2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Thermochemical Feedstock Interface

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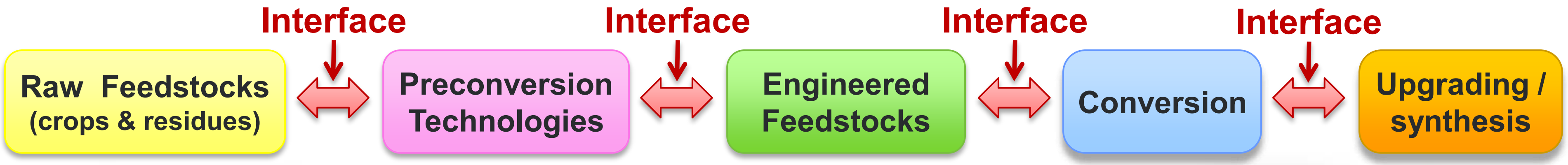
Goal Statement

Goals: (1). Develop models & tools to evaluate feedstock costs & quality for TC processes (pyrolysis, gasification, combustion). (2) Establish pathway(s) toward optimization and cost-reduction.

- Material specifications and rapid characterization tools are needed to facilitate effective material transfer from raw feedstocks to finished fuels
- Supports Thermochemical Conversion Pathway: “By 2017 Validate integrated conversion process for woody biomass to renewable-gasoline or -diesel via pyrolysis at pilot-scale”



Focus: Solve key challenges that require integration of Feedstock and Conversion Platforms

Project Quad Chart Overview

Timeline

- Start: October 2007
- End: September 2022

Budget

Total project funding: **$6,129K**

- DOE share: 100%

Funding in FY 2011-2013 ($1,000s)

	2011	2012	2013
INL	975 (150)	1950 (225)	2175 (450*)
NREL	145	800	500
PNNL	150	200	200

Total values shown; equipment in ()
* Intended to stock new facility

Barriers

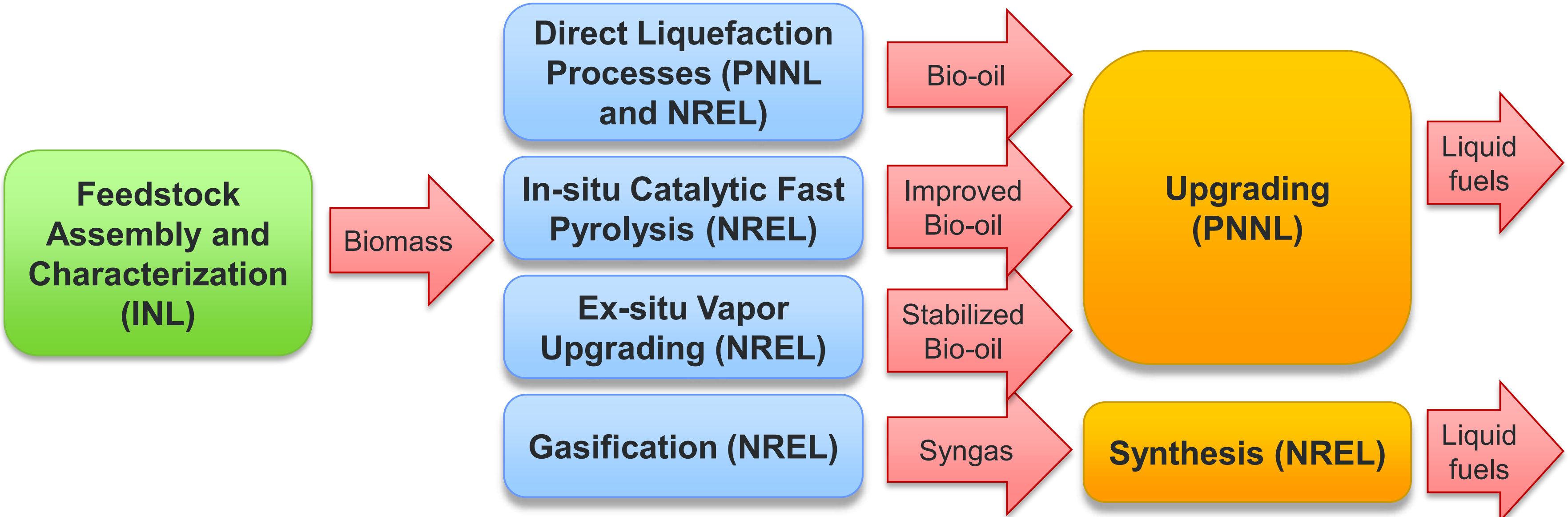
- Ft-A: Resource Availability & Cost
- Ft-G: Feedstock Quality and Monitoring
- Ft-K: Biomass Physical State Alteration
- Ft-M: Overall Integration and Scale-Up
- Tt-A: Feeding Dry Biomass
- Tt-C: Gasification of Biomass
- Tt-E: Pyrolyis of Biomass & Bio-Oil Stabilization
- Tt-K: Thermochemical Process Integration

Partners & Roles

- INL – Feedstock handling and assembly
- NREL – Oil generation and analysis
- PNNL – Oil generation, upgrading, and analysis
- WSU-IAREC/USDA – Agronomy & soil science
- NCSU/IBSS – TC conversion

Project Overview

1. Develop & define feedstock specifications (material performance)
   - Produce, characterize, & distribute feedstock, bio-oils, & bio-products
   - Techno-economic & life cycle analyses
2. Develop & deploy rapid analytical screening tools
   - For feedstocks: moisture, ash, calorimetry, thermogravimetry,
   - For vapors & oils: composition, similarities, & stability via MS & IR spectrometries (e.g. NIR, FT-IR, MBMS) & chromatographies (HPLC, GC, 2D-GC)
3. Interface (i.e. cross-cutting) sub-projects
   - Assess preconversion & conversion processes for benefits & costs to feedstock supply & conversion (solid, liquid, gas yields & qualities)



Feedstock Assembly and Characterization (INL)

Biomass

Direct Liquefaction Processes (PNNL and NREL)

In-situ Catalytic Fast Pyrolysis (NREL)

Ex-situ Vapor Upgrading (NREL)

Gasification (NREL)

Bio-oil

Improved Bio-oil

Stabilized Bio-oil

Syngas

Upgrading (PNNL)

Synthesis (NREL)

Liquid fuels

Liquid fuels

1 – Technical Approach (All)

- Overall Technical Approach:
  1. Produce, characterize, & share feedstocks & bio-oils (Task 1: "Specs")
  2. Assess preconversion processes for benefits & costs on feedstock supply & conversion (Tasks 1 & 3: "Specs" & "Sub-project")
  3. Assess impact of feedstock compositional characteristics on liquid, gas, and solid yield as well as oil quality (Task 1: "Specs")
  3. Develop methods for vapor and oil characterization (Task 1 & 2: "Specs" & "Screening")
  4. Rapid analytical screening tools: ash composition, FT-IR microscopy (Task 2: "Screening")
  5. Techno-economic analyses to optimize feed/conversion systems (Task 1: "Specs")
- Success Metrics
  - Predictive performance models for supply, preconversion, and conversion performance, including costs, for rapid determination of local least-cost pathways
  - Reduced costs for feedstocks & delivered fuels
    - Accomplished by optimizing preconversion operations and feedstock formulations to access full local supply of all low cost resources

1 – Approach (Managerial)

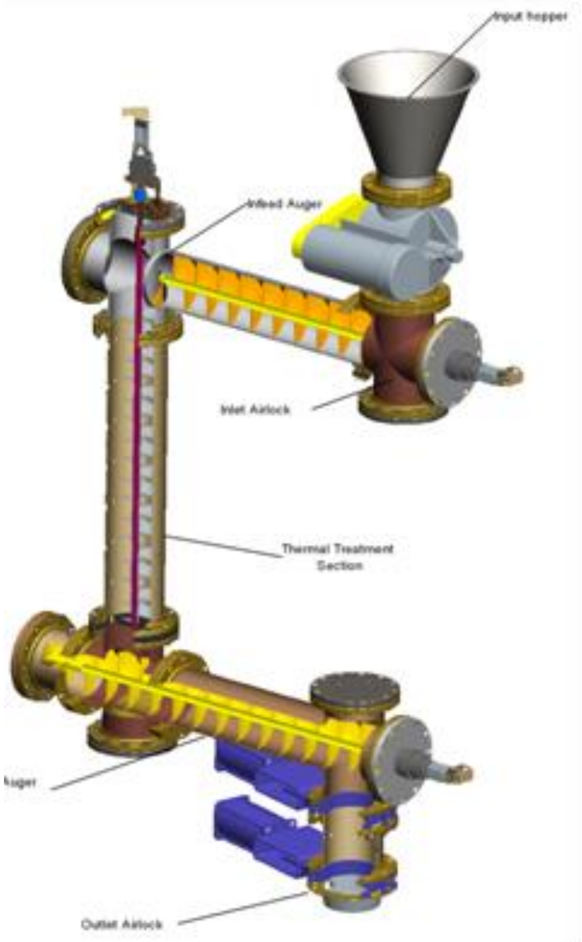
- Task Leadership: Plan, Prioritize, Coordinate, Review Progress:
  - Periodic inter-laboratory team meetings & visits
  - Weekly progress and coordination meetings
  - Quarterly BETO Review Meeting
- Leverage related BETO sponsored work (feedstock, pyrolysis, gasification, test equipment):
  - Share data with Feedstock Harvesting and Supply (data up to plant gate)
  - Standardize test procedures, including tests at representative conversion conditions
  - Data mining and assimilation of BETO program data into Biomass Resource Library
- Create & Follow Approved Project Management Plans
  - Regular milestones (1/quarter) and deliverables (annual reports)

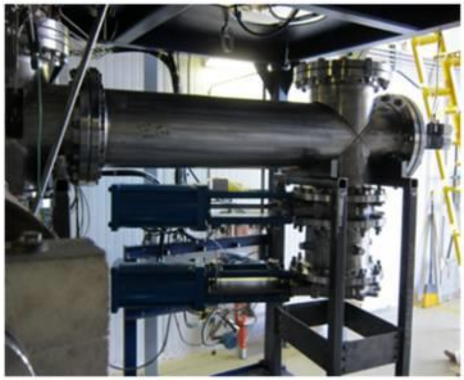
2 – Technical Progress (INL)

Preconversion Processes, 3.1.2.3 & 3.7.1.3

"Demonstrate interface of 4 grades of uniform format feedstock with conversion technology" *INL Milestone Report, 12/31/2012*

- Fabricated pilot-scale thermochemical preconversion system (20 kg/hr)
  - Temperature range: RT to 270ºC
  - Thermal oxidizer burns combustibles to recover energy to reinject into main reactor
  - Fixed gases (O2, CO, CO2, H2, CH4, & Total hydrocarbons)
  - Volatile gases (captured in Tedlar bags)
  - Semi-volatile gases (captured in IPA impinger train)
  - Complements batch-scale thermochemical preconversion system (6 kg/batch)





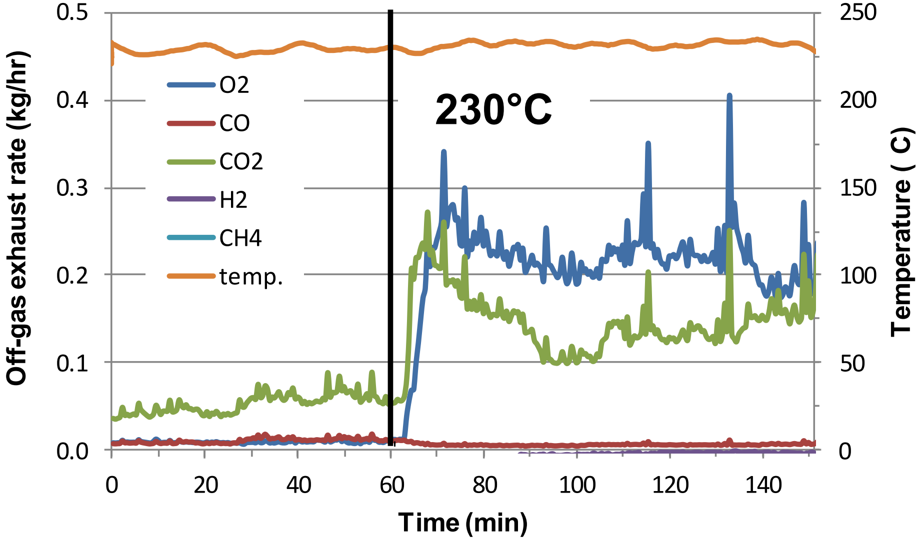
Continuous-feed thermochemical preconversion system

