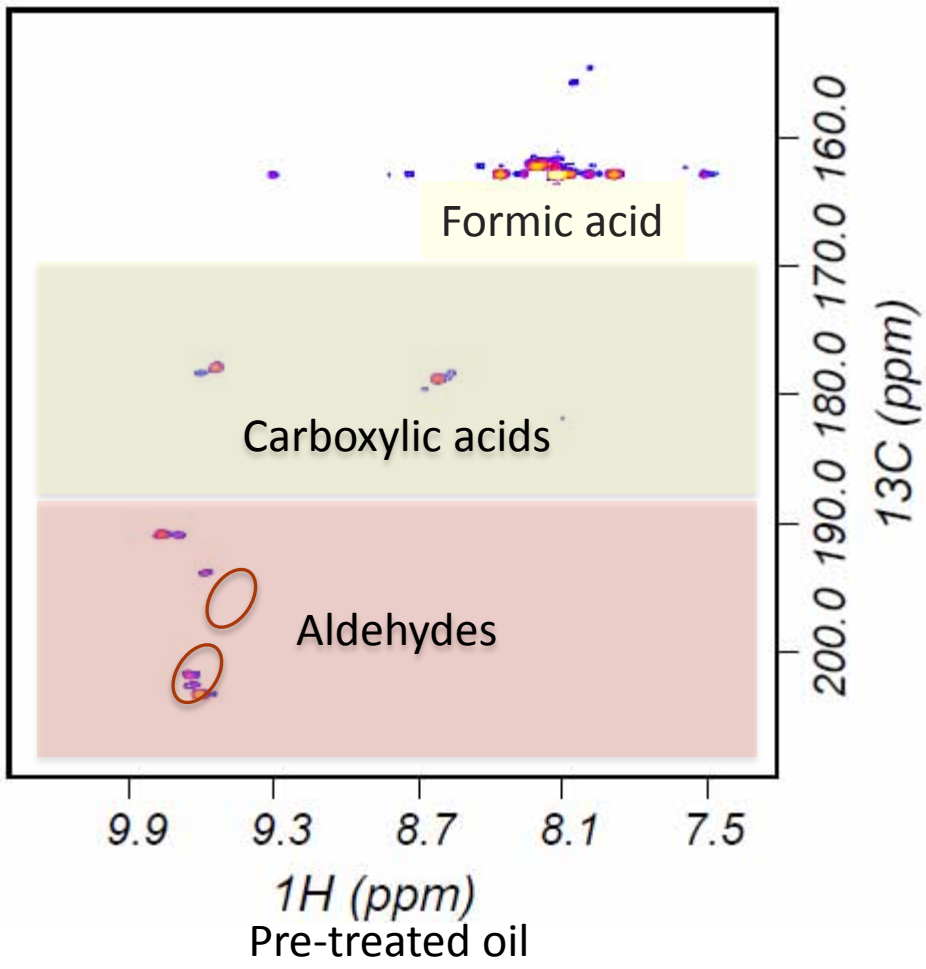


1 – Raw
2 – 80°C
3 – 140°C

2D-NMR Analysis of pre-treated oils



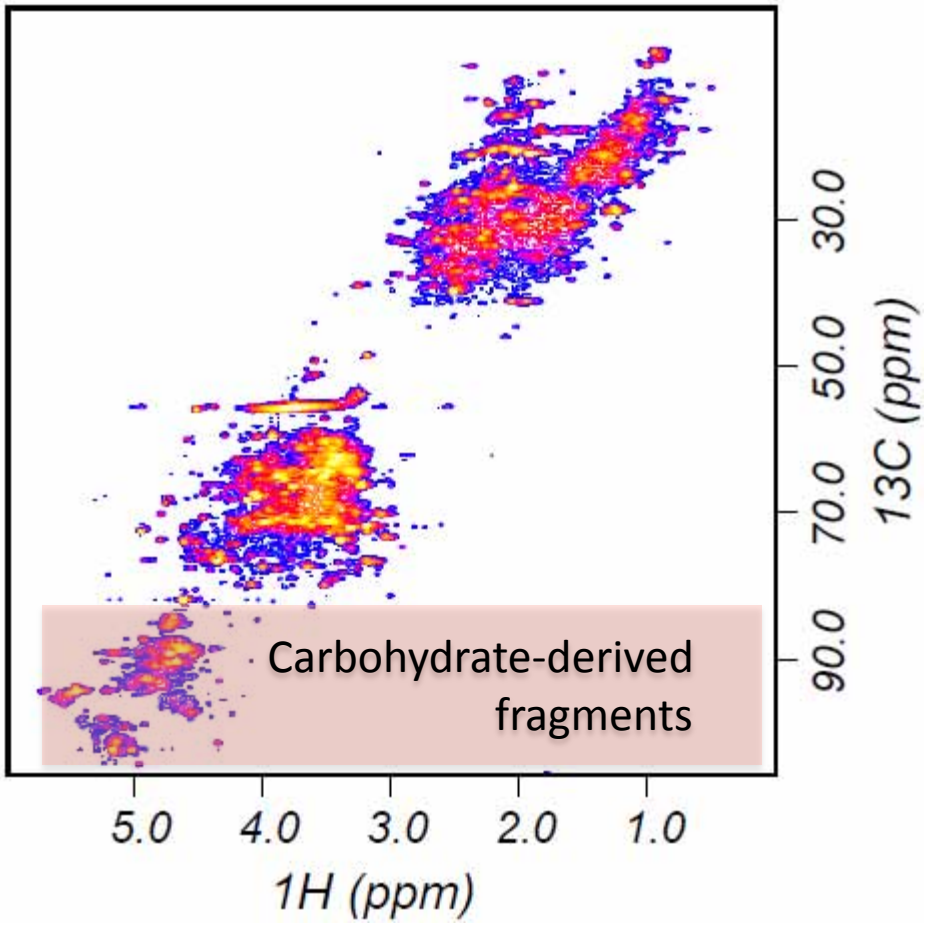
