2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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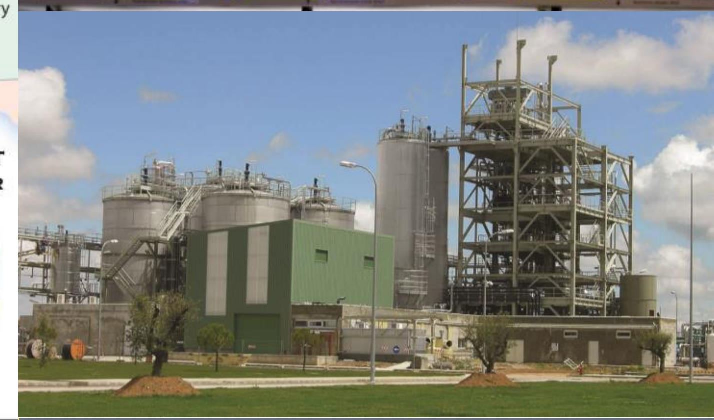

Thermochemical Feedstock Interface

March 23, 2015

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Goal Statement

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GOAL: Understand the effects of feedstock composition on thermochemical conversion processes to enable BETO's FY17 conversion cost target of $2.50/GGE (hydrocarbon biofuels) using a blended feedstock delivered at $80/dry ton.

Understanding how blended feedstocks (with variable ash, lignin, and protein) impact product yields, product quality, and catalyst lifetimes is critical to bringing down biofuel costs.

Outcome: In-feed compositional specifications that will help match biomass *resource development* with thermochemical *conversion technologies*, allowing these additional resources to be included at a reduced risk to the U.S. biofuels industry.

Project Quad Chart Overview

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Timeline

- Start: October 2010
- End: September 2017
- 70% complete

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$908K	$1,270K	$1,543K	$2,307K

Barriers

- Tt-C. Relationship Between Feedstock Composition and Conversion Process
- Ft-G. Biomass Material Properties and Variability
- Tt-E/F. Deconstruction of Biomass Feedstocks to Form Gaseous/Bio-Oil Intermediates
- Tt-I/J. Catalytic Upgrading of Gaseous/Bio-Oil Intermediates to Fuels and Chemicals
- St-C., At-C. Analysis and Sustainability Barriers

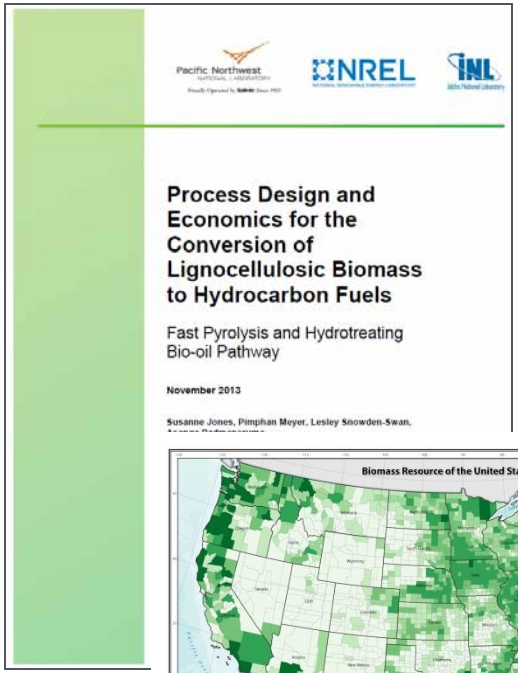
Partners

- **NREL** (80%) – TC conversion and product analysis (bio-oil production, vapor upgrading, syngas production)
- **PNNL** (20%) – Bio-oil production and upgrading, fuel product analysis
- **INL** – Feedstock characterization, handing, and logistics
- **NCSU/IBSS** – TC Conversion/Feedstocks
- **MIT/BP** – Gasification modeling
- **CPC** – Pyrolysis/reactor modeling

1 – Project Overview

Background

- Feedstock cost = ⅓ of each gallon of fuel, large **risk factor** for biorefinery developers
- What are the process **sensitivities to blending** low-cost feedstocks into the supply chain?
- Technoeconomic **analyses** identify areas for process cost reduction
- Resource **assessments** (e.g. Billion Ton Update) identify low-cost, high-impact feedstocks

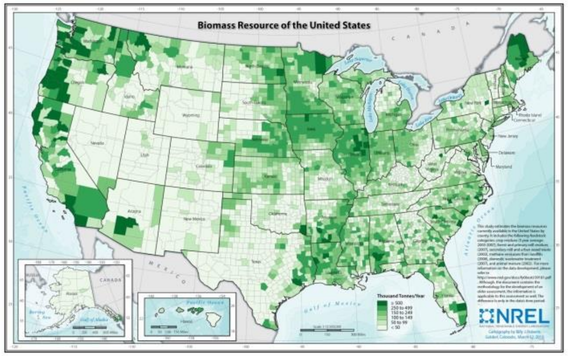

Pacific Northwest NATIONAL LABORATORY | NREL | INL

Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels

Fast Pyrolysis and Hydrotreating Bio-oil Pathway

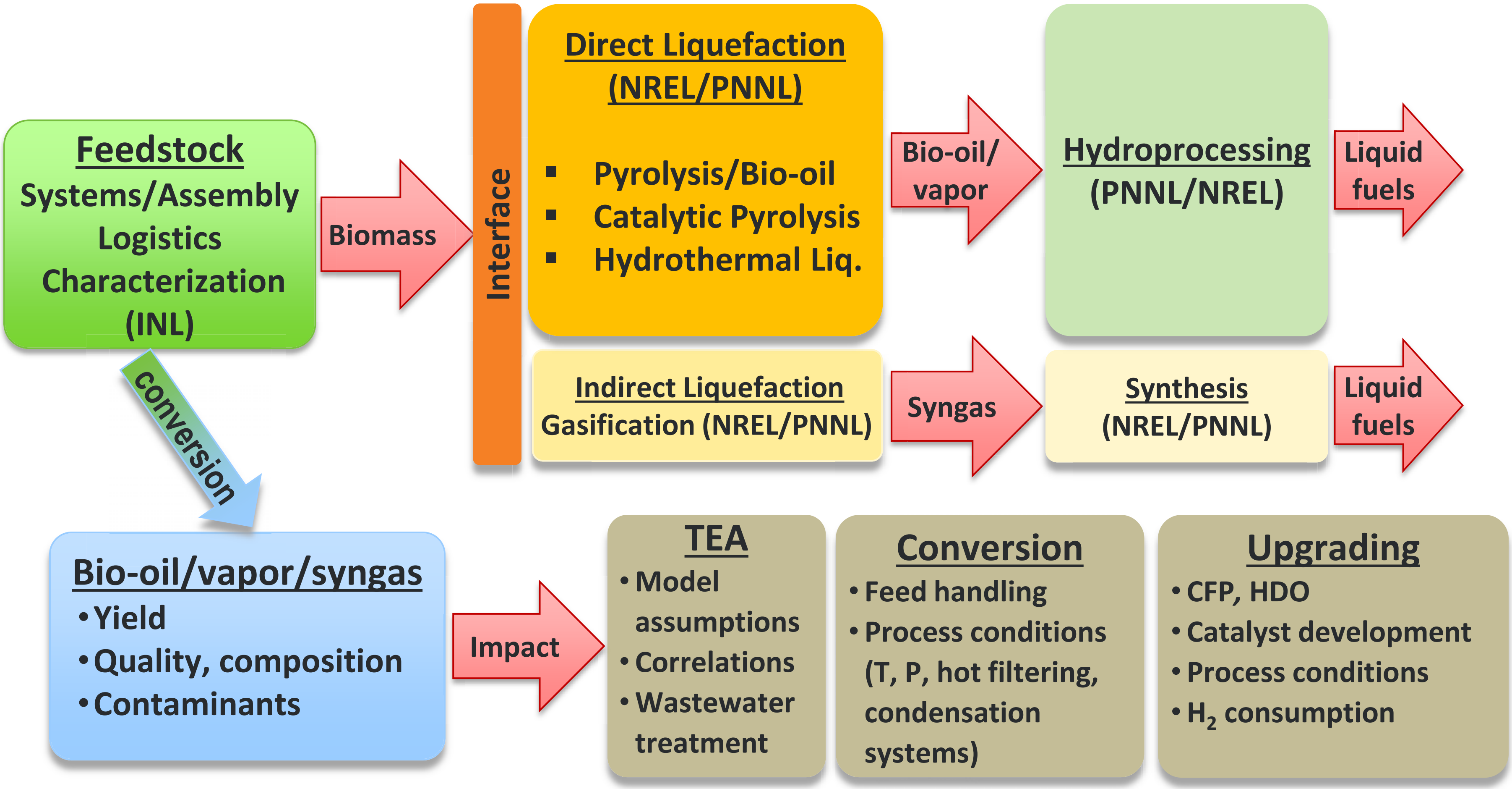
November 2013

Susanne Jones, Pimphan Meyer, Lesley Snowden-Swan,

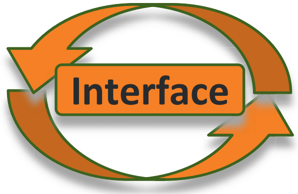


Overall Objective: Capture and analyze the key biomass interface interactions at the fundamental biomass and chemical process level needed to establish feedstock specifications for a given thermochemical conversion process.

1 – Project Overview



Process specifications impact feedstock development



Feedstock cost/properties impact conversion R&D decisions

2 – Technical Approach

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- Overall Technical Approach
  - Milligram-scale **rapid screening** of many feedstocks/blends/pretreatments
  - Process-relevant **conversion testing** of down-selected feedstocks:
    - NREL – Fast pyrolysis, catalytic fast pyrolysis, indirect liquefaction (gasification)
    - PNNL – Hydrothermal liquefaction, catalytic hydroprocessing
  - Detailed physical/chemical **analysis**:
    - GC/MS, SimDist, py-MBMS, CHNO, viscosity, TAN, XAS, carbonyls, phenols, ICP-OES
  - **TEA** to identify process cost reductions

- Critical Success Factors
  - **Quantified impacts** of feedstock on product yield/composition, catalyst life
    - ➢ *$/GGE as a function of product yield, contaminants, H_2 use*
  - **Demonstrated** technical targets can be met with **low-cost feedstocks**
    - ➢ *Ex-situ: 17.5% → 27.2% org. yield, 27% → 44% C_{eff}, $101.45 pine → $80 blend*
  - **Reduced risk to industry** – blends are adopted in commercial plant designs

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- Potential Challenges
  - **Broad scope** of feedstocks and (pre)conversion technologies to investigate
  - Inherent **variability** of delivered biomass (even within species)

2 – Management Approach

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- Project Leadership at Labs (plan, prioritize, coordinate, communicate)
  - Periodic intra-lab team meetings & site visits
  - Regular progress updates
  - Exchange of experimental data
  - Periodic project and AOP coordination calls
- Leverage related BETO-sponsored work
  - Adopt best practices within TC Platform (e.g. standardized feedstocks, catalysts, analytical methods and testing conditions)
  - Communicate and share data with early-stage conversion R&D projects regarding potential interface issues as new feedstock are considered
- Establish & Follow Approved Project Management Plan
  - Regular Milestones (quarterly progress) and Deliverables (manuscript submissions, annual reports)
  - Go/No-Go, e.g. Q2 FY16: identify blended feedstock that meets targets
  - Project risk/mitigation strategies
  - Disseminate results (peer-reviewed manuscripts, conference papers)