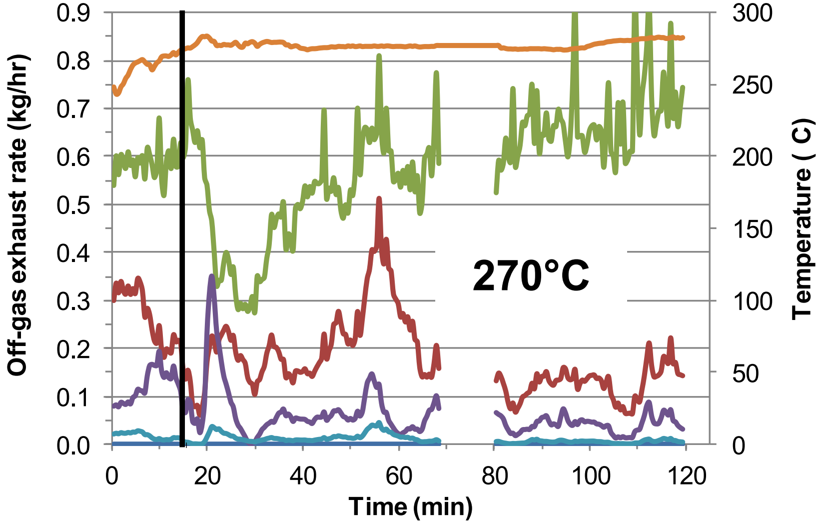
2 – Technical Progress (INL)

Preconversion Processes, , 3.1.2.3 & 3.7.1.3

- Pine chips thermally treated at 120, 180, 230, 270ºC

- Exhaust-gas recycled through thermal oxidizer to recycle heat in off-gases
- Exhaust gases monitored real time for O_2, CO, CO_2, H_2, CH_4





2 – Technical Progress (INL)

Preconversion Processes, , 3.1.2.3 & 3.7.1.3

Fuel properties of material treated in fixed-bed (FB) and continuous-feed (CF) systems

Proximate properties and heat content of pine chips (%, db) thermally treated in the fixed bed (FB), continuous-feed (CF) and thermogravimetric analysis (TGA) systems.

Treatment	MC(%, wb)	VM	Ash	FC	HHV (MJ/kg)
120°C	1.55 (0.02)[a]	79.1 (0.13)	1.82 (0.21)	17.8 (0.31)	18.4 (0.13)
180°C-FB	1.97 (0.02)	78.9 (0.21)	0.48 (0.01)	18.6 (0.21)	19.7(0.00)
180°C-CF	0.42 (0.03)	79.1 (0.12)	1.73 (0.14)	18.4 (0.23)	19.5 (0.02)
230°C-FB	2.39 (0.02)	76.9 (0.21)	0.49 (0.01)	20.2 (0.16)	20.1 (-)
230°C-CF	0.51 (0.02)	77.3 (0.39)	1.76 (0.08)	20.5 (0.38)	20.1 (0.01)
270°C-FB	3.24 (0.03)	68.6 (0.48)	0.57 (0.02)	27.6 (0.47)	22.3 (0.02)
270°C-CF	0.36 (0.03)	72.4 (0.19)	2.03 (0.15)	24.8 (0.26)	21.8 (0.08)
270°C-TGA	4.21 (0.19)	56.1 (2.07)	1.00 (0.07)	38.7 (1.94)	23.0 (0.17)

Elemental properties of thermally treated pine (%, db). Sulfur content of all samples is negligible.

Treatment	N	C	H	O[b]
120°C	0.18 (0.01)[a]	48.6 (0.34)	6.27 (0.05)	44.9 (0.38)
180°C-FB	0.52 (0.05)	50.5 (0.16)	6.41 (1.39)	42.1 (01.36)
180°C-CF	0.20 (0.02)	49.2 (0.08)	6.17 (0.10)	44.5 (0.10)
230°C-FB	0.47 (0.01)	51.8 (0.06)	6.19 (0.41)	41.1 (0.44)
230°C-CF	0.20 (0.02)	51.4 (0.09)	6.03 (0.04)	42.3 (0.10)
270°C-FB	0.50 (0.05)	56.2 (0.31)	6.25 (0.13)	36.5 (0.16)
270°C-CF	0.23 (0.00)	55.0 (0.09)	5.77 (0.03)	39.0 (0.07)
270°C-TGA	0.55 (0.02)	61.2 (0.12)	5.13 (0.52)	33.1 (0.40)

As temperature increases:

- FC, C, & HHV increase
- O decreases

2 – Technical Progress (INL)

Specific grinding energy & rate, 3.1.2.3

(a) Grinder power consumption

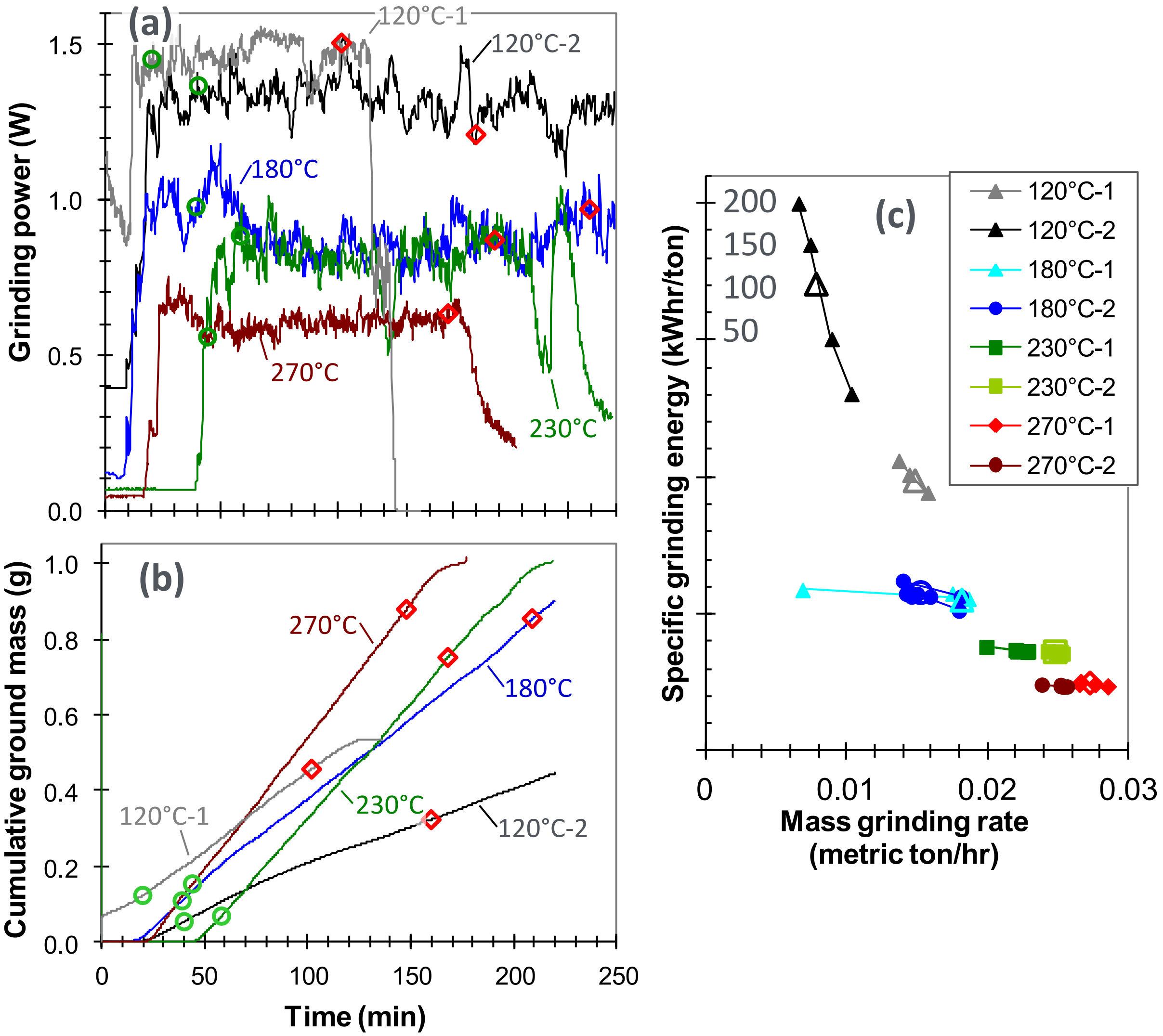
(b) Cumulative ground material mass for thermally treated pine chips as functions of time.

(c) Specific grinding energy in kWhr/metric ton as functions of the material grinding rate.

- Small solid symbols were calculated over short time periods of approximately 25 seconds over which the material grinding rate appeared constant.
- Large hollow symbols were calculated as the average over longer time intervals as marked in (a).
- Green circles and red diamonds represent the start and end, respectively, of the long time intervals used to calculate the large hollow symbols in (b).

As temperature increases:

- Grinding rate increases
- Grinding energy decreases



2 – Technical Progress (PNNL)

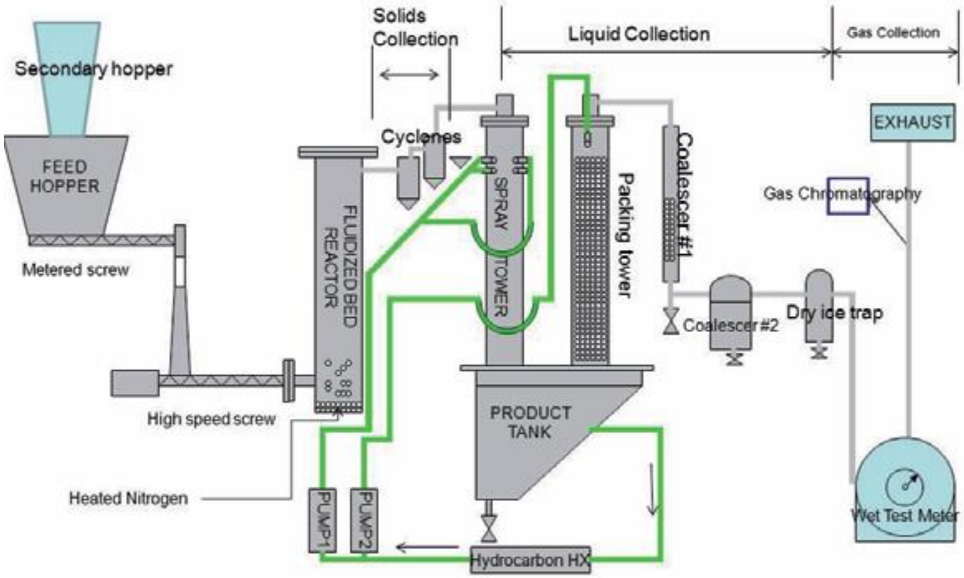
Pyrolysis, 3.1.2.3, 3.1.2.1

Yields and elemental analysis of bio-oil fractions and aqueous trap

Liquid Product Split between Oil and aq.	Bio-oil composite							Aqueous Trap			
	wt% as bio-oil	Dry Elemental anal.				H_2O (%)	TAN	wt% as aq.	Elemental Carbon	H_2O	TAN
		C (%)	H (%)	N (%)	O (%)						
Pine Flour (ref.)	87	53	7.0	0.1	39	14	80	13%	13	76%	47
120°C-CF	93	57	6.2	0.1	37	9.8%	78	7%	11	74%	37
180°C-CF	91	57	6.0	0.1	37	11%	72	9%	11	77%	35
230°C-CF	92	58	6.4	0.0	36	10%	72	8%	10	77%	39
270°C-CF	92	58	6.6	0.1	35	9.8%	72	8%	NA	NA	NA

CF: Continuous feed; NA: Not applicable; TAN: Total acid number

- **No strong impacts as *T* increases**
- **Minor impacts:**
    - Liquid yield decreased 1%
    - O% in bio-oil decreased 2%
    - Acid number decreased



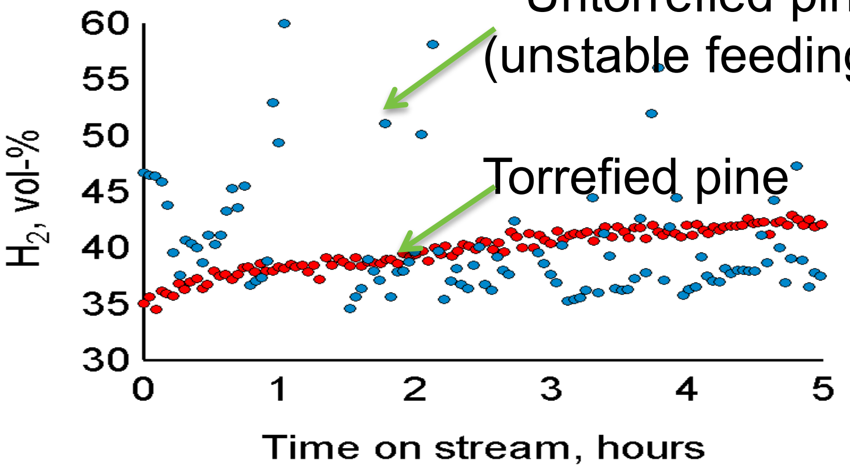
Fluid bed fast pyrolysis system (PNNL)