Pyrolysis oil



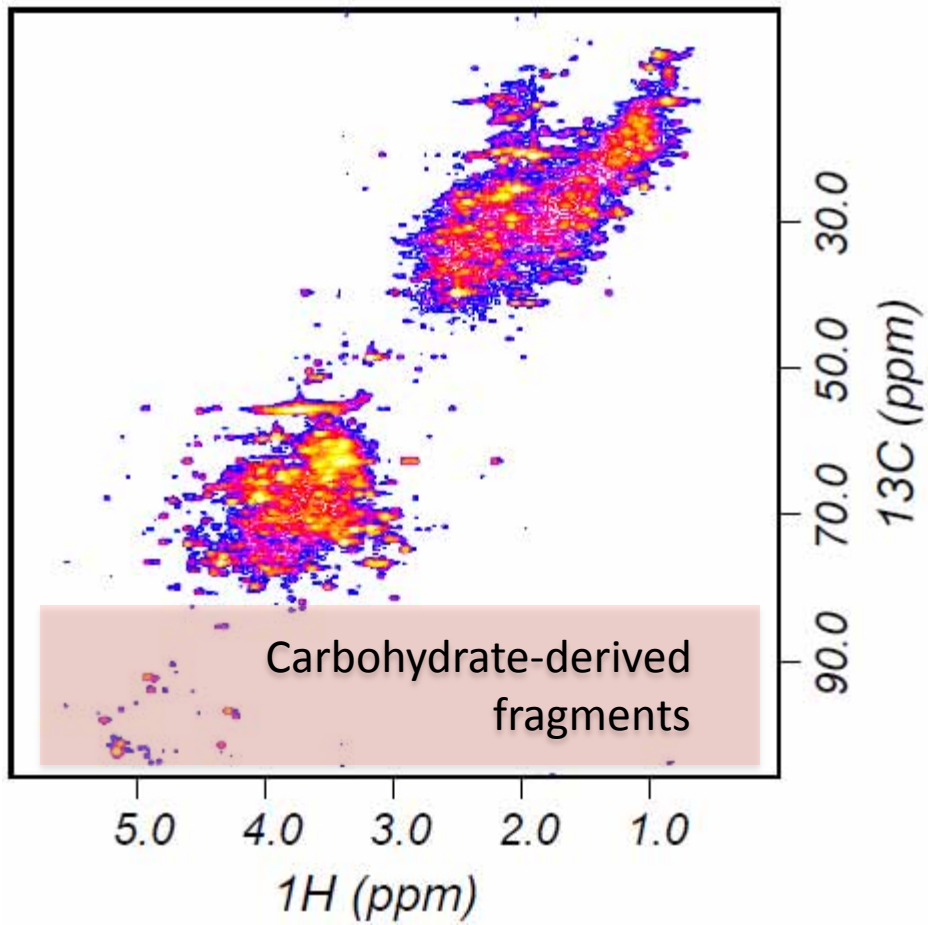
Pre-treated oil

Loss and decrease of certain aldehydes.