3 – Technical Progress (Summary NREL/PNNL/INL)

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1. Integrated Study of FP/HT Pathway (“Field-to-Fleet”)
   - Pyrolysis oils from 6 pure + 2 blended feedstocks produced and upgraded to hydrocarbon fuels
   - Fuel yields: 17-27% $g_{fuel}/g_{biomass}$, C_{eff}: 30-48%, conversion: \$2.50-\$4.10/GGE
   - py-MBMS rapid screening can potentially be used to predict final fuel yield
   - Demonstrated that feedstock impacts oil yield/composition, fuel yield/composition, H_2 use, \$/GGE
2. Catalytic Fast Pyrolysis vs. Feedstock
   - Hydrocarbon yield varies with feedstock, trend is different than bio-oil upgrading
3. Gasification of INL Feedstocks
   - At 850^{o}C, syngas yield & composition are largely insensitive to feedstock
   - Feeding, contaminants, bed interactions are potential issues with herbaceous feed
4. Analytical Development
   - Commissioned high-resolution mass spectrometer for pyrolysis vapor speciation
   - Developed X-ray absorption methods for bio-oil/char inorganic speciation

3 – Technical Progress
(Field-to-fleet – NREL/PNNL/INL)

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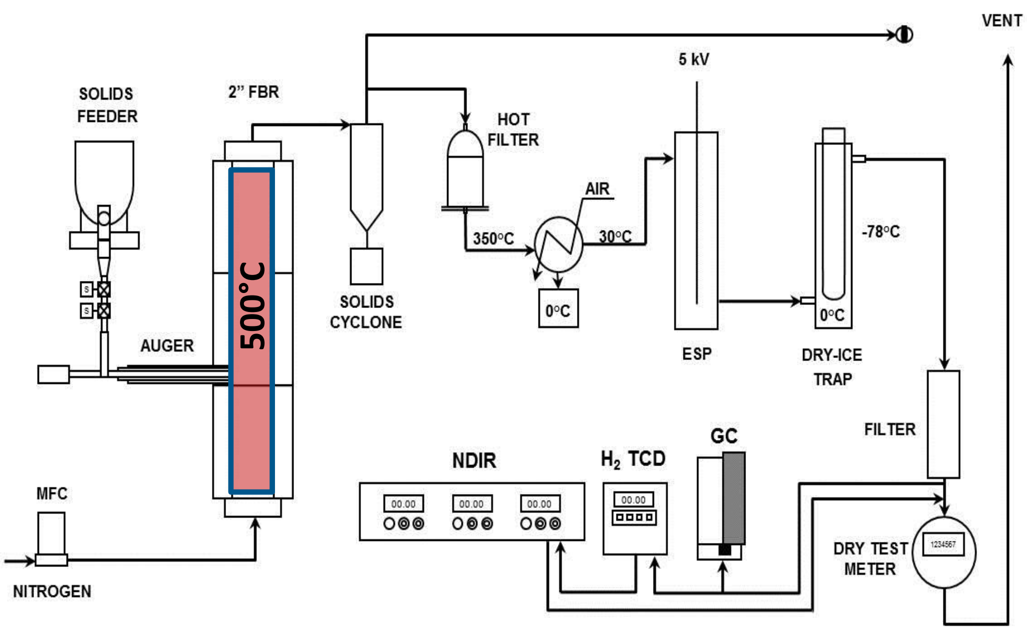
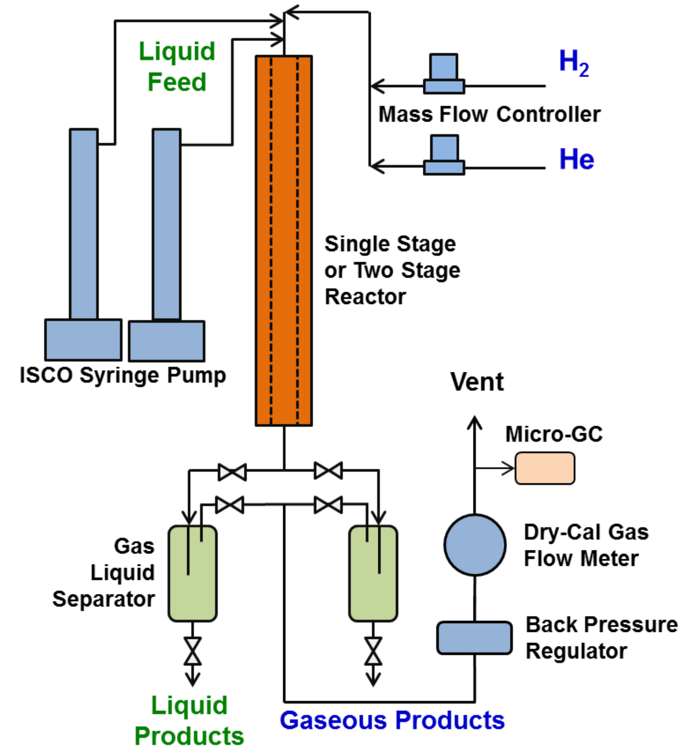
1. “Field-to-fleet” integrated fast pyrolysis/hydrotreating study

NREL Fast Pyrolysis Reactor



Feed rate: 0.5 kg/h
Reactor: 5.0 cm ID
T = 500°C
P = 1 atm.

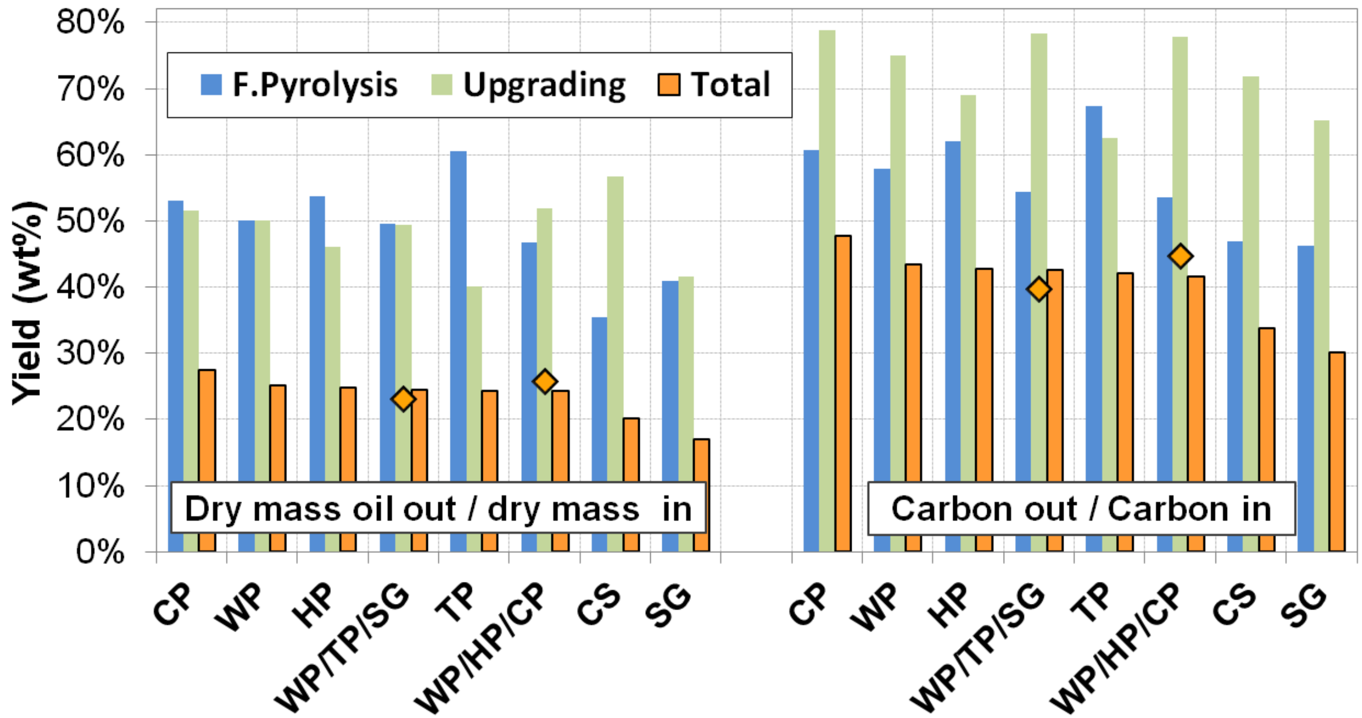
PNNL Hydrotreating Reactor



Feed rate = 48 mL/h   T = 220°C/400°C
Reactor = 1.3 cm ID   P = 1550 psi

3 – Technical Progress (cont.)
(Field-to-fleet – NREL/PNNL/INL)

Feedstocks
Clean pine
Whole tree pine
Hybrid poplar
Tulip poplar
Corn stover
Switchgrass
B1: TuPo/WhPi/SwGr
B2: WhPi/ClPi/HyPo



- Bio-oil yields: 35% (corn stover) to 60% (tulip poplar), dry basis (results validated within 20% by PNNL using similarly sized fast pyrolysis system)
- Fuel blendstock yields: 40% (tulip poplar) to 57% (corn stover)
- Overall field-to-fleet yields ($g_{fuel\ oil}/g_{biomass}$): 17% (switchgrass) to 27% (clean pine), 30-48% carbon efficiency
  - ➢ **High oil yield does not necessarily mean high fuel yield downstream!!**

3 – Technical Progress (cont.)
(Field-to-fleet – NREL/PNNL/INL)