2 – Technical Progress (NREL)

Gasification, 3.1.2.2

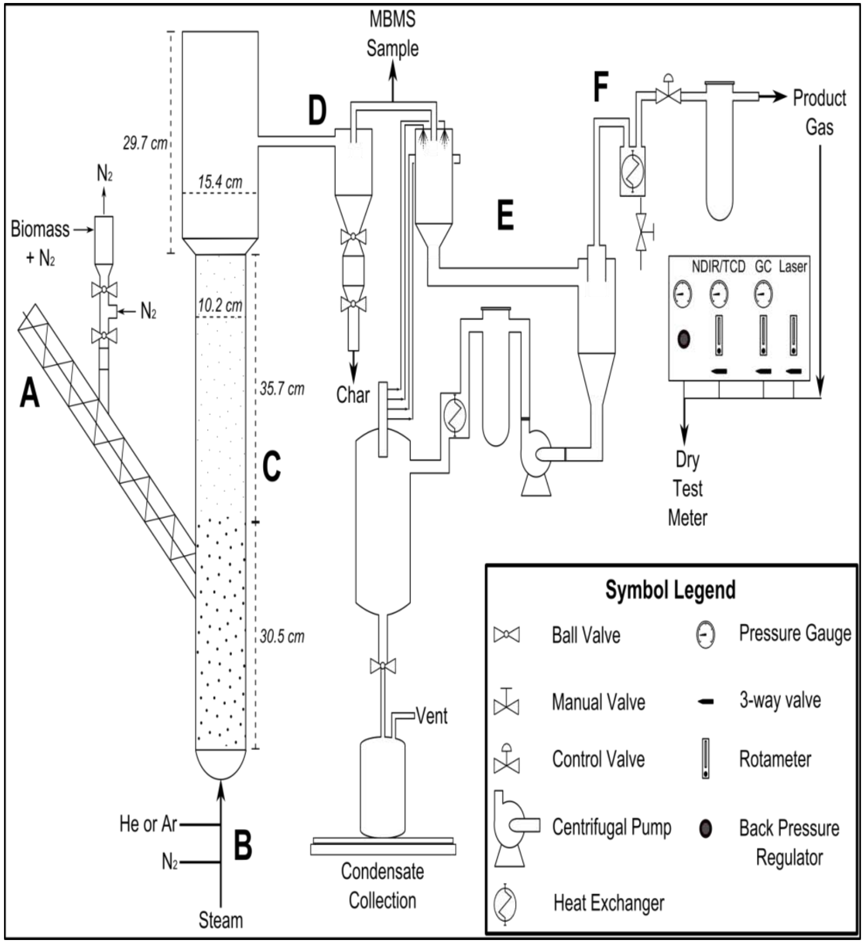
Gasification of Thermally Treated Feedstocks

- Whole pine, clean pine (debarked), oak, switchgrass, torrefied whole and clean pine
- Conditions: 800C, 0.6 kg/h biomass, steam:biomass=1
- On-line NDIR, GC, MBMS (tars), diode laser spectrometer (H_2S, NH_3)



Untorrefied pine (unstable feeding)

Torrefied pine



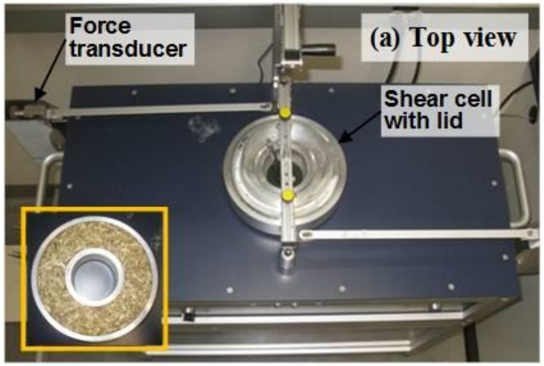
4” fluid bed gasifier

2 – Technical Progress (INL)

“Flowability”, 3.1.2.3

“Flowability” via Schulze ring shear tester

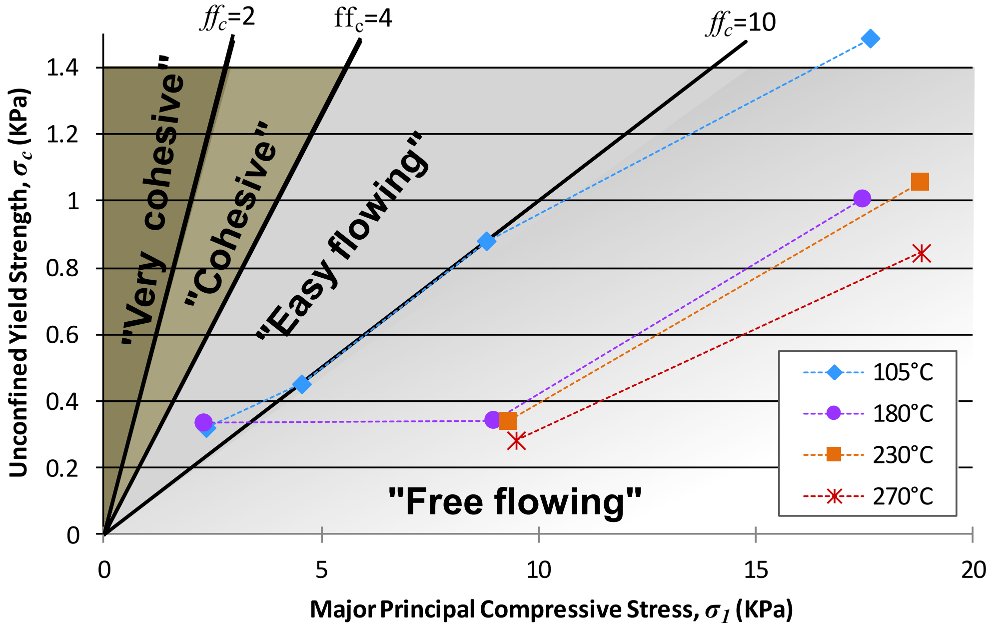
- Tendency of bulk solid to flow increases as compressive stress increases relative to material’s shear strength (σ_1 / σ_c = flowability, ff_c)
- Cases in which ff_c > 10 are generally considered ‘free flowing,’ although flow problems can still occur.



Schulze ring shear tester

- Additional hopper feeding tests indicate that flow behavior of thermally treated material is similar to cohesionless dry sand

- Thermal treatment greatly increases flowability
  - Treatment at T >180°C greatly improves flow properties



Measured unconfined yield (shear) strength, σ_c, as a function of major principal compressive stress, σ_1, for pine chips thermally treated at 105, 180, 230, and 270C.

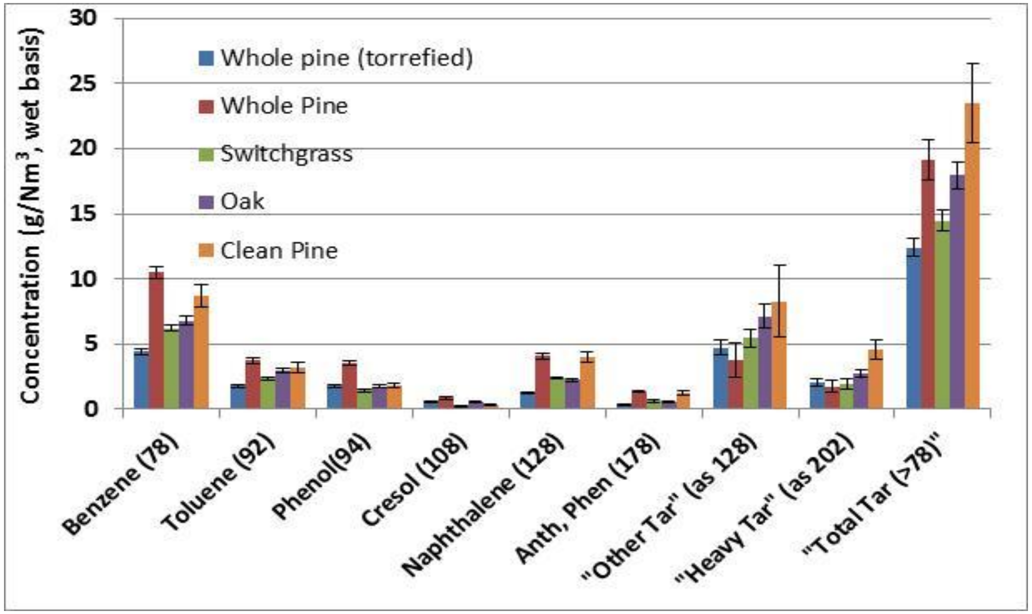
2 – Technical Progress (NREL)

Gasification, 3.1.2.2

Gasification of Thermally Treated Feedstocks (cont.)

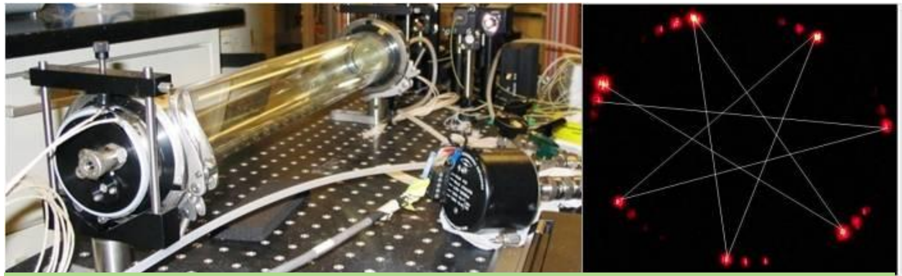
With torrefied pine:

- No significant change in bulk syngas composition
- Improved feeding
- Lowered selectivity to tar (as % of feed carbon)



Diode laser spectrometer results:

Feedstock	H_2S (ppm)	NH_3 (ppm)
Oak	< 2	NA
Clean Pine	2 ± 2	69 ± 2
Whole Pine	12 ± 3	<2
Switch Grass	134 ± 22	116 ± 8

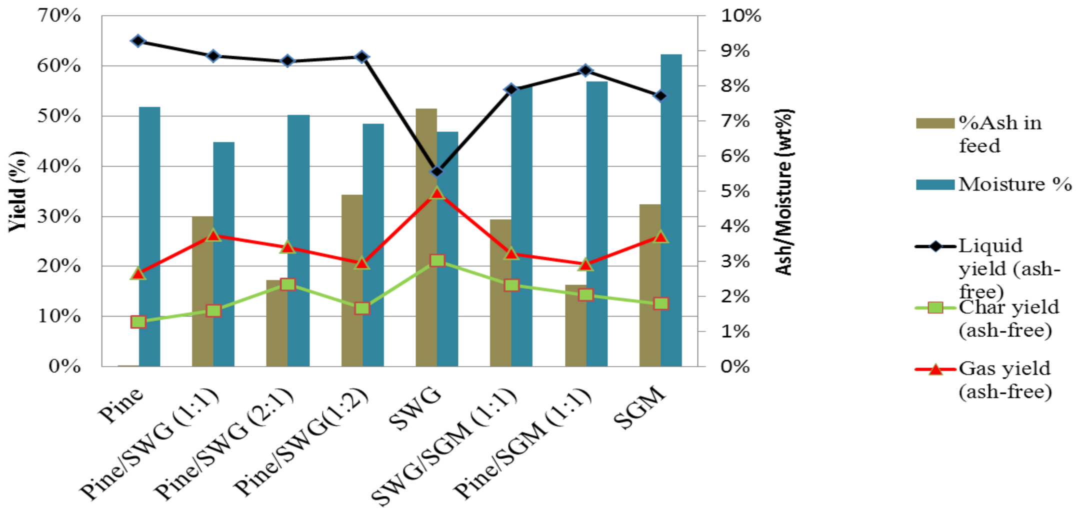


Herriott cell (left) and multipass pattern observed on 2” mirror using 660 nm alignment laser (right). Effective pathlength ~ 49 meters.