2D-NMR Analysis of pre-treated oils



Pyrolysis oil



Pre-treated oil

Loss of anomeric C, potentially reduced to alcohols

2D-NMR Analysis of pre-treated oils

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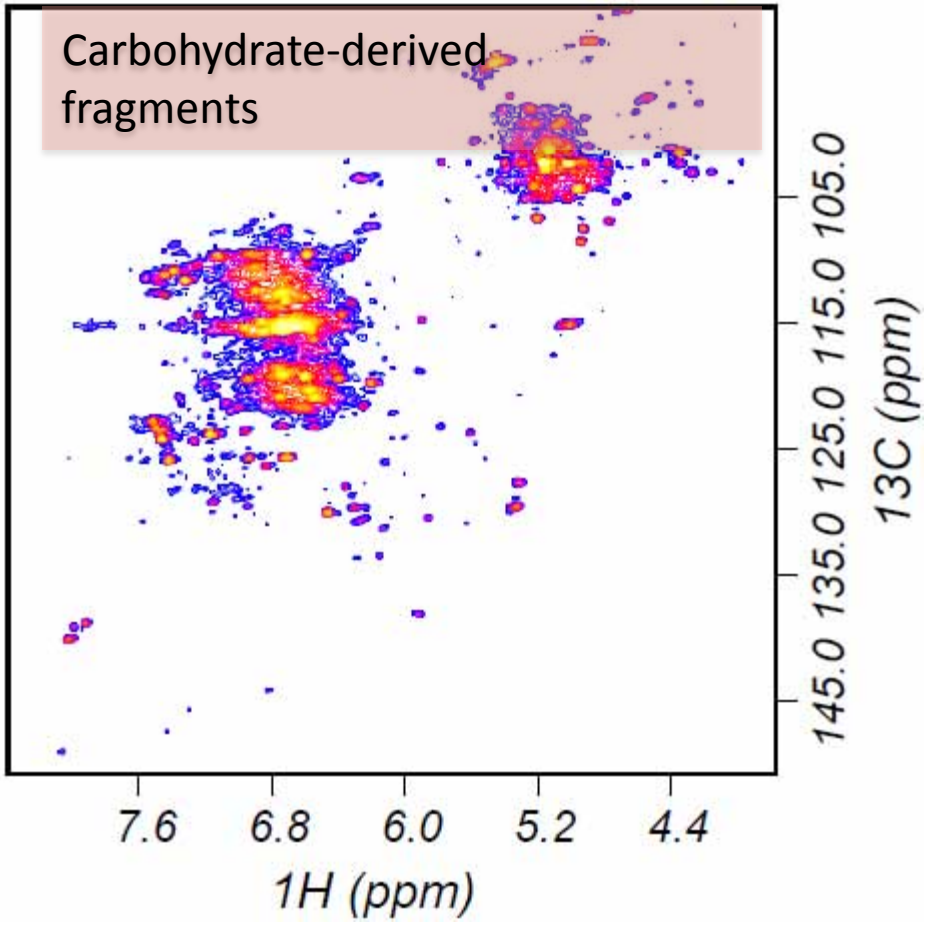
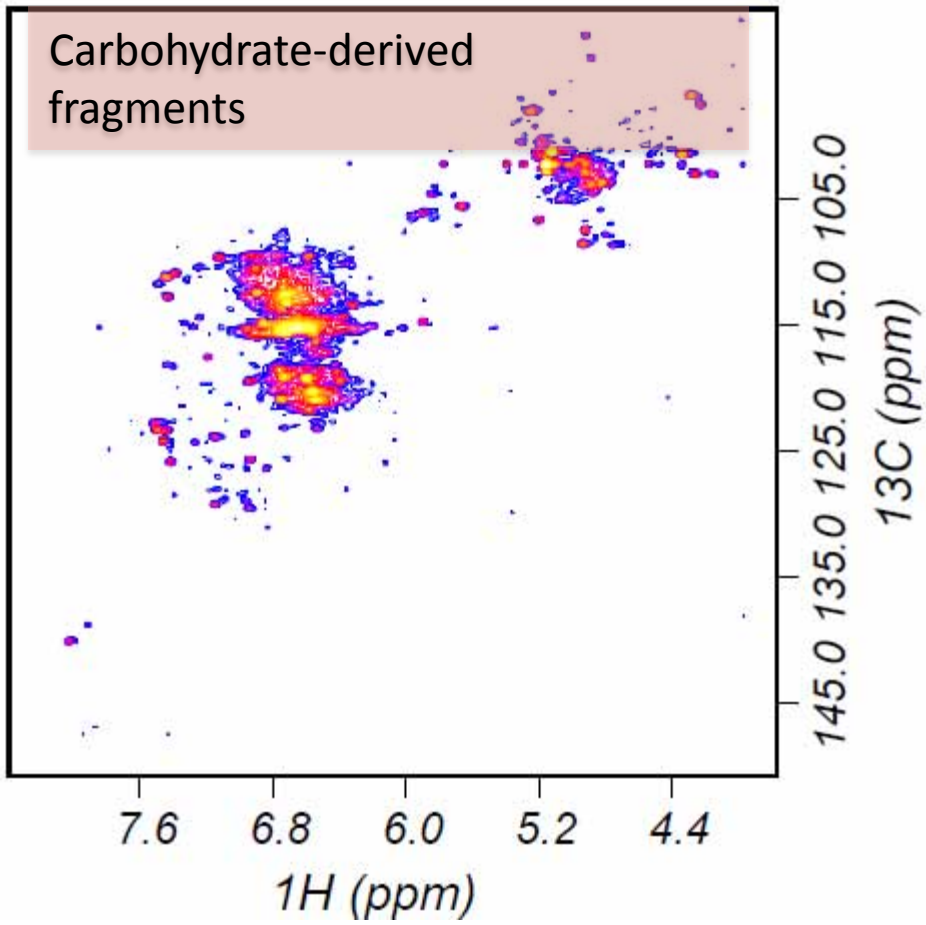


Pyrolysis oil



Pre-treated oil

Loss of anomeric C, potentially reduced to alcohols