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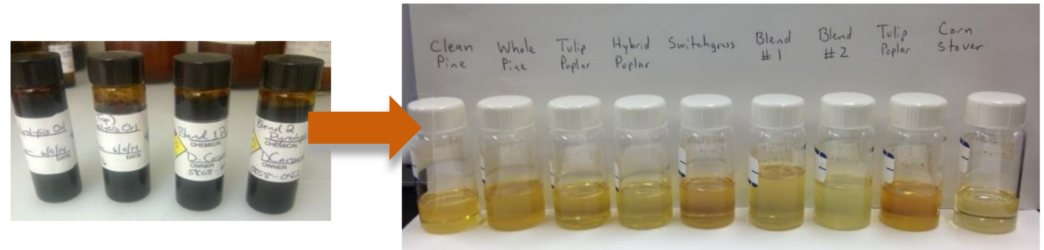
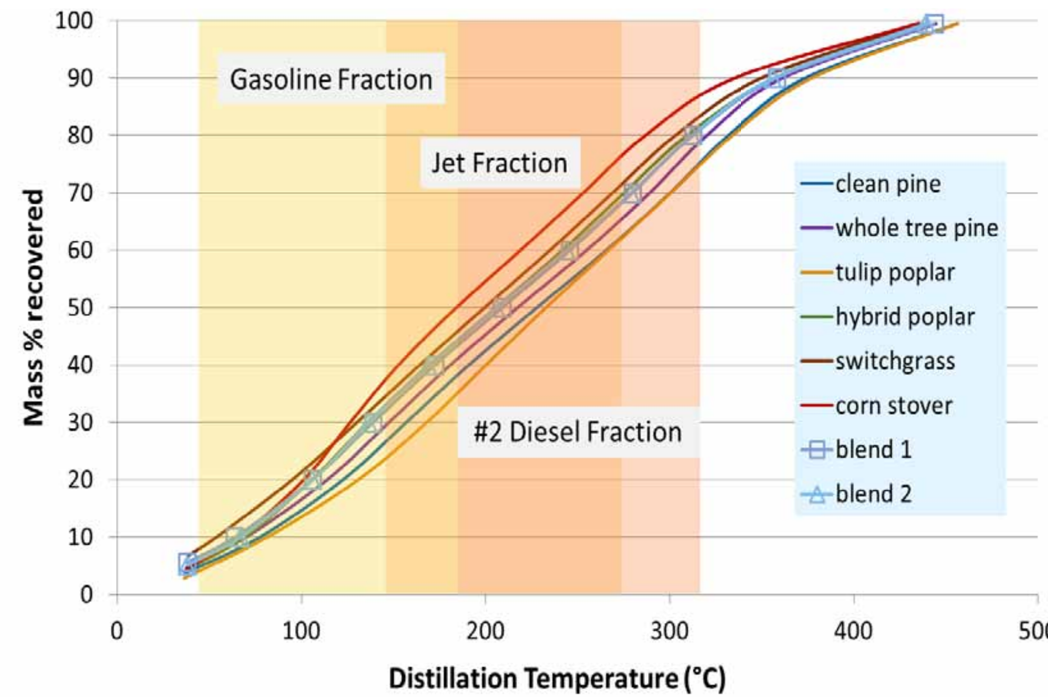
- SimDist gives fuel blendstock composition
  - Compounds separated by boiling point (fractions may not represent finished fuel)
  - Gasoline ranges from 39% (clean pine) to 51% (corn stover)
  - Diesel ranges from 40% (corn stover) to 46% (tulip poplar)
  - Jet fraction near constant at 11-12%
  - **Feedstock impacts fuel composition**

    * *blending could potentially be used to influence desired products*





3 – Technical Progress (cont.) (Field-to-fleet – NREL/PNNL/INL)

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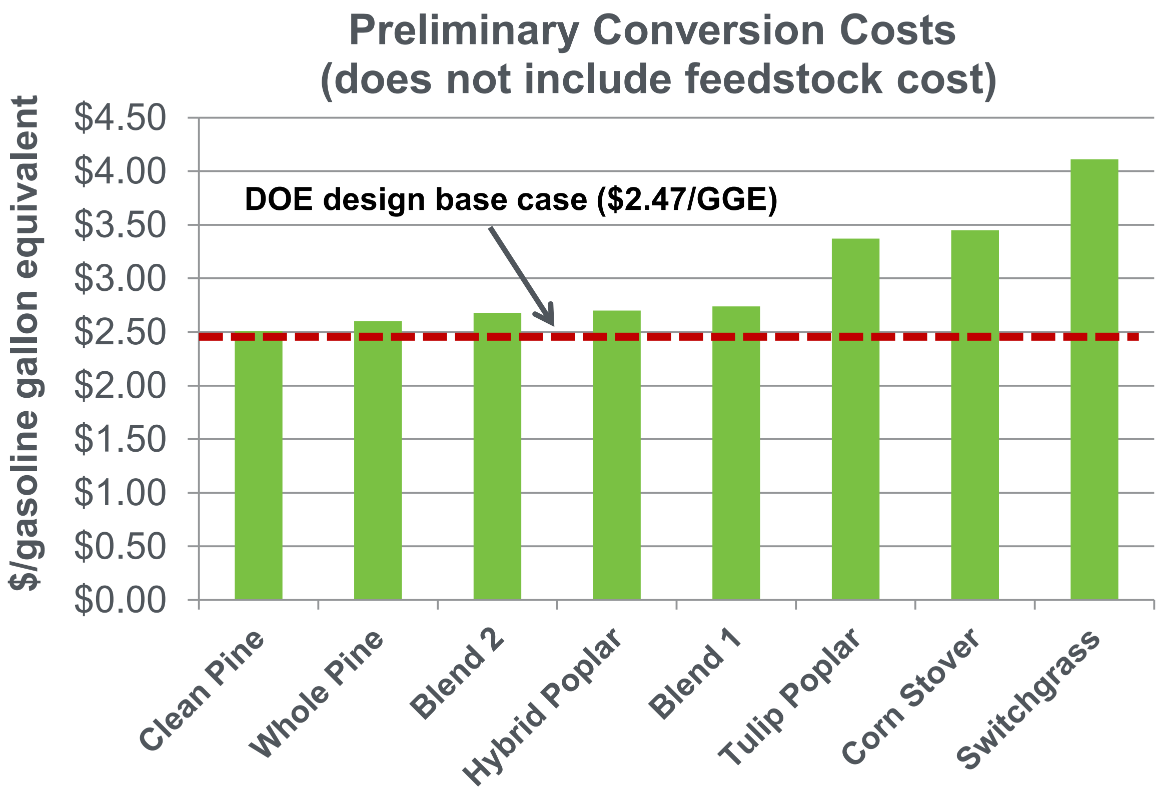
- Modeled n^{th} plant conversion costs for bio-oil upgrading
- Demonstrated performance with blended feedstocks similar to woody feedstocks, but at a lower projected cost

Feedstock affects multiple points in the process:

- Fast pyrolysis yields
- Bio-oil composition
- Hydrotreating yields
- Fuel composition
- H_2 consumption
- **Fuel production cost**



3 – Technical Progress (py-MBMS rapid screening - NREL)

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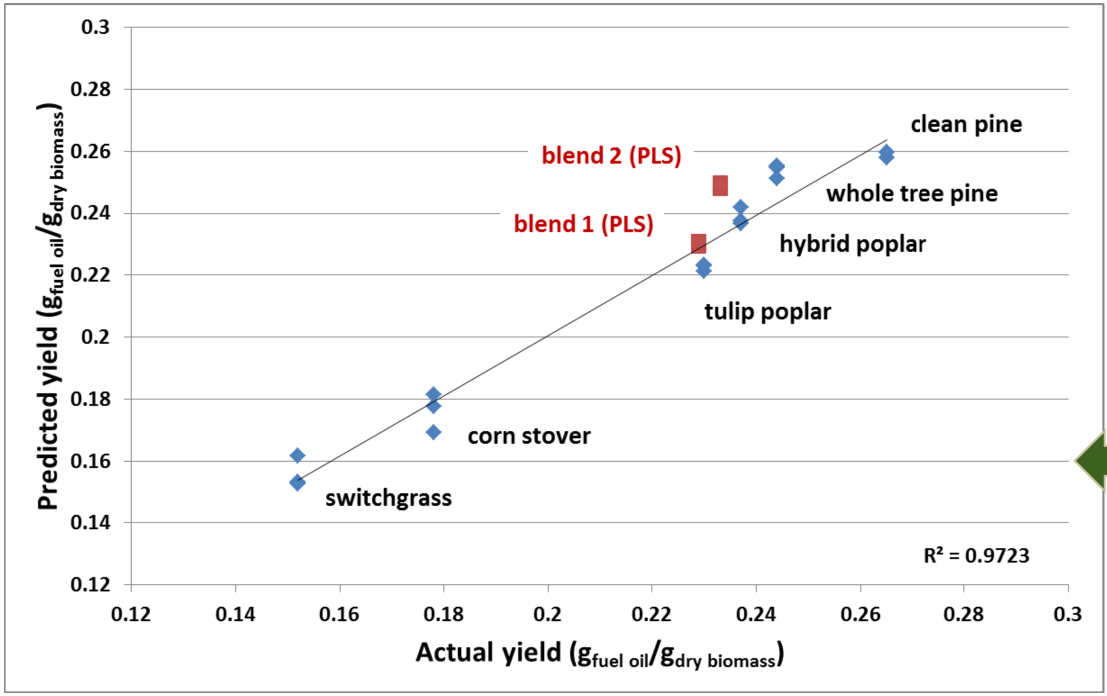
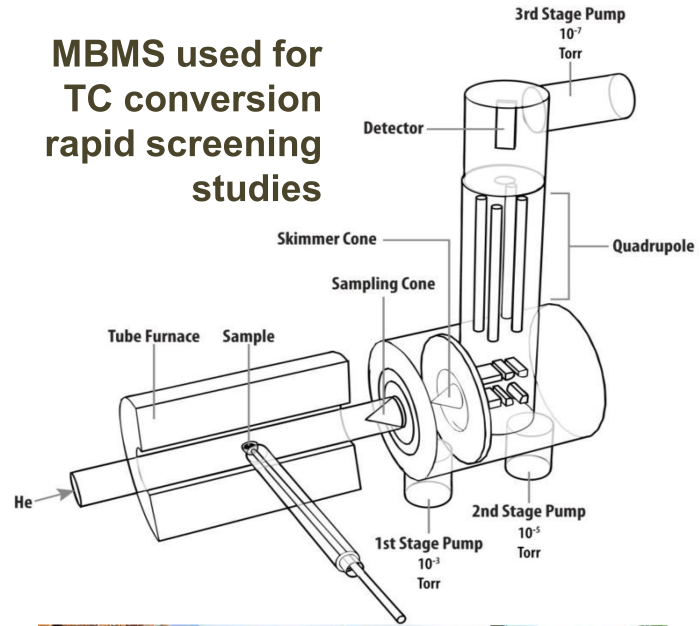
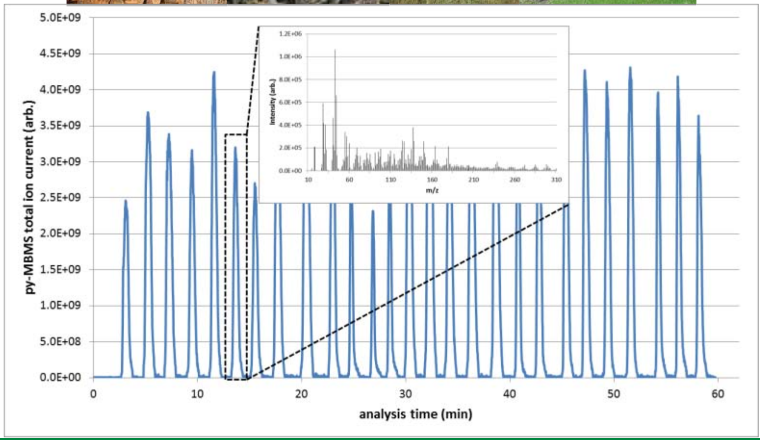
- Rapid screening to estimate product yields, analyze pyrolysis vapor composition, examine solid and/or vapor interactions in blends
- PLS model built to predict fuel blendstock yields based on mass spectral signature
- Good correlations, but larger sample set is needed for robust predictions