2 – Technical Progress (PNNL)

Pyrolysis, 3.1.2.1

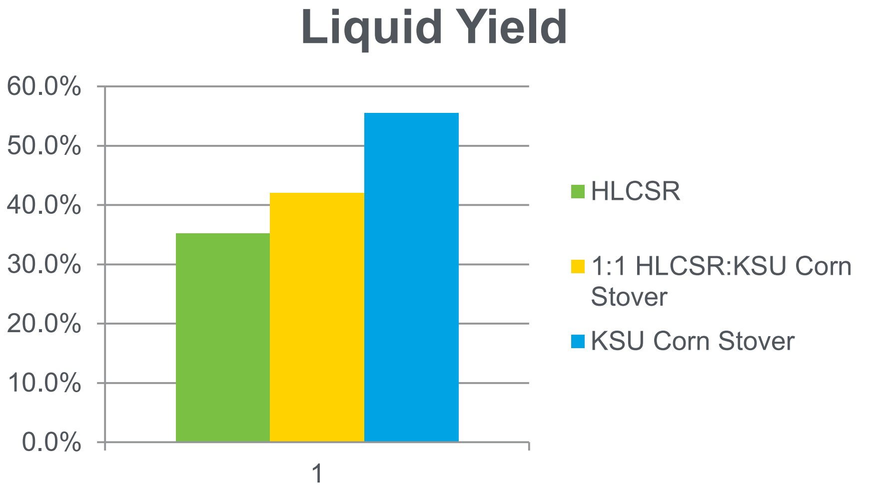
- In conjunction with Core Pyrolysis Program, pine, switchgrass, and sorghum blended at various ratios and processed via fast pyrolysis at identical conditions
  - Decreasing ash content trends with increasing liquid yield
  - Large variations despite constant polymer (organic) content
- Data was used to generate a target "uniform" specification for ash and extractives content of blended feedstocks
  - 1:1 Pine:switchgrass chosen based on large differences between composition and processing behavior

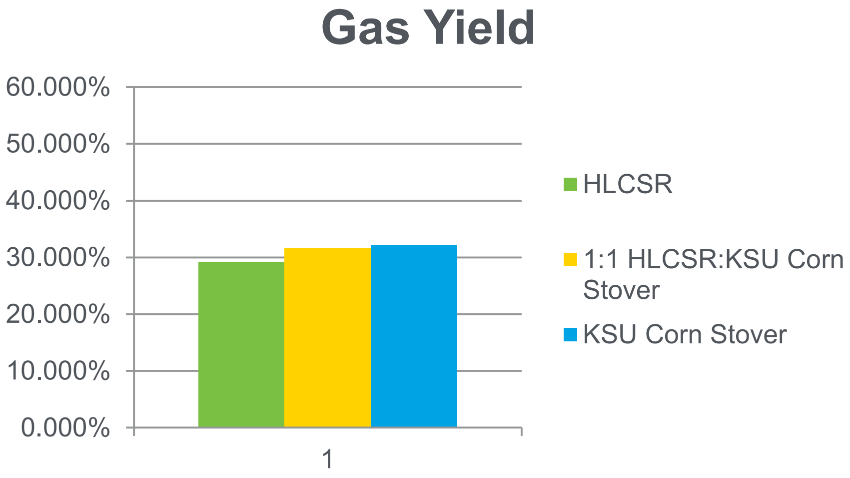


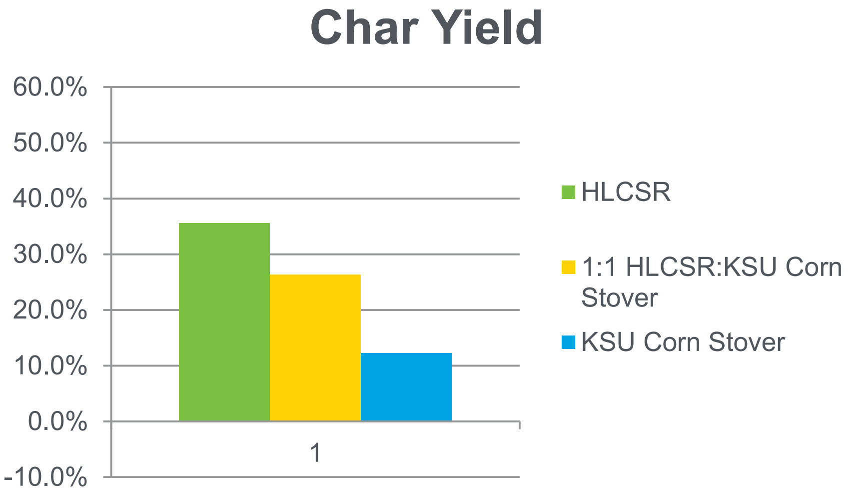
2 – Technical Progress (PNNL)

Pyrolysis, 3.1.2.1

- Residue from SSF digestion of corn stover acquired from NREL, pelletized by INL
  - High lignin (37%) and ash (16%) falls outside traditional lignocellulosic feedstock levels
- Pyrolysis experiments conducted with pure SSF residue, 1:1 SSF residue:corn stover, and pure corn stover



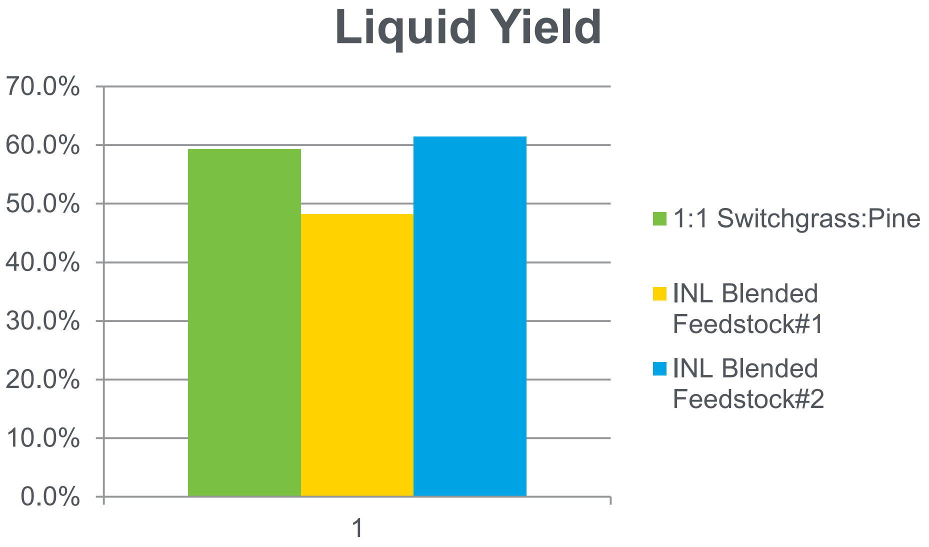


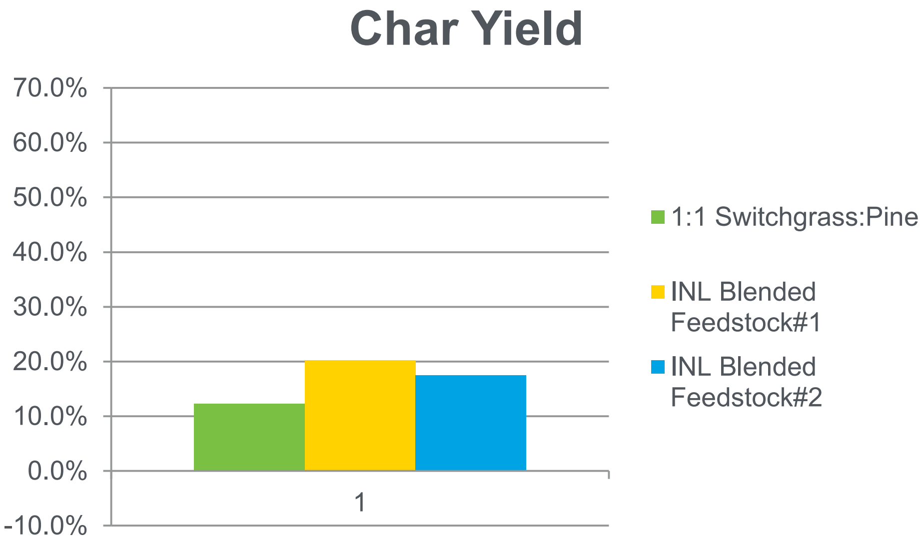


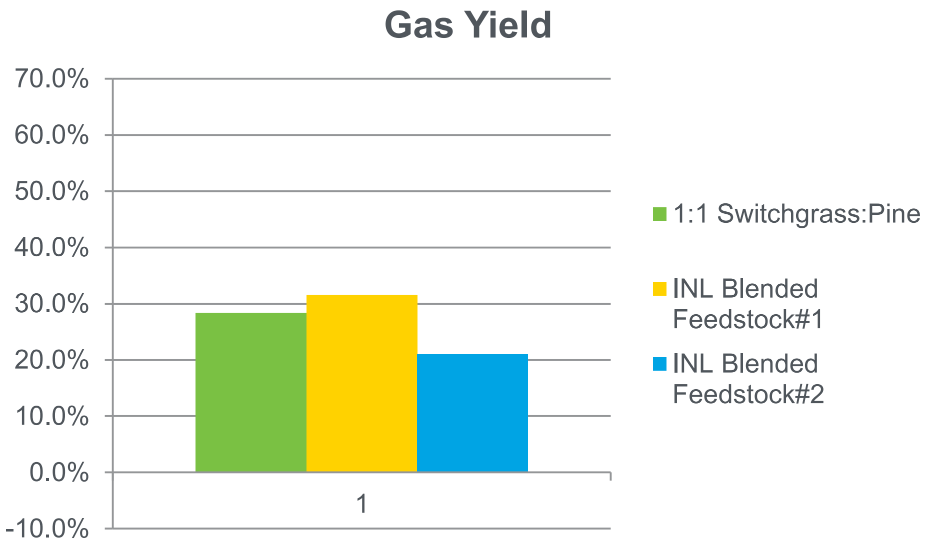
2 – Technical Progress (PNNL)

Pyrolysis, 3.1.2.1

- Feedstocks blended by INL to match ash and/or extractives content of 1:1 Pine:Switchgrass
  - Blend 1 matches extractives
  - Blend 2 matches ash
  - Blend 3 matches both
- Fast pyrolysis experiments conducted

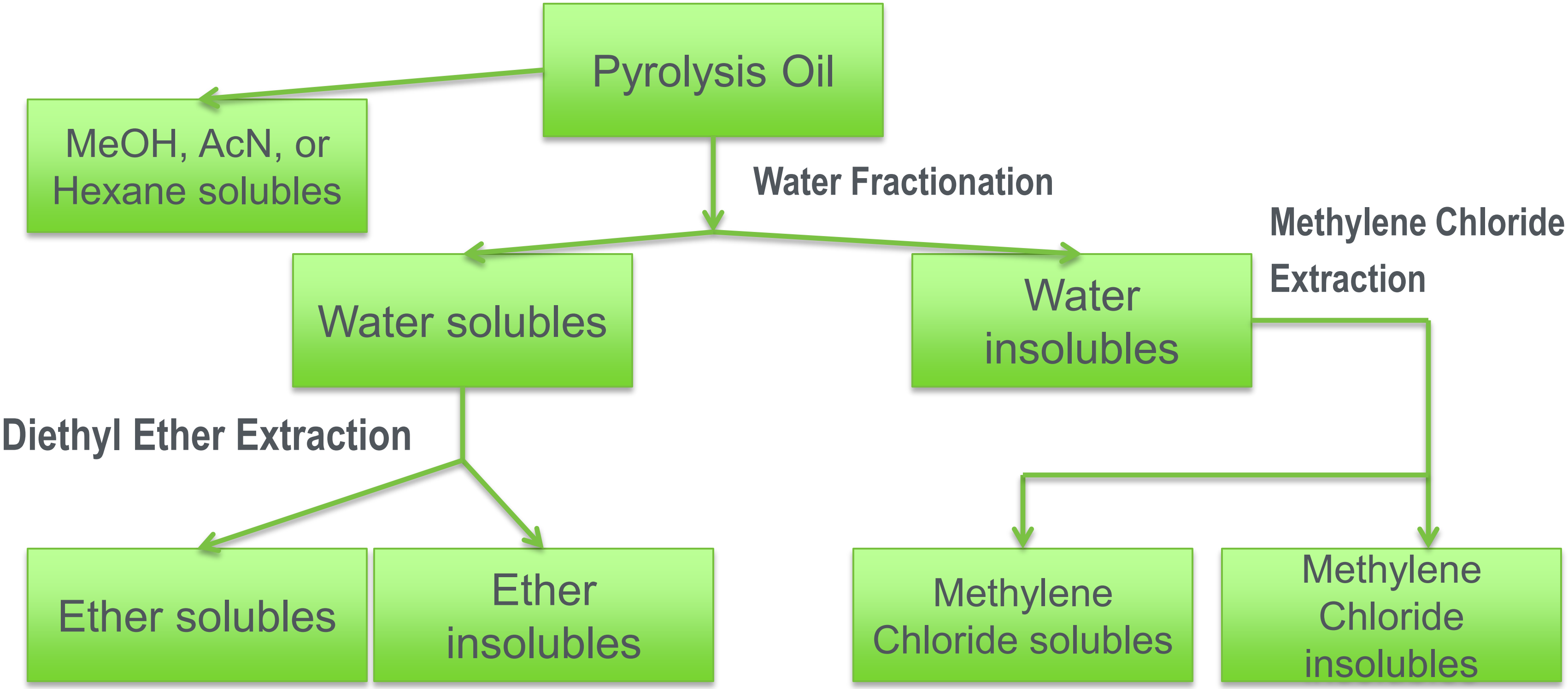






2 – Technical Progress (PNNL)

Pyrolysis, 3.1.2.1



Pyrolysis Oil

MeOH, AcN, or Hexane solubles

Water Fractionation

Water solubles

Water insolubles

Methylene Chloride Extraction

Diethyl Ether Extraction

Ether solubles

Ether insolubles

Methylene Chloride solubles

Methylene Chloride insolubles

- VTT fractionation scheme[1] used to simplify analysis of bio-oil
- Major compounds in each fraction identified via 2D GCxGC
- GC-FID calibrated with standards and used for quantification of identified species

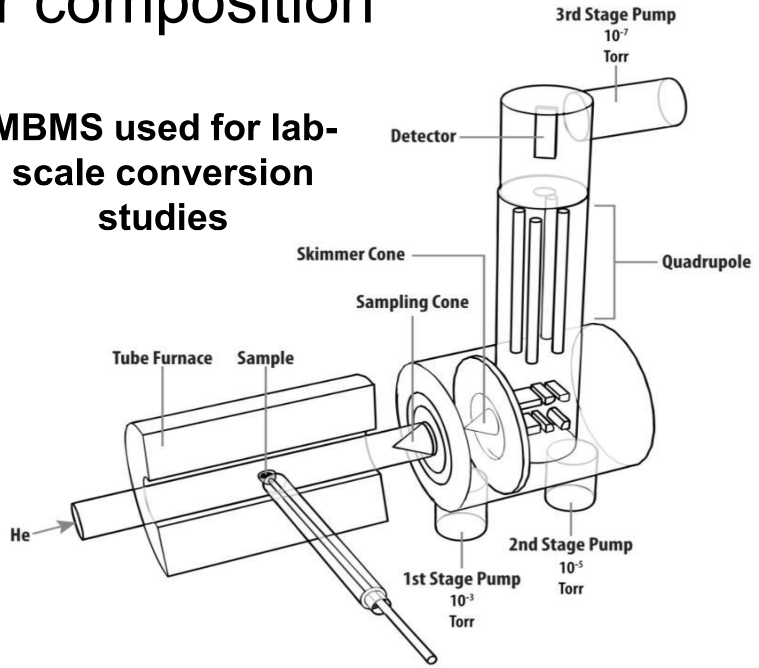
[1] Oasmaa, *Energy & Fuels*, **2003**, *17*

2 – Technical Progress (NREL)

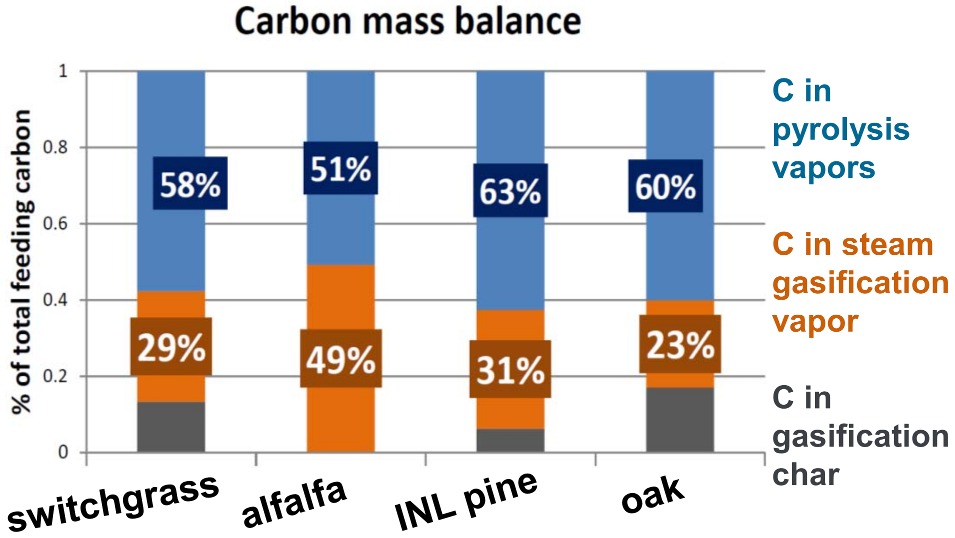
Pyrolysis vapor, 3.1.2.2

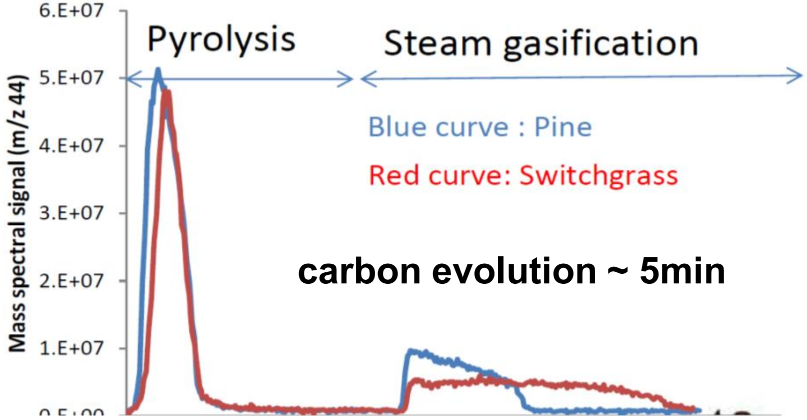
Feedstocks effects on pyrolysis vapor composition

- Collaboration with North Carolina State U, investigating feedstock effects on pyrolysis vapor composition and fate of carbon
- Developing rapid screening methods for:
  - Devolatilization rates
  - Volatile yields
  - Residual char reactivity



MBMS used for lab-scale conversion studies





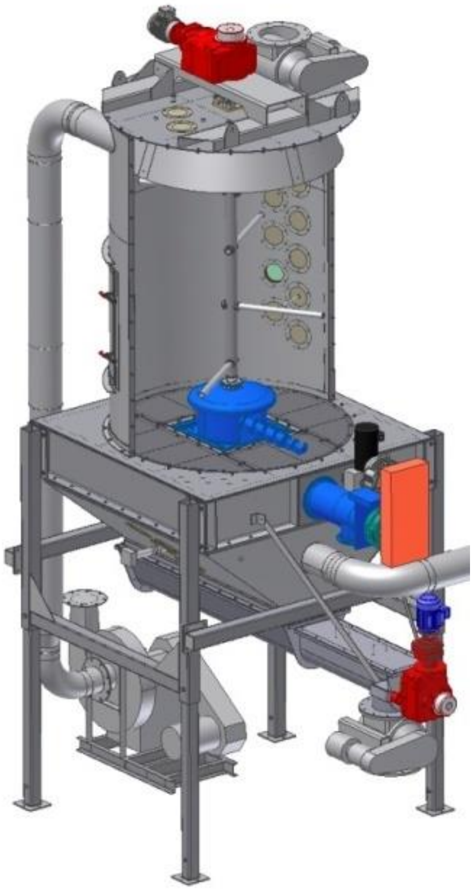
carbon evolution ~ 5min

2 – Technical Progress (INL)

Waste-heat drying 3.1.2.3

"Evaluate residence time drying efficiency to take advantage of low quality waste heat at biorefinery", *INL Milestone Report, 03/31/2012*

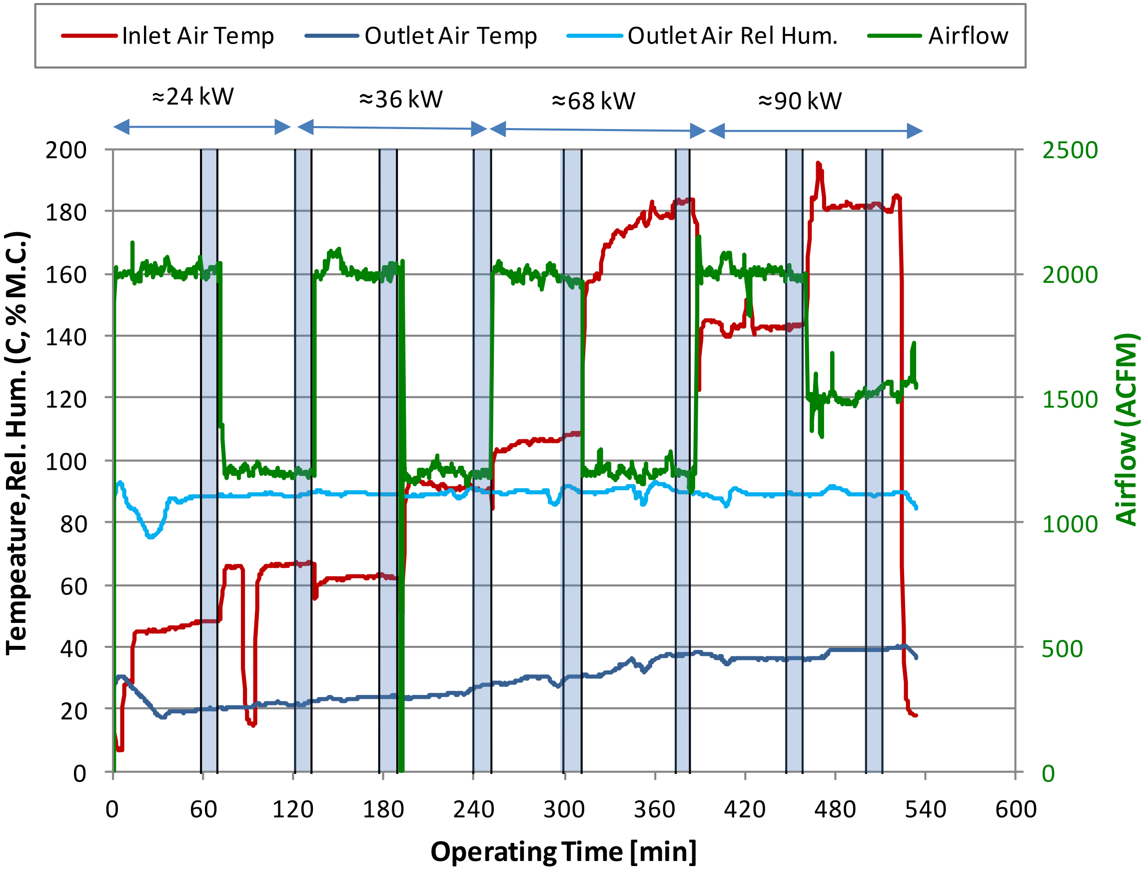
- Fabricated pilot-scale residence dryer
  - Material flows down 2 m diameter hopper
  - Heated air flows up through bed (≈1.3 m deep)
  - Rotating reclaimer feeds dry material from bottom
- Performed experiments to verify drying effectiveness
  - Inlet air temperature range: 50-180ºC
  - Air flow range: 36-60 m^3/min
  - 0.7 kg H_2O removed per KJ supplied heat using inlet air at 60ºC
  - As inlet air temperature rises to 120ºC, efficiency drops only slightly while capacity nearly doubles
  - Validated that waste heat from 2009 NREL Gasification Design is sufficient alone to achieve target drying, thus reducing drying costs



Schematic of residence dryer

2 – Technical Progress (INL)

Waste-heat drying, 3.1.2.3



Pulp Grade Wood Chips

Actual residence dryer

Experiments conducted holding 'steady-state' for 1 hr and 6 hrs yielded similar results

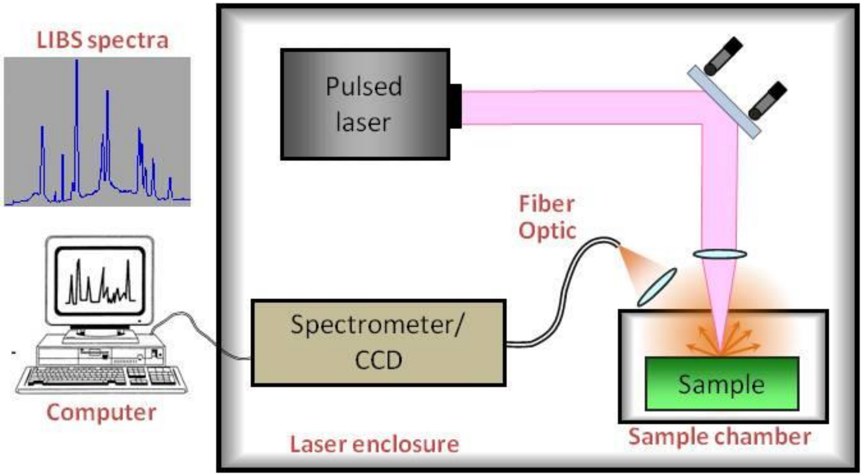
	Heat input	Inlet air temp	Airflow	Outlet air temp	Outlet air RH	Water Removed
	kW	ºC	ACFM	Deg C	%	kg/min
1 hr	0.97	62.5	57	23.9	89.0	0.72
6 hr	0.97	63.4	57	22.8	86.7	0.70