MBMS used for TC conversion rapid screening studies





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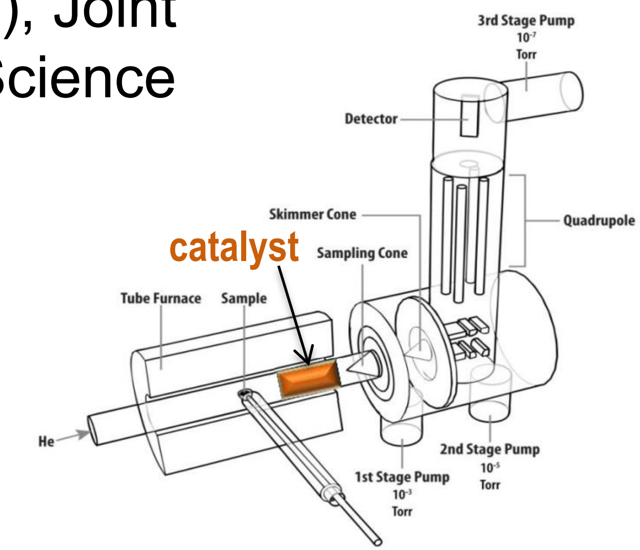
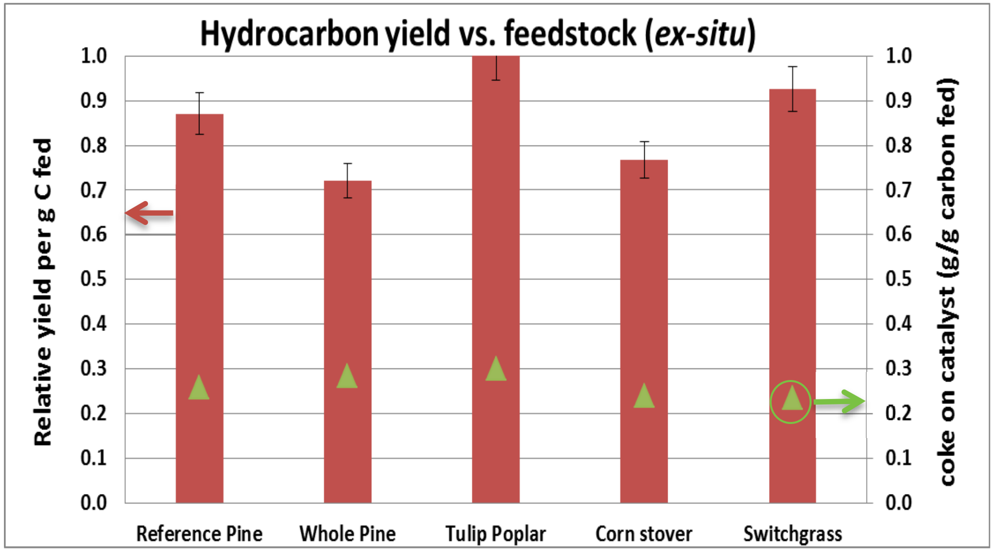
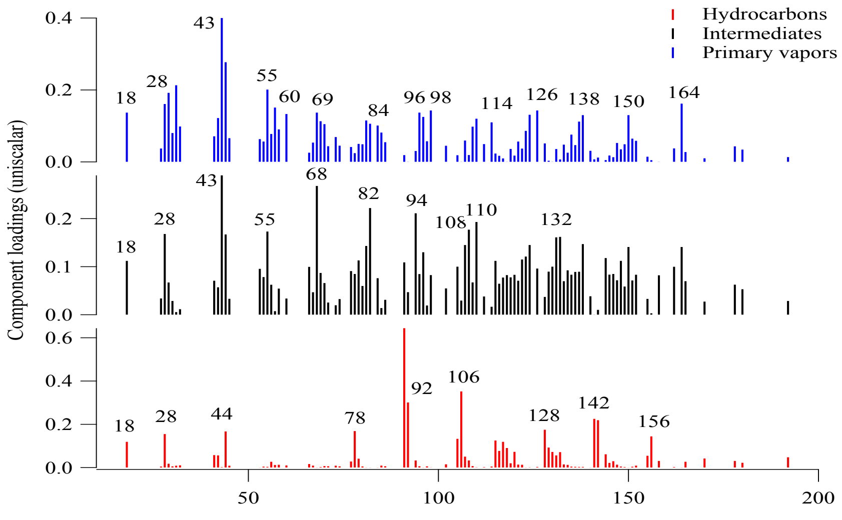
2. Catalytic Fast Pyrolysis (*ex-situ* upgrading), Joint with NREL 2.3.1.313, Catalytic Pyrolysis Science

- Significant variation in hydrocarbon yield ($g_{HC}/g_{carbon\ fed}$) observed between feedstocks
- Initial trends are different than trends seen in bio-oil upgrading studies
- Switchgrass performed relatively well possibly due to less lignin (~17% vs 30% for wood)
- Bench-scale experiments are planned to validate micro-scale trends



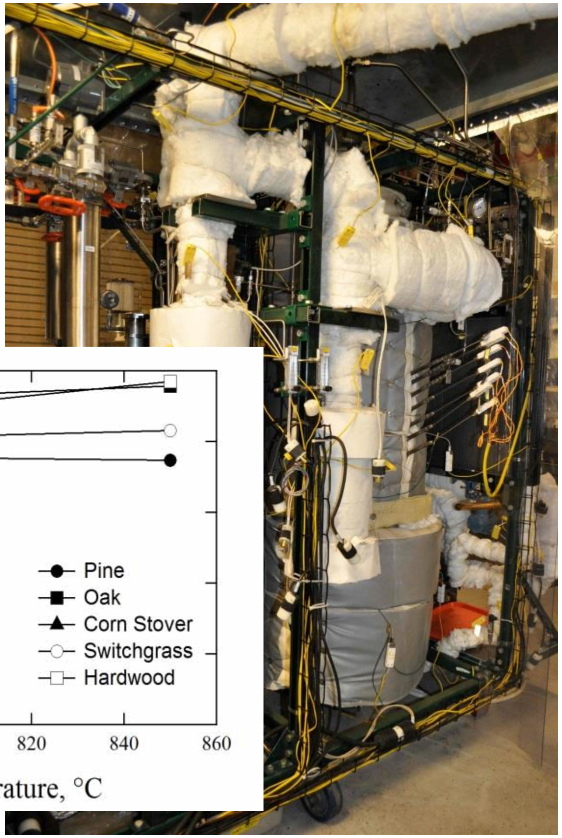


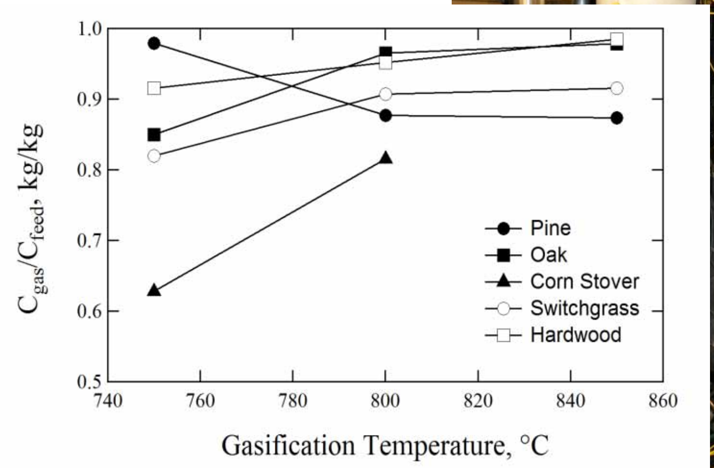


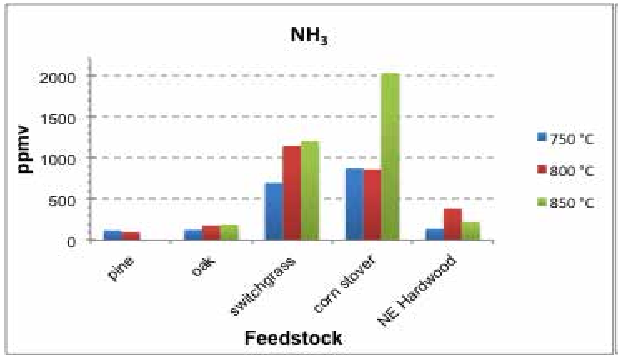
3. Gasification of INL feedstocks

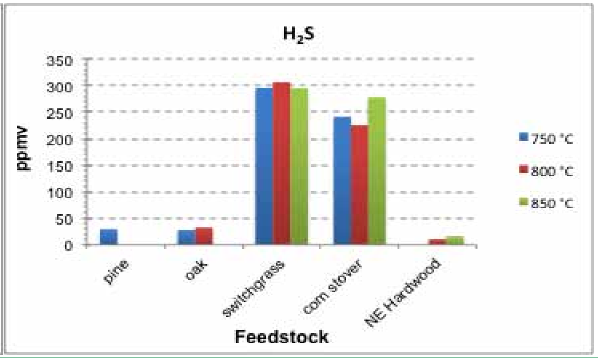
- Assessed gasification performance of several baseline INL feedstocks (pine, oak, switchgrass, corn stover, mixed hardwood) at three temperatures (750, 800, 850°C)
- Measured distribution of inorganic components (esp. S, N, Cl) in syngas, liquid condensate, and bio-char
- At 850ºC, syngas yield and composition are **largely insensitive to feedstock**
- Biomass feeding, contaminants, interactions with bed materials could be problematic for **herbaceous** feedstocks