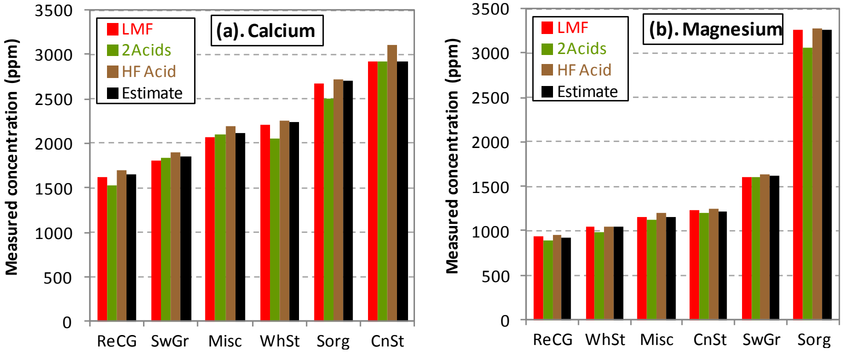
2 – Technical Progress (INL3.1.2.3)

Rapid Screening: LIBS, 3.1.2.3, 3.7.1.3

"Screening Methods for Ash Composition Using Laser Breakdown Spectroscopy (**LIBS**)" *INL Milestone Report, 9/30/2012*

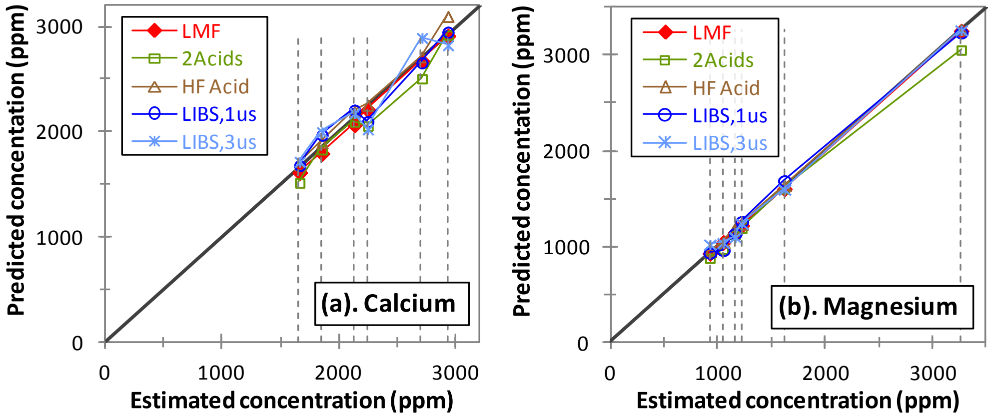
- Advantages
  - Rapid analysis with little sample prep
  - Configurable as field-portable system
- Challenges
  - Material differences can require extensive calibrations
  - Material heterogeneity





Calibration data for 6 feedstocks using lithium metaborate fusion method, and nitric and refluxing perchloric (2 acid) and HF acid digestions with ICP-MS

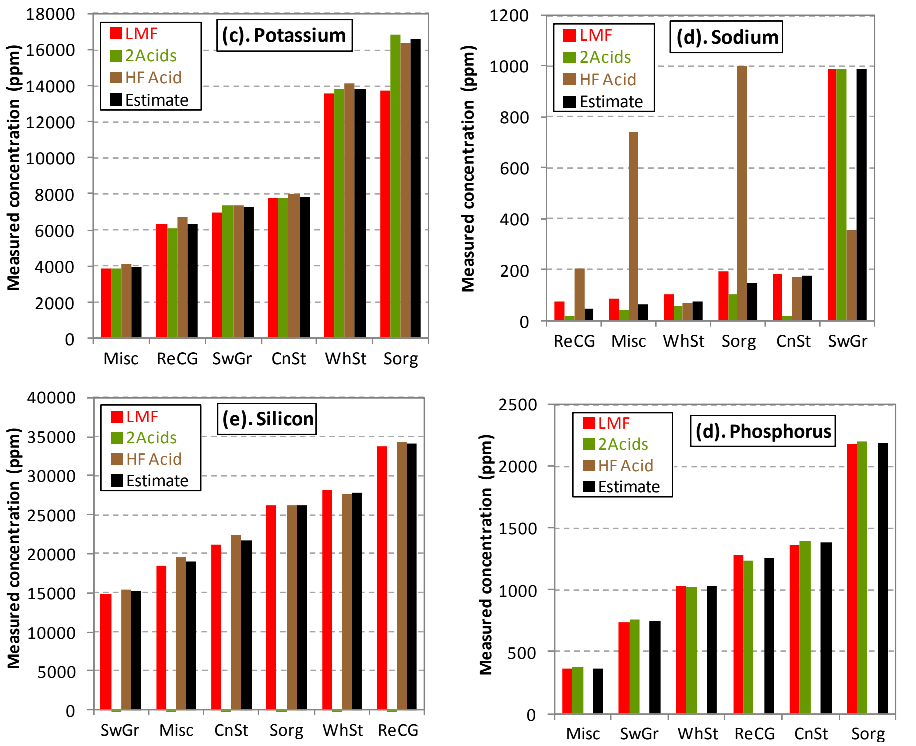
LIBS demonstrated good agreement for feedstocks tested



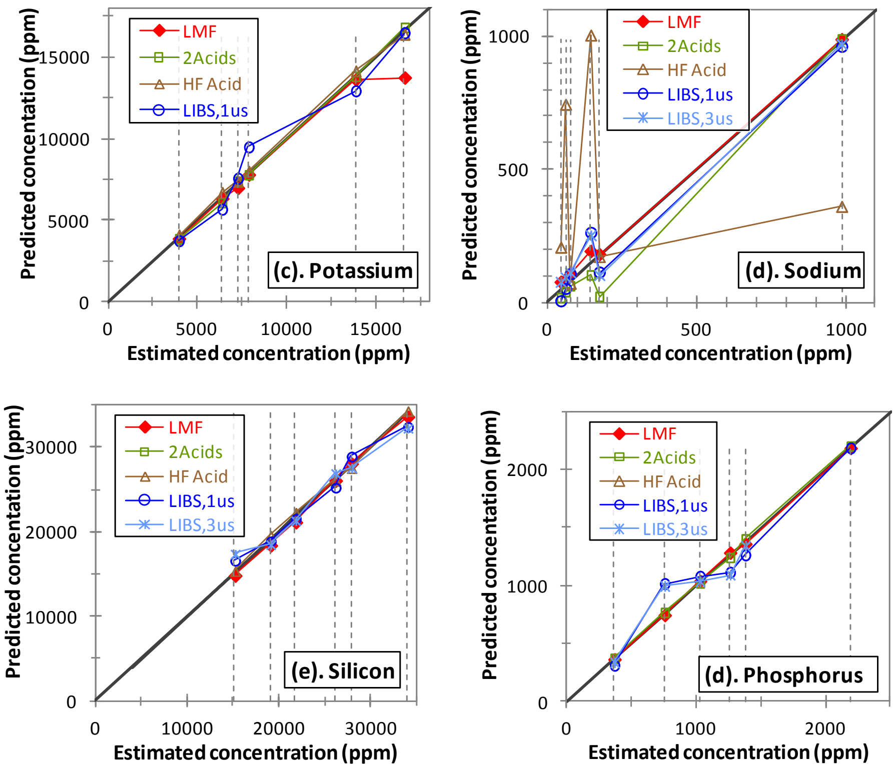
Comparison of calibration data with LIBS predictions for calcium and magnesium

2 – Technical Progress (INL3.1.2.3)

Rapid Screening: LIBS, 3.1.2.3, 3.7.1.3



Calibration data for 6 feedstocks using lithium metaborate fusion method, and nitric and refluxing perchloric (2 acid) and HF acid digestions with ICP-MS

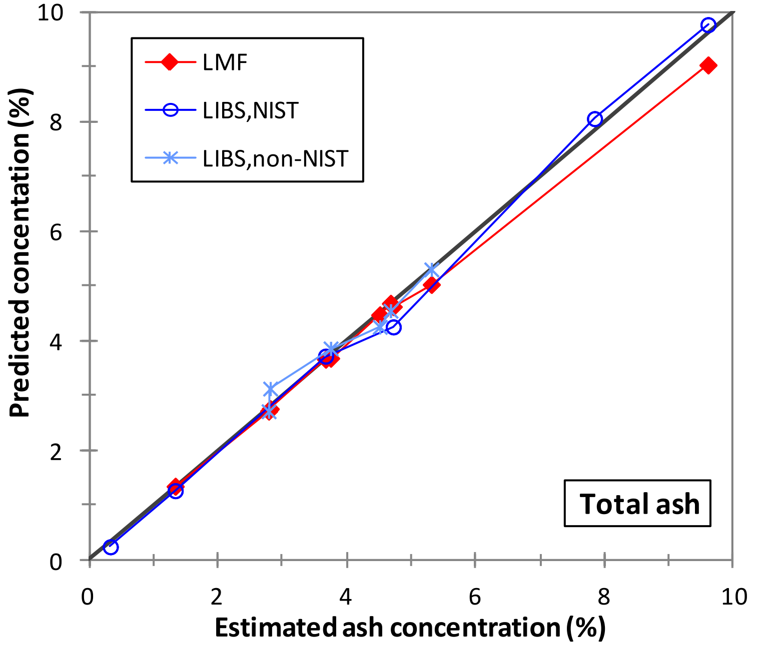


Comparison of calibration data with LIBS predictions

LIBS demonstrated good agreement for K, Na, Si & P

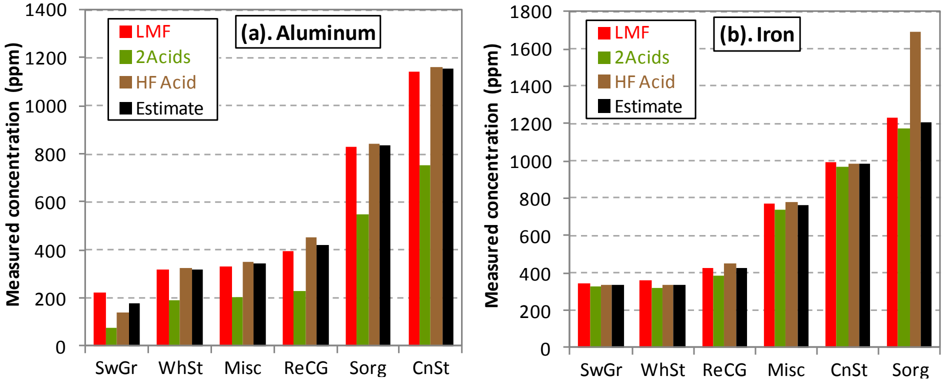
2 – Technical Progress (INL3.1.2.3)

Rapid Screening: LIBS, 3.1.2.3, 3.7.1.3

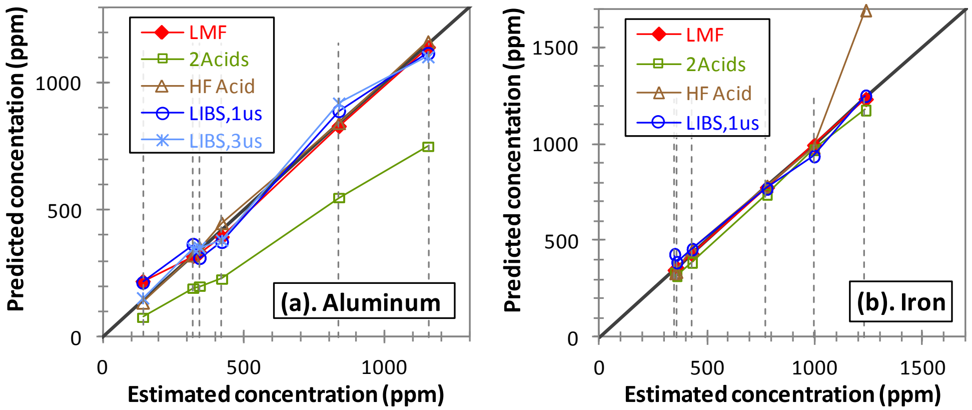


Concentrations of total ash (calculated as sum of Al, Ca, Fe, Mg, Mn, P, K, Na and Si) 6 NIST reference materials and 6 non-NIST samples. Solid black line indicateds best estimated value (NIST value for NIST samples).