NREL's 4" fluidized bed research gasifier





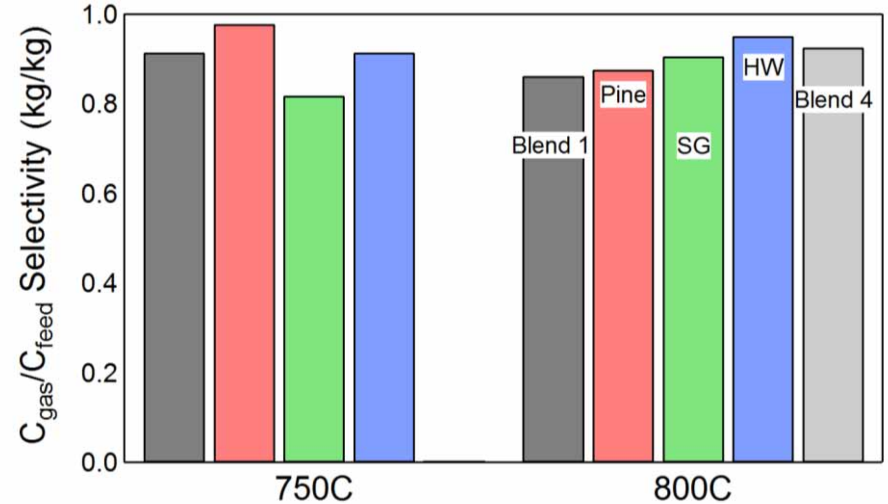


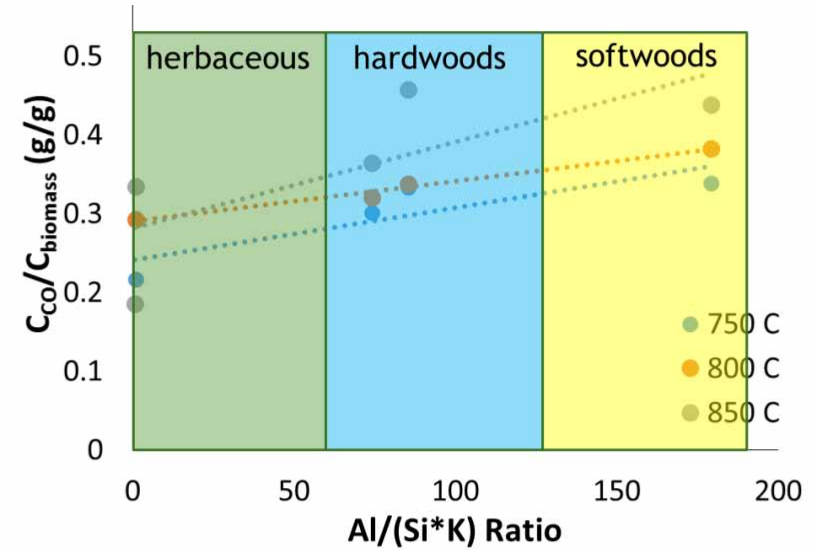


Agglomerated bed material after feeding corn stover

3. Gasification of blended feedstocks/MIT Practice School

- MIT Practice School students spent 4 weeks at NREL operating 4FBR and analyzing data
- Herbaceous materials can be blended at ~30% without detriment to efficiency or C selectivity to gas
- Found correlations with syngas composition and certain ash components (e.g. Al, Si, K)
- Recommended further study of blends (synergies?), and air gasification of corn stover to improve performance

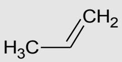
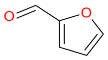
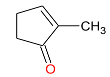
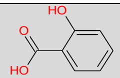
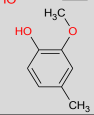
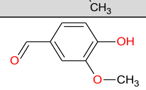
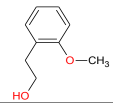


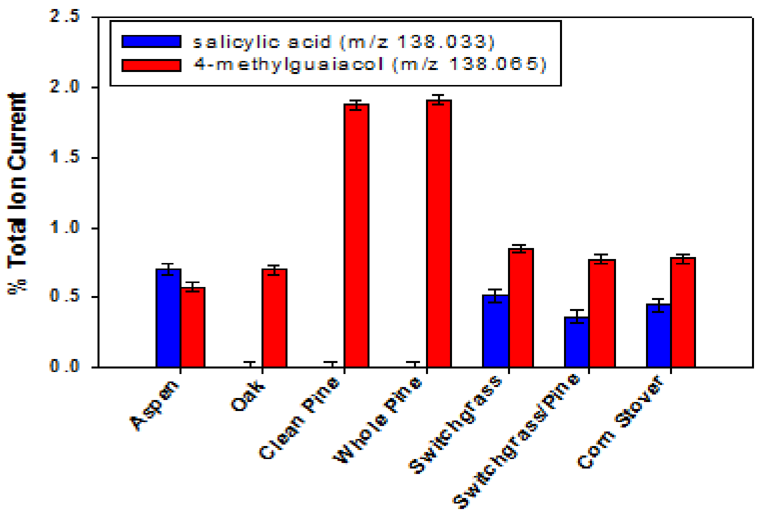


MITei MIT Energy Initiative

4. Analytical development

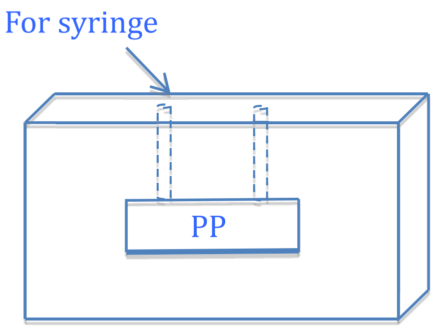
- Commissioned high-resolution mass spectrometer (HRMS) for detailed pyrolysis vapor analysis
- ‘Exact mass’ measurements revealed new molecular detail, differences between feedstocks
- Added chemical specificity enables new mechanistic insights (e.g. formation of ketene, a possible cross-linking agent)
- As formulated feedstocks are considered for *in-situ* and *ex-situ* vapor upgrading pathways, this information will help with rational design of upgrading catalysts

Tentative ID	Formula	Structure	Measured *m/z*
ketene	C_2H_2O	$H_2C{=}C{=}O$	42.018
propene	C_3H_6		42.054
furfural	$C_5H_4O_2$		96.011
2-methyl-cyclopentenone	C_6H_8O		96.046
salicylic acid	$C_7H_6O_3$		138.033
4-methylguaiacol	$C_8H_{10}O_2$		138.065
vanillin	$C_8H_8O_3$		152.050
4-ethylguaiacol	$C_9H_{12}O_2$		152.086

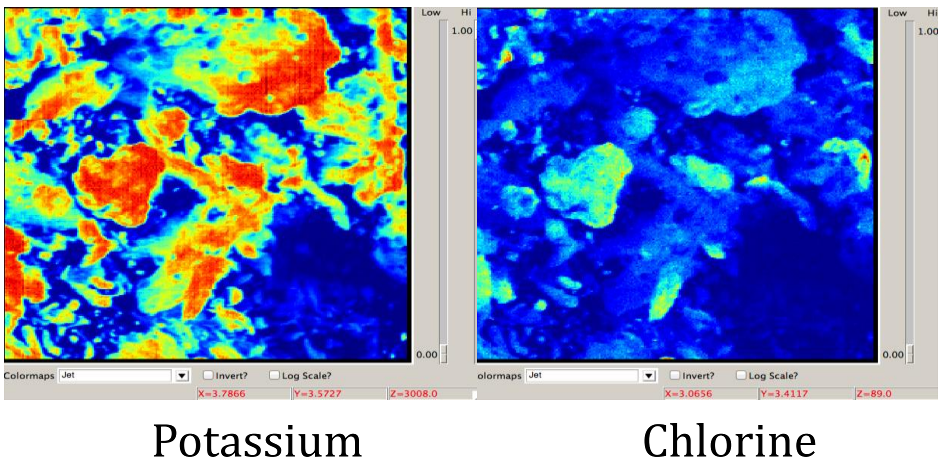


4. Analytical development

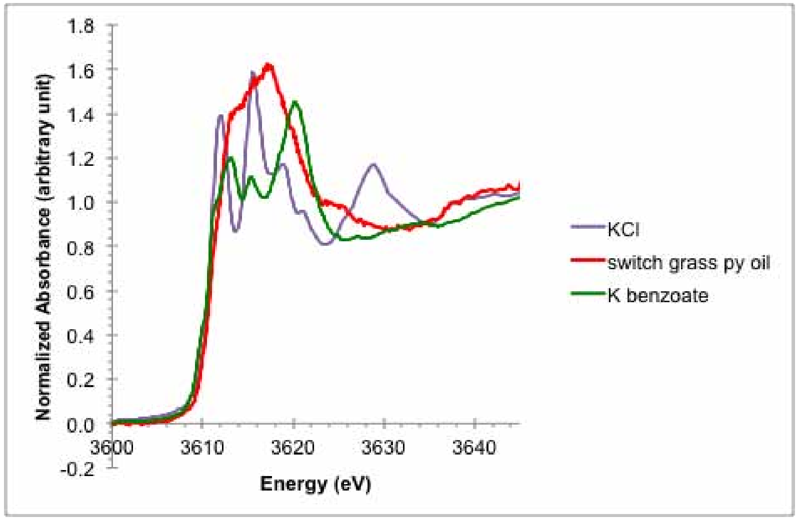
- Awarded beam time at Stanford Synchrotron Radiation Laboratory for X-ray spectroscopy experiments
- Developed methods to analyze specific mineral species & chemical forms in bio-oil and char
- Important to understand mineral species transport in regards to oil stability, and downstream implications when using high-ash feedstocks



Bio-oil sample cell designed for XAS studies.



X-ray microprobe maps of potassium and chlorine in corn stover <u>bio-chars</u>.



X-ray absorption spectra of switchgrass <u>bio-oil</u>.

4 – Relevance (cont.)

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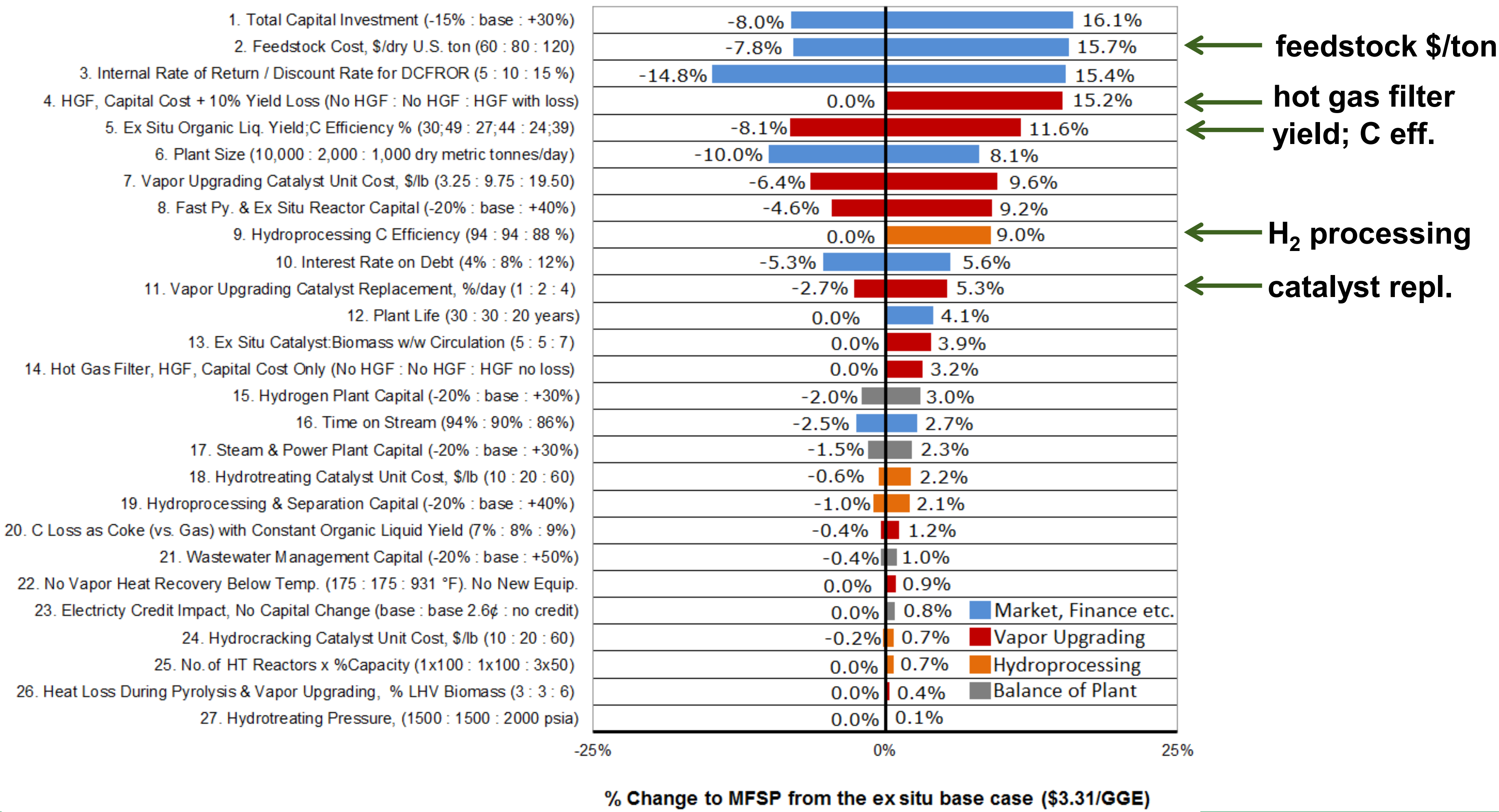
Cost sensitivities show potential impacts of feedstock on MFSP (*ex-situ* upgrading case).



4 – Relevance

BETO FY17 Performance Goal:

"…deliver **feedstock**…at required conversion process in-feed **specifications** at or below $80/dry ton…"

BETO 2022 Milestone:

"By 2022, validate the Office performance goal of $3/GGE…using **on-specification blended, low-cost feedstock** via a thermochemical pathway that produces gasoline and diesel blendstock fuels."

Barriers

- **Tt-C.** Relationship Between Feedstock Composition and Conversion Process
- **Ft-G.** Biomass Material Properties and Variability
- **Tt-E/F.** Deconstruction of Biomass Feedstocks to Form Gaseous/Bio-Oil Intermediates
- **Tt-I/J.** Catalytic Upgrading of Gaseous/Bio-Oil Intermediates to Fuels and Chemicals
- **St-C., At-C.** Analysis and Sustainability

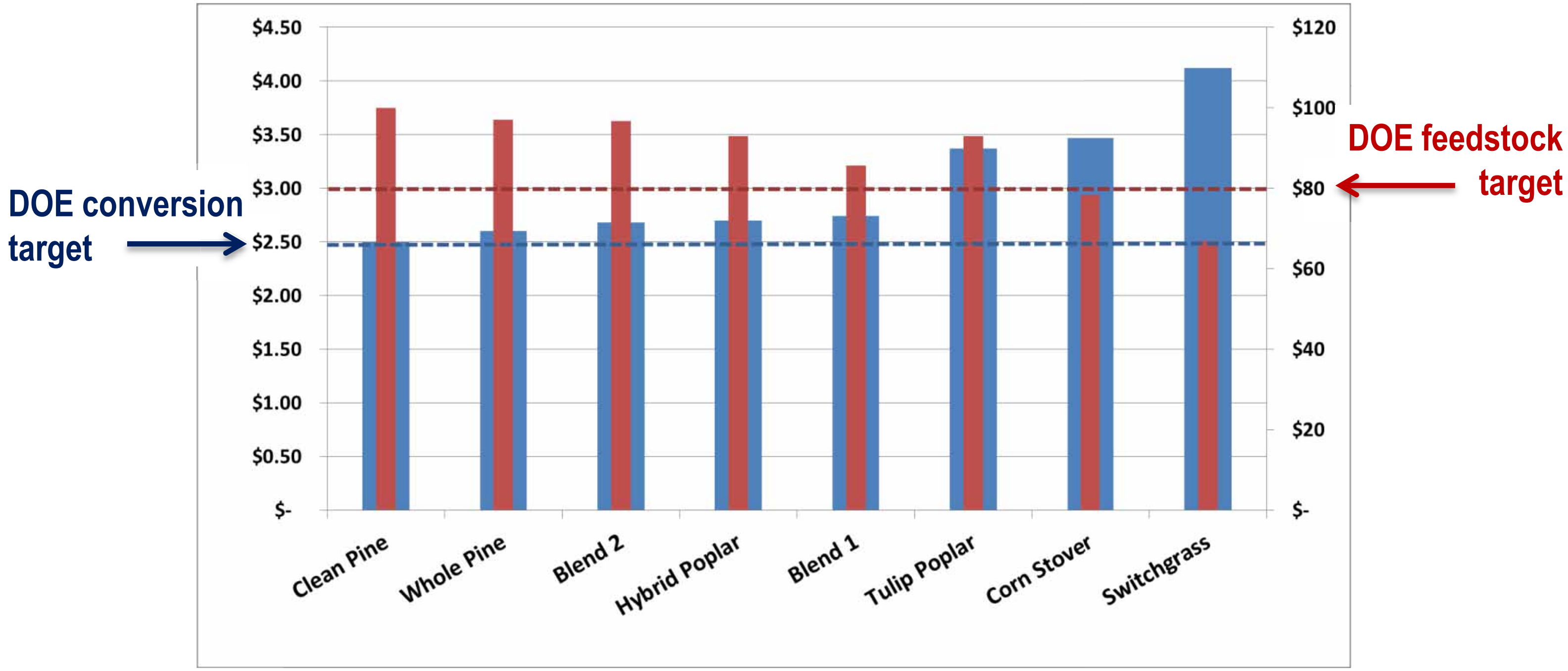
***Process-relevant data** – feeding & handling, product yield & composition vs feedstock – leading to in-feed **specifications** will help feedstock and biorefinery developers during commercialization.*

5 – Future Work

- Remainder of FY15: continue 'field-to-fleet' performance testing (bio-oil upgrading) of new and blended feedstocks
  - Feedstock prep (INL), bio-oil production (NREL), hydrotreating (PNNL), and detailed analysis of feedstock and product streams
  - Confirm linearity of blends
  - Oriented strand board (OSB, to represent C&D waste) and pinon/juniper
  - Effect of pyrolysis temperature on upgrading of switchgrass bio-oil
- FY16/FY17: understand impacts of specific feedstock components and process variables on product yields, product distributions, and overall conversion costs
  - Mineral species (transport phase of ash components, effects on yield)
  - Lignin content/composition (effects on hydrotreating)
  - Protein content (char formation)
  - Aerosol formation (effects on vapor upgrading)
  - Evaluate INL pretreated feedstocks
  - Process variables vs. feedstock (temperature, hot gas filter)
- Environmental and sustainability metrics (validate model assumptions)
  - Char combustion (reactivity, emissions)
  - Wastewater effects with high N and S feedstocks

Summary
Thermochemical Feedstock Interface

- Understanding how blended feedstocks impact conversion is key to matching biomass *resource* development with *conversion* technologies
- Feedstock impacts multiple parts of process: bio-oil yield & composition, fuel blendstock yield & composition, and \$/GGE (~\$1.60 variation)
- 30% switchgrass Blend1 performed similar to wood, but costs less



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***Project Leads at respective labs**

Additional Slides

Manuscripts

1. Howe, D.; Westover, T.; Carpenter, D.; Santosa, Emerson, Deutch, Starace, Kutnyakov, Lukins, "*Field to Fleet Performance Testing of Lignocellulosic Feedstocks: An Integrated Study of the Fast Pyrolysis/Hydrotreating Pathway*", Submitted to Energy and Fuels, February 2015
2. Trendewicz, A.; Evans, R.; Dutta, A.; Sykes, R.; Carpenter, D.; Braun, R. "*Evaluating the effect of potassium on cellulose pyrolysis reaction kinetics.*" Biomass and Bioenergy 2015, 74, 15-25, DOI: 10.1016/j.biombioe.2015.01.001.
3. Cheah, S.; Malone, S.; Feik, C. "*Speciation of sulfur in biochar produced from pyrolysis and gasification of oak and corn stove*r." Environmental Science and Technology 2014, 48(15), 8474−8480, dx.doi.org/10.1021/es500073r.
4. Carpenter, D.; Westover, T.; Jablonski, W.; Czernik, S. "*Biomass Feedstocks for Renewable Fuel Production: A review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors.*" Green Chem., 2014, DOI: 10.1039/C3GC41631C, http://xlink.rsc.org/?doi=C3GC41631C).
5. Cheah, S.; Olstad, J.; Jablonski, W.; Barthelemy, K.; Carpenter, D.; Robichaud, D.; Westover, T. "*Effect of feedstock torrefaction and catalytic gasification on product gas composition.*" To be submitted.
6. Cheah, S.; Olstad, J.; Black, S.; Jablonski, W.; Laroco, N.; Starace, A.; Robichaud, D.; Mukarakate, C.; Carpenter, D. "*Partitioning of inorganic species during biomass gasification*." To be submitted.
7. Christensen, E.; Carpenter, D.; Evans, R. "*High-resolution mass spectrometric analysis of biomass pyrolysis vapors.*" To be submitted.
8. Starace, A.; Carpenter, D.; Evans, R. "*Effect of torrefaction temperature on oak, pine and switchgrass composition, torrefaction products and pyrolysis products.*" Submitted to Journal of Analytical and Applied Pyrolysis, March 2015.
9. Jablonski, W.; Olstad, J.; Carpenter, D.; Dutta, A. "*Gasification of pretreated and blended feedstocks: syngas and tar compositions, mass and energy balances.*" To be submitted.
10. Carpenter, D.; Mukarakate, C.; Budhi, S. "*Catalytic upgrading of biomass-derived pyrolysis vapors: comparison of softwoods, hardwoods, and herbaceous feedstocks.*" To be submitted.

Presentations/Posters

1. Cheah, S.; Laroco, N.; Olstad, J. "*From plant materials to bio-chars: speciation and transformation of sulfur and potassium during biofuel production*." Oral presentation, 249th American Chemical Society National Meeting, Denver, CO, March 2015.
2. Jablonski, W.; Cheah, S.; Olstad, J.; Black, S.; Carpenter, D. "*Towards Blended Feedstocks: Parametric gasification study comparing traditional and blended feedstocks at varying conditions*" Oral Presentation, AIChE National Meeting, November 2014, Atlanta, GA.
3. Jablonski, W.; Cheah, S.; Olstad, J.; Black, S.; Carpenter, D. "*Towards Blended Feedstocks: Parametric gasification study comparing traditional and blended feedstocks at varying conditions*." Oral Presentation, TCS2014, September 2014, Denver, CO.
4. Carpenter, D.; Westover, T.; Howe, D.; Evans, R.; French, R.; Kutnyakov, I.; Santosa, D. "*Field-to-fuel performance testing of various biomass feedstocks: production and catalytic upgrading of bio-oil to refinery blendstocks*." Oral Presentation, TCS2014, September 2014, Denver, CO.
5. Starace, A.; Evans, R. Olstad, J.; Magrini-Bair, K.; Carpenter, D.; Cheah, S. "*Evaluation of effect of torrefaction temperature on carbon content, pyrolysis vapor composition and surface chemistry of woody and herbaceous feedstocks*." Poster, TCS 2014, September 2014, Denver, CO.
6. Cheah, S.; Jablonski, W.; Olstad, J.; Carpenter, D.; Robichaud, D.; Westover, T. "*Impact of feedstock torrefaction and catalytic gasification on product gas composition*." Oral Presentation, TCS 2014, September 2014, Denver, CO.
7. Carpenter, D.; Westover, T.; Howe, D.; Jones, S.; Evans, R.; French, R.; Kutnyakov, I.; Santosa, D. "*Conversion of lignocellulosic biomass to hydrocarbon fuels via hydroprocessing: case study for eight high-volume U.S. feedstocks*", Oral Presentation, 2nd International Symposium on Energy Challenges & Metrics, Aberdeen, Scotland, August 2014.
8. Jablonski, W.; Olstad, J.; Carpenter, D.; Black, S.; Oddo, M.; Robichaud, D. "*Bench scale gasification of torrefied woody feedstocks: comparison of syngas and tar compositions to traditional woody and herbaceous feedstocks*," Poster, tcbiomass2013, Des Plaines, IL.