LIBS appears to be the most reliable method for ash % by components, followed by lithium metaborate fusion (LMF) method



Calibration data for 6 feedstocks using lithium metaborate fusion method, and nitric and refluxing perchloric (2 acid) and HF acid digestions with ICP-MS



Comparison of calibration data with LIBS predictions for alumunim and iron

2 – Technical Progress (INL3.1.2.3)

Fourier Transform Infrared (FTIR) Microscopy, 3.1.2.3, 3.7.1.3.

“Screening methods for feedstock quality and micro/macro-scale variability using FT-IR microscopy” *INL Milestone Report, 12/31/2013 (in progress)*

Capability

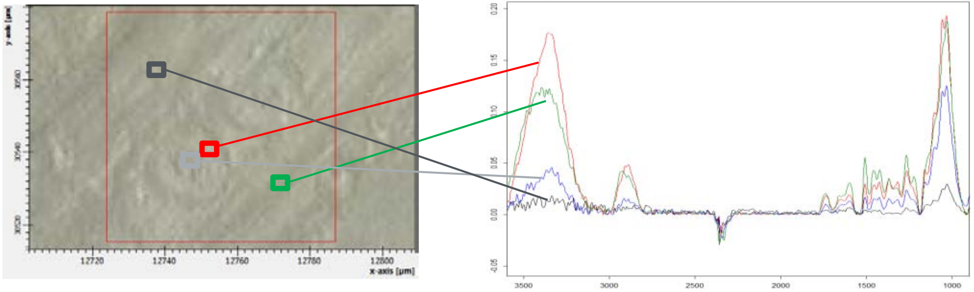
- Capture FTIR spectra from128x128 pixel detector (focal plane array) in seconds to build micron-scale hyperspectral ‘maps’
- Potentially track spatially resolved physiochemical changes at cell level real time during thermochemical processes

Progress

- Methodologies developed to analyze biomass samples using reflectance, transmission, & total attenuated reflectance (ATR)
- Pine and corn stover samples
- Analyzed qualitatively
- Calibration models for quantitative models are being built

Video image

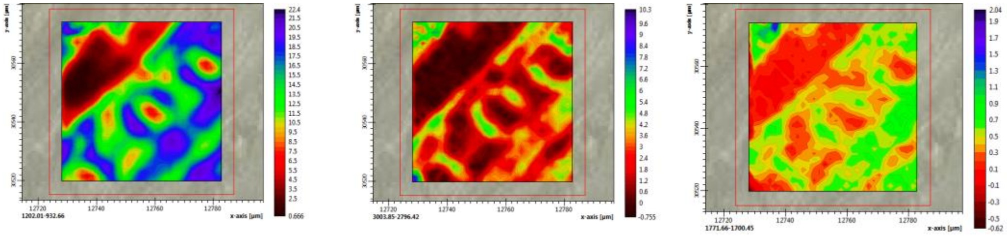
Representative spectra



Cellulose (≈1200-933cm^{-1})

CH stretching (≈ 3003-2795cm^{-1})

Ester carbonyl (≈1770-1700cm^{-1})



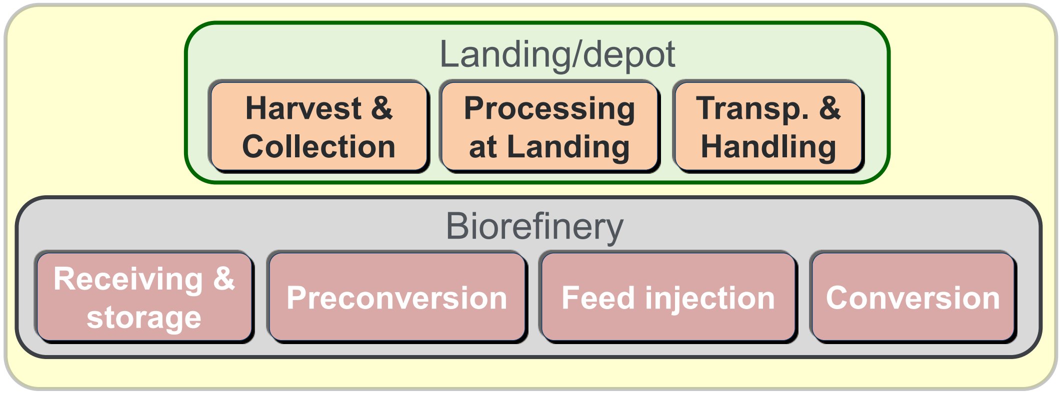
Images of a pine chip dried at 105°C.

2 – Technical Progress (INL)

Techno-economic Analysis, 3.1.2.3

"Validate the cost of feedstock at $61.57/dry US ton for the production of ethanol via thermochemical conversion ($46.37 w/o grower payment)", *INL Milestone Report, 12/31/2012*

2012 Conventional Woody Design (2" wood chips at 10% MC, <1% ash)



Plant size[a]	800,000 DM/yr
Harvested land area	40,800 acres/yr
Feedstock draw radius[b]	5.8 miles
Landing to biorefinery distance	50 miles

[a] U.S. short ton = 2,000 lb.

[b] Assume an equal distance distribution of acres throughout the draw radius.

Primary changes from 2009 Woody Design

- **New track-type feller buncher**
- **Field drying from 50% to 40% MC**
- **Increased chipper efficiency due to pneumatic assist (w/ drying to 35% MC)**
- **Drying during storage to 30% MC**
- **Waste heat drying to 10%**

2 – Technical Progress (INL)

Techno-economic Analysis, 3.1.2.3

Gasification Cost Assessment from Harvest to Conversion Reactor Inlet	Metric	**2009**	***2012***	% Decrease Per Item / Total
	Year $ Basis	2007	2007	-
Total Feedstock Logistics (harvest to conversion reactor inlet, grower payment not included)	*$/DM ton*	***$71.05***	***$46.37***	35 / 35
	$/gall (ETOH)	$1.00	$0.65	35 / 35
Harvest and Collection				
Total Cost Contribution	*$/DM ton*	$22.30	$18.75	16 / 5
Capital Cost Contribution	*$/DM ton*	$6.40	$5.60	13 / 1
Operating Cost Contribution	*$/DM ton*	$15.90	$13.15	17 / 4
Depot Preprocessing				
Total Cost Contribution	*$/DM ton*	$13.60	$11.42	16 / 3
Capital Cost Contribution	*$/DM ton*	$3.50	$4.20	-20 / -1
Operating Cost Contribution	*$/DM ton*	$10.10	$7.22	29 / 4
Transportation and Handling				
Total Cost Contribution	*$/DM ton*	$12.50	$8.95	28 / 5
Capital Cost Contribution	*$/DM ton*	$4.10	$2.95	28 / 2
Operating Cost Contribution	*$/DM ton*	$8.40	$6.00	29 / 3
Plant Receiving, Storage and Queuing, and In-Feed Preprocessing				
Total Cost Contribution	*$/DM ton*	$22.65	$7.25	68 / 22
Capital Cost Contribution	*$/DM ton*	$5.45	$2.10	61 / 5
Operating Cost Contribution	*$/DM ton*	$17.20	$5.15	70 / 17

Primary sources of cost savings

- **Higher efficiency of new track-type feller buncher**
- **Transportation costs due to field drying**
- **Use of waste heat at biorefinery**

3 – Relevance (INL, NREL, PNNL)

Feedstock Supply (FS)

1. Identify sustainable, high-quality feedstock and quantify risk
2. Assess effects across full supply chain
3. Establish baselines and target for improving sustainability
4. Develop best practices

Conversion (C)

1. Lower costs/improve quality of intermediates
2. Enable high performance separations technologies
3. Improve catalyst performance – cleanup/conditioning & fuel synthesis
4. Maximize carbon utilization
5. Develop best practices
6. Optimize reactor performance
7. Define & validate technology
8. Assess progress

Deployment (D)

1. Support advanced biofuels compatibility testing

- Techno-economic analyses to optimize feed/conversion systems (FS1-2; C1,8)
- Rapid analytical screening (FS3-4; C1-5)
- Produce, characterize, & distribute shared feedstock materials (FS2-4; C5-7)
- Assess preconversion processes for benefits & costs to feedstock supply & conversion (FS2-4; C1-7)
- Bench-scale bio-oil production (C6-8)
- Develop methods for vapor and oil characterization (C6-8)
- Assess impact of feedstock compositional characteristics on liquid, gas, and solid yield as well as oil quality (FS3-4; C3-7)

Results:

- Predictive models for supply, preprocessing,and conversion performance, including costs, for rapid determination of local least-cost formulations
- Reduced costs for feedstocks and delivered fuels

4 – Critical Success Factors

- Development of predictive performance models, including costs, for rapid determination of local least-cost pathways
  - Integrated models for supply, preconversion, and conversion
- Reduced costs for feedstocks and delivered fuels
  - Better understanding of thermochemical conversion parameter space will enable inclusion of low-cost resources to achieve least-cost formulations
  - Reduced cost of preconversion operations to make low-cost resources compatible with conversion technologies
- Challenges
  - Rapid screening techniques tend to be expensive.

    → *Economic and field-portable technologies must be developed*
  - Non-linear effects in thermochemical conversion reactions complicate predictive models for optimizing least-cost formulations

    → *Many feedstocks must be tested for model construction & validation*
  - Results from lab-scale tests must be transferable to pilot-scale.

    → *Pilot scale tests are needed to confirm lab results*

2 – Technical Progress (INL)

Milestone	Planned Completion Date	Completion
Screening Methods for Ash Composition Using Laser Breakdown Spectroscopy (LIBS)	30 Sept, 2012	✓
Demonstrate interface of 4 grades of uniform format feedstock with conversion technology	31 Dec, 2012	✓
Report inter-lab collaborative efforts to characterize feedstock supply chain & conversion attributes	30 Jun, 2013	In preparation
Evaluate dry thermal treatments to reduce variability & impacts on supply chain and conversion quality metrics	30 Sept, 2013	In preparation
Screening methods for feedstock quality and micro/macro variability using FT-IR microscopy	30 Sept, 2013	Planning underway

2 – Technical Progress (PNNL)

Milestone	Planned Completion Date	Completion
Develop method for bio-oil characterization	31 Dec, 2012	✓
Conduct testing on high lignin mixed feedstocks	31 Jan, 2013	✓
Conduct testing on uniform feedstocks obtained from INL	31 March, 2013	✓
Conduct testing on torrefied feedstocks obtained from INL	30 June, 2013	Planning underway
Conduct testing on high yield feedstock	30 Sept, 2013	Planning underway

2 – Technical Progress (NREL)

Milestone	Planned Completion Date	Completion
Provide detailed gasification product composition and material balance for three INL feedstocks	15 Dec, 2012	✓
Review state of the art analytical tools for pyrolysis oil speciation	29 Mar, 2013	✓
Determine the impact of feedstock treatment and catalytic gasification on product gas composition	30 Jun, 2013	experiments underway
Determine feedstock chemical changes from torrefaction and densification through compositional and spectroscopic analysis	30 Aug, 2013	Planning underway
Assessment of feedstock impact on pyrolysis vapor composition	30 Sep, 2013	Planning underway

5 – Future Work

1. Evaluate impacts of dry thermal treatments on supply chain and conversion quality metrics (including feedstock variability)
    - Supply chain properties (grinding energy, flowability, density) – INL
    - Conversion metrics (yield, quality) – NREL, PNNL
    - Techno-economic analysis – INL
2. Pyrolysis baseline tests of 6 feedstocks & 2 blends
    - Prepare 200 kg of each feedstock at 12 mm particle size
    - Round-robin characterizations (physical, chemical, & fuel properties). Use results to standardized methods and results from labs (INL, NREL, PNNL)
    - Pyrolysis oil generation and characterization (NREL, PNNL)
    - Upgrading of pyrolysis oil and characterization (PNNL)
3. Develop predictive performance models, including costs, for rapid determination of local least-cost pathways
    - Integrated models for supply, preconversion, and conversion
4. Develop rapid screening tools for predicting feedstock conversion performance
    - Py-MBMS, GC-MS, TGA-DSC, FTIR Microscopy,
5. Evaluate mild alkaline and acid leaching for removal of ash
    - Whole tree pine, forest thinnings
    - Complete batch-scale and continuous-feed (20 kg/hr) experiments
    - Techno-economic analysis of ash removal process

5 – Future Work (Selected Milestones)