Note: All three INL/NREL/PNNL interface projects were combined for the 2013 Peer Review

4). Critical Success Factors

Please evaluate the degree to which:

- The project performers have identified critical factors (including technical, market, and business) that will impact the potential technical and commercial success of the project.
- The project performers have presented adequate plans to recognize, address, and overcome the top two to three challenges (technical and non-technical) that need to be overcome for achieving successful project results.
- Successful completion of the project will advance the state of technology and impact the viability of commercial bioenergy applications.

Reviewer Comments

a). The CSF's are reasonable. There is a balance between a need for specificity (i.e., knowing precisely what the conversion process "customer" is doing) and generality (i.e., the conversion process in vogue today may be on tomorrow's trash heap, so measurements and processes must apply across a range of conversion technologies). This work could shift a bit toward generality, since the conversion work at the Labs is typically some years behind the state of the art. The real risk is in major changes in direction, like cellulosic ethanol waning while hydrothermal liquefaction waxes, gasification declining while pyrolysis work increases, etc. The balance of this project should be carefully assessed vs. the MYPP as it evolves over time.

b). Seem to understand critical factors

c). Good goal, but may be difficult to achieve. Tests that can be used in the field vs run at a national lab need to be developed. This can be a huge hurdle. Non-linearity of blends creates other hurdles. Lastly, ash composition vs feedstock and ash vs yields creates a possible way of valuing alternative biomass feedstocks.

d). Significant success has already been made. The investigators seem to understand the barriers to progress.

Presenter Response:

a). We agree that this task must evaluate a broad range of technologies and feedstocks, so generality is given greater weight than specificity. However, comparing different technologies and feedstocks require that specific examples be explored and the results generalized where possible. This project closely watches the MYPP to assist in guiding research efforts.

c). A principal focus of this project is to develop tools and test methods that can be applied in the field real time, such as LIBS and FTIR spectroscopies and possibly TGA/DSC. An important aspect of conducting the research is assuring that research performed in the laboratory used 'field-run' material that is truly representative of material that is harvested at full commercial scale.

5). Future work

Please evaluate the degree to which:

The project performers have outlined adequate plans for future work, including key milestones and go/no go decision points.

The project performers have addressed how they plan to deal with upcoming decision points and any remaining issues.

Reviewer Comments

a). The Future Plans are sound.

b). Still several methods to evaluate to be done
Go back and figure out what funds left to do needed tasks

c). May not have time and scope to achieve the goal, considering the complex scope of this task. A good plan though.

d). Future work is well defined and planned.

Presenter Response:

b). There are still many technologies and feedstocks (including blends) that need to be evaluated. This task cannot evaluate all possible methods, so it is essential that we prioritize what technologies and feedstocks are evaluated with the available funds. We look for and appreciate guidance from Industry regarding how the prioritization should be made.

c). See response to b).

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6). Technology Transfer and Collaboration

Please comment on the degree to which the project coordinates with other institutions and projects to provide additional benefits to both BETO and the industry. Please provide suggestions on additional opportunities for encouraging further coordination.

Reviewer Comments

a). The collaboration is almost 100% focused on the other Labs, which is understandable, but over time, there should be more emphasis on engaging industry partners, even if it is only informally via sample exchanges and periodic discussions / workshops. Tunnel vision based on what the other Labs are doing in the conversion arena is the biggest risk here.

b). Articles and conference proceedings published.

c).

d). This is a well coordinated project and will be transferable to many other bio-oil projects.

Presenter Response:

a). Although industry partners are not explicitly listed as partners in the quad chart, this project does work indirectly with industrial partners through the Core Feedstock and Conversion Platforms. The process is like a pipeline or flow chart: Industry (feedstocks) → Feedstock Platform (DOE) → Interface Task (DOE) → Conversion Platform (DOE) → Industry (Conversion & Upgrading). If the Interface Tasks engages in substantial effort directly with industry, it runs the risk of cutting out the Feedstock and Conversion Platforms, which could cause confusion and duplicate effort.

Recent Milestones (2.2.1.304 NREL)

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Milestone	Planned Completion Date	Completion
Baseline pyrolysis testing of INL feedstocks	6/30/14	✓
Preliminary feedstock/conversion correlations	9/30/14	✓
Partitioning of inorganic species during gasification	9/30/14	✓
Effect of feedstock on deactivation of *in-situ* and *ex-situ* vapor upgrading catalysts	12/31/15	✓
Optimization of syngas quality from formulated feedstocks	3/31/15	Experiments complete
Pyrolysis conversion testing of formulated feedstocks	6/30/15	Experiments underway
Formulated feedstock specifications for bio-oil upgrading pathway	9/30/15	Planning underway

Milestones (2.2.1.305 PNNL)

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Milestone	Planned Completion Date	Completion
Submission of manuscript to peer reviewed journal detailing results of Field to Fuel Performance Testing	31 Dec, 2014	✓
Literature review and report on feedstocks, feed preparation (wet milling), and processing parameters for HTL	31 March, 2015	✓
Complete upgrading of FY15 blend formulations for FP	30 June, 2015	Planning underway
Complete upgrading of FY15 blend formulations for HTL	30 June, 2013	Planning underway

5 – Future Work (cont.)

Lab	Milestone Description	FY15		FY16			
		Q3	Q4	Q1	Q2	Q3	Q4
NREL	Complete Pyrolysis Conversion Testing of Formulated Feedstocks						
PNNL	Complete Upgrading of FY15 Blend Formulations for FP						
NREL	Formulated Feedstock Specifications for Bio-Oil Upgrading Pathway						
PNNL	Complete Upgrading of FY15 Blend Formulations for HTL						
PNNL	Annual progress report						
PNNL (Go/No Go)	Determine Viability of a Higher Ash Feedstock for FP Based on Ash Species Composition						
NREL (Go/No Go)	At Least One Feedstock Formulation Identified at $80/ton Delivered That Meets $2.47/GGE Conversion Target						

5 – Future Work (cont.)

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Project timeline:

SOT	FY14	FY15	FY16	FY17 Targets
Plan >	Test 8 *baseline feedstocks*, preliminary conversion model	Test 10 *blends*, propose 1-3 blends for demo, validate model	Validate yield model with 1-3 blends, optimize conversion	Demonstration with blended feedstock **($80/ton)**
Pulpwood **($120/ton)** Materials used >	Pine, poplar, corn stover, switchgrass, two blends	Combinations of pine, poplar, log. res., switchgrass, MSW	1-3 blends (per FY15 results)	1 blend for optimized conversion conditions
Carbon eff. (% feed carbon)	FP wood: **58-60%** HT wood: ?	→	→	FP blend: **69%** HT blend: **47%**
Example spec: Total ash < 1%	Propose > 1%, but limit specific elements (N, S, K, P, etc.)	Set initial chemical and physical specifications	Finalize specifications for demonstration	Update specifications as needed

Project Overview (PNNL)

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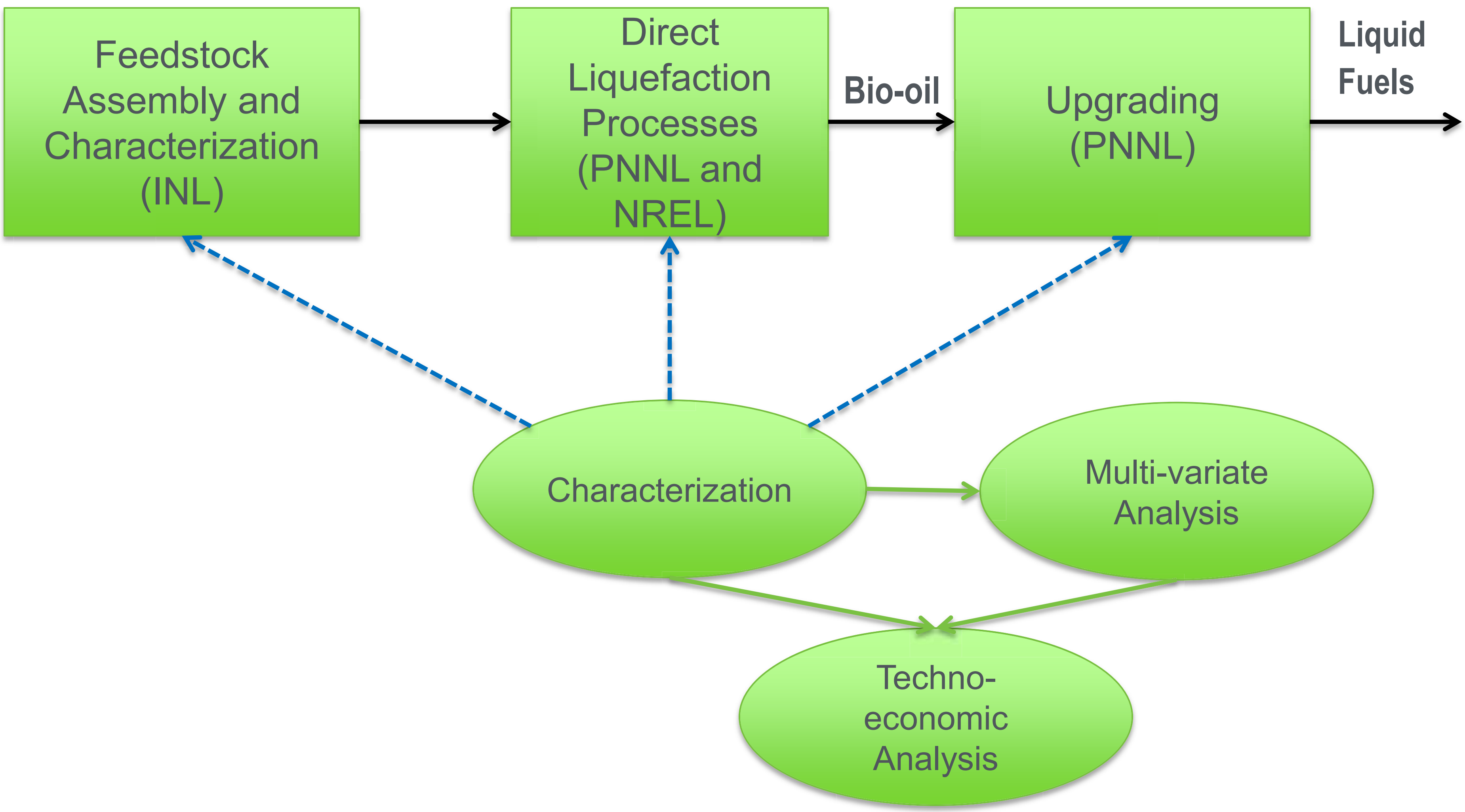

Supply-cost curves for some key feedstocks (BT2)

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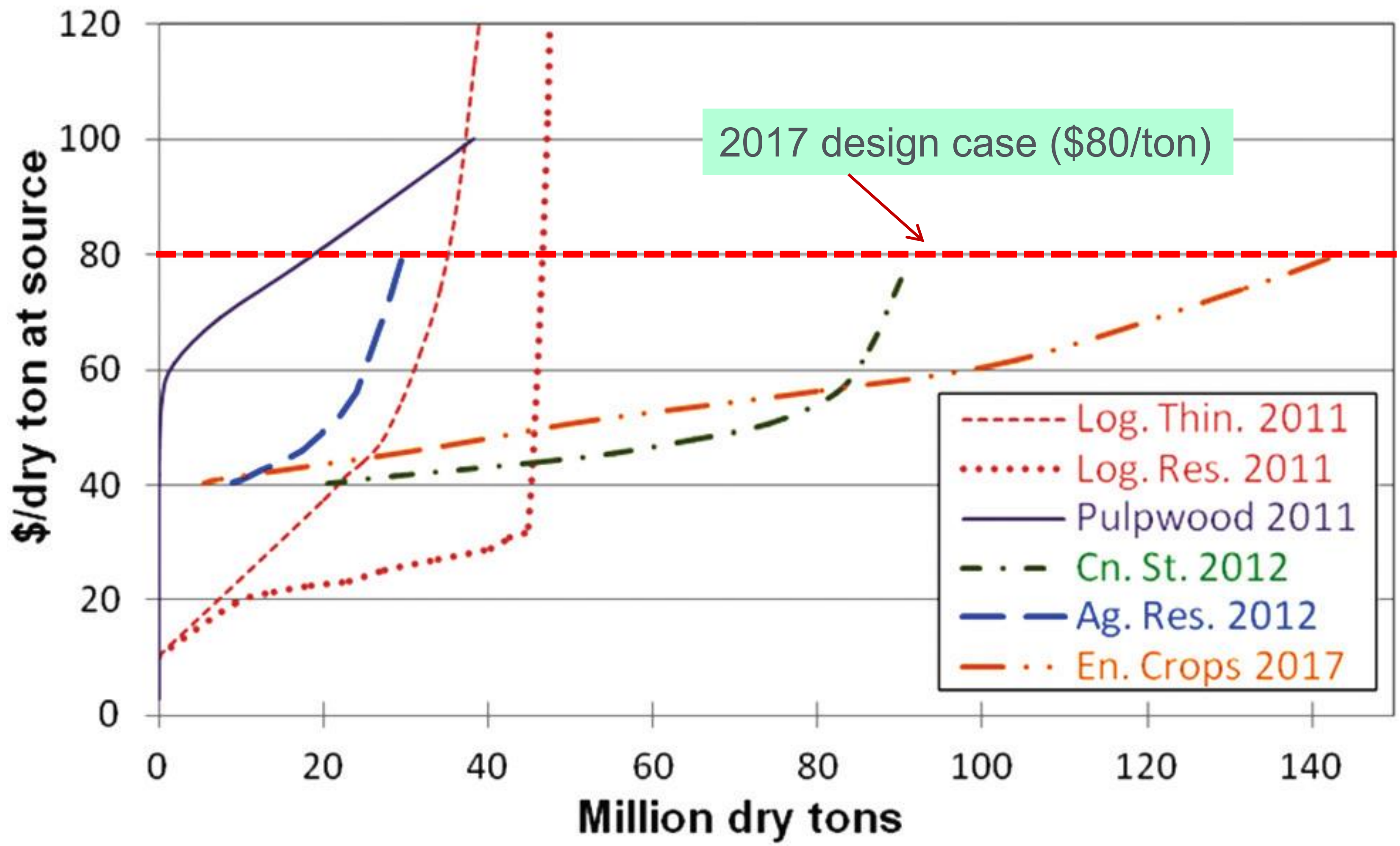

Carpenter, Westover, Jablonski, Czernik, Green Chem., 2014, 16, 384, adapted from BT2

Formulated feedstocks

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Move toward formulated feedstocks…to mitigate variability, reduce/stabilize cost
- commoditize feedstocks for biofuels production
- establish composition-based specifications (precedence for this is coal and animal feed industries)

Example blend *(from Jones, et al design report):*

Feedstock	Reactor Throat Feedstock Cost ($/dry ton)[2]	Formulation Fraction (%)	% Ash Delivered to Throat of Conversion Reactor
Pulp	99.38	30	0.5
Logging Residues[1]	74.83	35	1.5
Switchgrass	80.54	10	2.8
C&D Wastes	63.77	25	0.5
Formulation Totals	**80.00**	**100**	**1.1**

[1] residues do not include costs for harvest and collection; they are moved to landing while attached to the merchantable portion of the tree (for example, timber or pulpwood)

[2] includes ash mitigation

How will the process tolerate different feedstocks? Biomass resource development and process optimization need to be closely-coupled!

3 – Technical Progress (cont.)
(Field-to-fleet – NREL/PNNL/INL)

Raw feedstock properties from proximate, ultimate, calorific, and elemental ash analysis reported on a dry basis. Syringal/guaiacol (S/G) ratio from pyrolysis-molecular beam mass spectrometry (Py-MBMS) is also included. Numbers in parentheses indicate differences between results obtained from duplicate analyses of samples at different grind sizes. All numbers are reported on dry feedstock basis.

	Cl-Pn	Wh-Pn	Hy-Pop	Tu-Pop	Cn-St	Sw-Gr	Blend 1	Blend 2
Ash (%)	0.71	0.70	0.91	0.46	4.27	4.20	1.75	0.62
Vol. matter (%)	85.0	83.9	84.9	88.2	79.0	80.2	82.59	84.78
Fixed C (%)	14.3	15.4	14.2	11.4	16.7	15.6	15.66	14.6
HHV (BTU/lb)	8614	9063	8561	8519	7990	8077	8473	8873
LHV (BTU/lb)	7269	7728	7199	7151	6614	6749	7111	7504
C (%)	49.6	50.2	49.9	49.2	48.7	47.2	49.27	50.36
H (%)	5.9	5.9	5.8	5.8	5.7	5.7	5.85	5.86
N (%)	0.2	0.2	0.2	0.2	0.7	0.5	0.33	0.19
S/G ratio (-)	0.13	0.14	1.21	2.32	0.56	0.54	0.83	0.35
Al (ppm)	199 (1)	184 (7)	76 (8)	39 (8)	62 (3)	60 (9)	106 (5)	89 (16)
Ca (ppm)	942 (10)	1094 (21)	1703 (79)	934 (36)	2810 (158)	2312 (284)	1153 (65)	1359 (56)
Fe (ppm)	293 (218)	424 (506)	142 (28)	62 (28)	354 (42)	538 (135)	143 (32)	383 (53)
Mg (ppm)	266 (1)	290 (5)	377 (3)	258 (10)	1598 (73)	2580 (295)	293 (10)	929 (10)
Mn (ppm)	68 (1)	73 (5)	7 (0)	35 (2)	32 (3)	65 (8)	48 (1)	57 (2)
P (ppm)	75 (1)	93 (7)	252 (2)	70 (3)	551 (67)	830 (60)	133 (1)	317 (2)
K (ppm)	757 (6)	754 (18)	1956 (42)	813 (24)	9325 (36)	6090 (173)	1129 (25)	2495 (107)
Si (ppm)	1555 (34)	1293 (247)	524 (109)	562 (8)	10043 (572)	10848 (1076)	667 (64)	3627 (559)
Na (ppm)	51 (0)	54 (2)	79 (4)	23 (1)	25 (0)	504 (24)	49 (1)	182 (7)
S (ppm)	68 (0)	73 (3)	107 (2)	69 (2)	386 (23)	465 (29)	78 (4)	180 (4)
Ti (ppm)	13 (1)	10 (1)	7 (1)	3 (1)	3 (0)	4 (3)	6 (0)	6 (1)

3 – Technical Progress (cont.)
(Field-to-fleet – NREL/PNNL/INL)

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Characterization of the liquid products from the hydrotreater.

	Oil Phase						Aqueous Phase			
	C	H	O	S	N	TAN	C	H	S	N
Feed	wt%	wt%	wt%	wt%	wt%	mg KOH/g	wt%	wt%	wt%	wt%
Clean Pine	87.15	12.52	1.08	0	0	0.018	0.19	11.92	0	0.06
Whole Pine	87.52	12.67	1.03	0	0	0.000	0.15	11.65	0	0.04
Tulip Poplar	87.73	12.37	1.05	0	0	0.000	0.14	10.98	0	0.00
Tulip Poplar (Repeat)	86.05	11.99	0.69	0	0	0.000	0.16	10.98	0	0.09
Hybrid Poplar	86.76	12.42	1.01	0	0	0.000	0.15	11.88	0	0.01
Switchgrass	87.30	12.94	0.80	0	0	0.743	0.48	10.71	0	0.42
Corn Stover	85.30	12.89	0.66	0	0	0.063	0.78	10.77	0	0.94
Blend 1	87.18	12.64	0.83	0	0	0.180	0.53	11.41	0	0.27
Blend 2	87.05	12.56	0.77	0	0	0.000	0.20	11.56	0	0.08

3 – Technical Progress (cont.)
(Field-to-fleet – NREL/PNNL/INL)

Inorganic analysis of the oil and aqueous phases.

Oil Phase	Al	Ca	K	Mg	Mn	Na	P	Si	S
Clean Pine	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	11.1	< 5.5
Whole Pine	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5
Tulip Poplar	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0
Hybrid Poplar	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5
Switchgrass	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	12.4	< 5.5	6.0	49.4
Corn Stover	4.4	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	26.0	< 4.0
Blend 1	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5	< 5.5
Blend 2	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0
Aqueous Phase	Al	Ca	K	Mg	Mn	Na	P	Si	S
Clean Pine	< 0.8	< 0.8	< 2.0	< 0.8	< 0.8	20	< 0.8	41	9.4
Whole Pine	< 0.8	< 0.8	< 2.0	< 0.8	< 0.8	16	< 0.8	42	43
Tulip Poplar	< 0.8	< 0.8	< 2.0	< 0.8	< 0.8	18	< 0.8	150	59
Hybrid Poplar	< 0.8	< 0.8	< 2.0	< 0.8	< 0.8	20	< 0.8	130	88
Switchgrass	< 0.8	< 0.8	2	< 0.8	< 0.8	15	< 0.8	24	180
Corn Stover	< 0.8	< 0.8	< 2.0	< 0.8	< 0.8	14	< 0.8	81	570
Blend 1	< 0.8	< 0.8	< 2.0	< 0.8	< 0.8	10	< 0.8	13	140
Blend 2	< 0.8	< 0.8	2	< 0.8	< 0.8	11	< 0.8	19	65