Lab	Milestone Description	FY13		FY14			
		Q3	Q4	Q1	Q2	Q3	Q4
INL	Evaluate impacts of dry thermal treatments on supply chain and conversion quality metrics		🟩				
PNNL	Conduct testing on high yield feedstock		🟩				
NREL	Assessment of feedstock impact on pyrolysis vapor composition		🟩				
ALL	Pyrolysis baseline tests of 6 feedstocks & 2 blends)				🟩		
PNNL	Conduct hydrotreating testing on round robin feedstocks					🟩	
ALL	Round robin characterizations					🟩	
INL	Assessment of mild leaching to remove ash from woody materials					🟩	

6 – Summary

- Approach
  - Rapid analytical screening tools: ash, moisture, TGA, MBMS, GC, 2D-GC
  - Techno-economic analyses of optimized feed & conversion systems
  - Produce, characterize, & distribute shared feedstock materials
  - Assess preconversion processes for benefits & costs
  - Bench-scale bio-oil production
  - Develop methods for vapor and oil characterization
  - Impact of feedstock composition on yield (liquid, gas, & solid) and oil quality
- Success metrics
  - Reduced ‘grower payment’ for feedstock
    - Better understanding of thermochemical conversion parameter space will enable inclusion of low-cost feedstocks to achieve least-cost formulations
  - Reduced cost of supply & preconversion operations (transportation, comminution, de-ashing,)
    - Low cost preconversion operations are needed to make low-cost feedstocks compatible with conversion technologies

Publications/Presentations

Publications

- Westover, T.L., Phanphanich, M., Clark, M.L., Rowe, S.R., Egan, S.E., Zacher, A.H., Santosa, D., "Impact of scale on thermochemical pretreatment of southern pine for pyrolysis conversion." Biofuels 4(1), 45-61 (2013).
- Olstad, J.; Jablonski, W.; Carpenter, D.; Westover, T.; Dutta, A. "Gasification of torrefied feedstocks: syngas and tar compositions, mass balances, and energy balances." submitted to …
- Westover, T.L., "Ash Composition Analysis of Herbaceous Biomass Using Laser-Induced Breakdown Spectroscopy." submitted to Biotechnology and Bioengineering.

Presentations

- Olstad, J. (2011). "Determining and Addressing Feedstock Variability for Thermochemical Biomass Conversion," AIChE 2011 Annual Meeting, Minneapolis, MN.
- Westover, T.L., Gresham G. (2012). "Rapid Analysis of Ash Composition Using Laser-Induced Breakdown Spectroscopy (LIBS).", AIChe Annual Meeting in Pittsburgh, PA. Oct. 28 – Nov. 2, 2012.
- Carpenter, D.; Pomeroy, M.; Robichaud, D. (2012). "Challenges and opportunities in on-line monitoring of thermochemical biomass processes." 39th National Meeting of the Society of Applied Spectroscopy, Book of Abstracts: 30 September-5 October, Kansas City, MO, pg 221.
- Xiao, L.; Evans, R.; Carpenter, D.; Davis, M.; Park, S.; Jameel, H.; Kelley, S. (2013). "Evaluation of the effects of biomass feedstock on syngas and tars composition using pyrolysis molecular bema mass spectrometry." 245th ACS National Meeting, 7-11 April, New Orleans, LA.
- Park, S.; Gwak, K.; Kelley, S.; Jameel, H.; Xiao, L.; Evans, R.; Carpenter, D.; Sykes, R. (2012). "Biomass screening and reactivity: molecular beam mass spectroscopy (MBMS) study." IBSS Annual Meeting, 12 December, Auburn, AL.

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Criteria	Avg Score	Std Deviation	Count
Approach	8.33	0.75	6
Progress	7.83	0.69	6
Relevance	7.83	0.69	6
Critical Success Factors	7.67	0.94	6

1. Project Approach (1-10)

Reviewer Comments

Criteria Score: 9 This is a sound approach to collect, analyze and communicate fundamental properties of the different feedstocks. Sound approach and well-defined work plan that targets DOE priorities. The work is clearly connected to other elements of program, and has clear milestones, and understanding of risks.

Criteria Score: 8 Project should be organized so that a future user of this data can look at an opportunity feedstock and determine how to use it to the fullest value. For example, the project should deliver data on how the feedstock would behave in a thermochemical process as is versus an optimum treatment (pelletization, drying, torrefaction, etc.). It would be helpful to see more information on the project management plan such as the schedule and milestones.

Criteria Score: 9 Biomass resource library with relational data base Impact of feedstock type on tar formation Torrefaction for feedstock preprocessing Laser-induced breakdown spectroscopy for rapid feedstock characterization

Criteria Score: 7 Focus is on all different kind of feedstocks, conventional as well as advanced feedstocks (torrefied, pellets) which makes sense. To understand the interface interactions between biomass feedstock and conversion technology is really important. Systematic screening of the feedstock is very good.

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1. Project Approach (1-10) continued….

Reviewer Comments

Criteria Score: 8 It is good that they are casting a wide net to gather info. The comprehensive of the program is good. I do wonder, however, why the program is taking 8 years to complete. This seems long.

Criteria Score: 9 Good teaming approach between national labs Good management plan across very complex project Mining data from public sources - good use of interns to keep cost down

Presenter Response

The project management plan in general is to establish the Relational Data Base in FY-11, with a wide set of sample analysis pertinent to the Regional Partners, augmented with sample analysis data extracted from credible journal articles and pertaining to preprocessing, torrefaction, gasification, and pyrolysis. This will be an on-going activity; however, a major milestone will be making the data base accessible and complete for many biomass species. There is present need to verify the analysis methods are consistent and accurate, and this is being undertaken in the current year with respect to U.S. ASTM and other established methods. In addition to Round-Robin analysis, the team will begin to glean European analytical methods which have been tailored for biomass.

The emphasis to this point has been on establishing the analytical methods and sample data base. The plan is to move toward understanding the feed specifications for the TC processes by correlating relative reaction rates and conversion efficiencies of gasification and pyrolysis to feed characteristics.

This information will in turn inform the SOT bases - technology and fuel costs. The aim is to attain the lowest cost fuels.

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2. Technical Progress and Accomplishments (1-10)

Reviewer Comments

Criteria Score: 8 This is a systems approach to a complex set of issues; feedstock properties needed to inform process, products. They are working to understand how feedstock specifications match the different TC process. The connection with ORNL for densification, pellets, performance testing is useful. The database in development using rapid analysis tools - NIR, LIBS, py-MBMS, etc., will be a very useful biomass resource library - includes reference samples Measuring TC conversion behavior and connecting this behavior to the mechanical and chemical properties of the feedstock is very important, but very complex. INEL should continue to collect and provide reference samples. LIBS techniques pretty well-known, not clear why the baseline is being

Criteria Score: 8 Project has met one Joule Milestone - feedstock delivered at $55/dry ton. The Biomass Resource Library will be a useful tool for sharing information. Project has identified some key learning's such as the relationship of milling energy to the particle size. When investigating torrefaction, the overall energy balance should be monitored - as energy content is densified, some of the energy is lost. Losses must be balanced against the densification.

Criteria Score: 9 achieved Joule milestone - $55/DT feedstock (wood), delivered to reactor throat developed feedstock sampling process (w/ bar coding)

Criteria Score: 7 Database is really valuable, especially the exchange with the biochemical platform. Clear milestones are stated. Systematic screening and measurement of different feedstocks are really helpful for the use in different conversion technologies. Clear progress has been made in feedstock handling related to tar production, torrefaction and pelletization. The following screening tests using a reactor as well as the analytical tools like LIBS give the full picture of the performance of the tested feedstock.

Criteria Score: 7 The sample custody, characterization & supply task is coming together after 2-3 years. The LIBS analysis looks promising.

Criteria Score: 8 Very good progress against milestones, e.g.: established biomass resource library and relational database, Joule milestone for $55/DT feedstock, set up pedigree sample bank, and initiated screening process screening tests for gasification and pyrolysis.

2011 Peer Review Comments

2. Technical Progress and Accomplishments (1-10) continued…

Presenter Response

In addition to assimilation of the ORNL data, the program is taking notice of university and industry efforts to develop and possibly on-board torrefaction and densification operations.

Expanding the data base will indeed help evaluate both situational as well as the envisioned uniform feedstock supply. The LIBS system will be useful for screening feedstock entering the supply system. The thinking is similar to coal, where the ash content and composition may have negative impact on plant operations, up to catalyst impacts in this case. The LIBS system has the potential to rapidly speciate the ash, thus avoiding costly and time consuming wet chemistry methods. As noted, the complexities of spectrophotometric techniques are many, and as a minimum require calibration standards as well as well-defined techniques. In many cases, only an approximation of the ash composition will be needed. The Project will be using the sample library to provide calibration standards. In this manner, the methods can be developed for a wide set of biomass native materials or fractional tissues.

3. Project Relevance (1-10)

Reviewer Comments

Criteria Score: 8 Biomass costs and properties will dictate the commercial success for any conversion technology. Connections between the conversion process performance and the feedstock is well-known for biochem process, for thermochem this less well understood but equally important. The minor components and ash (amount and composition) will be critical for TC process.

Criteria Score: 8 The project is contributing to meeting several of the MYPP specifications. It is unclear how the data developed by the project will be used to make decisions. It may be helpful to obtain input from biomass conversion technology developers on how they may use the data and develop tools to support this.

Criteria Score: 9 Project identifies feedstock quality characteristics important for thermochemical conversion

Criteria Score: 7 Very important for having the whole picture of the process chain. The development of rapid analysis screening tools is really important for being economically viable.

2011 Peer Review Comments

3. Project Relevance (1-10) continued….

Reviewer Comments

Criteria Score: 8 Relevance was clearly identified in the presentation. I think it is good that they are looking at torrefaction, but I would like to see more info as it relates to overall process efficiency/yield, when you get to finished product from torrefied biomass. I think we understand the basic motivation for torrefaction, but it would still be good to see if it is possible to quantify the benefits.

Criteria Score: 7 I applaud the effort to consolidate knowledge relating feedstock specifications to process performance. On the other hand I suspect much of the data related to thermochemical processes is available in the literature, so not sure of incremental value of generating additional data in lab experiments. Utilizing standardized test methods will at least produce internally consistent data. Establishing feedstock SOT costs is a key need for DOE MYPP and process cost targeting.

Presenter Response

The comments and suggestions are useful. The program is funded to review the open literature for thermal conversion process data and to add this to the data base. This task was initially scheduled for completion in FY-10, but is now scheduled to complete in FY-11 with funding carried into this year. We agree that the larger base of experience should be assimilated to better focus the current program development of the relationship between feedstock specifications and conversion outcomes.

4. Critical Success Factors (1-10)

Reviewer Comments

Criteria Score: 8 Most of the DOE lab projects understand the OBP program goals and the need to focus on the barriers. The team understands the risk with the natural variations in species. The variations from harvest and storage. They also understand the need for preprocessing to minimize variation and improve reactivity. The project understands the state of the art, and is driving much of the innovation in this area.

Criteria Score: 7 At $55 per dry ton, the cost of feedstock will be one of the largest costs contributing to the total cost to produce a gallon of biofuel. Consequently, the relationship between "raw" biomass and the costs of preparing feed including energy losses are important. The project needs to develop a relationship of the tradeoffs involved in the feedstock preparation. This was not clearly communicated in the presentation.

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4. Critical Success Factors (1-10) continued…

Reviewer Comments

Criteria Score: 9 Presentation identifies goals Identify and characterize dependent feedstock specifications Measure TC conversion performance behavior Input and link data in Biomass Resource Library Establish and supply premium samples Develop rapid analysis screening tools

Criteria Score: 6 A feedback loop towards the problems faced by industry is missing.

Criteria Score: 8 what about gasifier variations? Test procedures are on existing lab units. The presenter indicated he was satisfied that they are covering a broad enough spectrum, with possible exception of high-temp entrained flow. Nevertheless, I still emphasize that it is very important that this project ensure that its results are as relevant as possible to the wide range of gasifiers available. I would also like to see more on energy balance issues

Criteria Score: 8 Project aims to understand the tradeoffs between additional upstream feedstock processing and total cost to produce fuel products. Understanding this tradeoff is a key success factor.

Presenter Response

The project does have a milestone in FY-11 to characterize the relationship of the tradeoffs involved in the feedstock preparation. This could have been covered in the presentation, but unfortunately was not. The remark regarding the problems facing industry is valuable. INL will survey the OBP Integrated Biorefinery and take note of the feedstock specifications that are relevant to in-feed or conversion issues. Such barriers may indeed be mitigated in the supply chain.

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5. Technology Transfer and Collaborations

Reviewer Comments

Many industrial partners in terms of equipment providers. Less clear on how environmental considerations are included, and ENGO or other interest groups are engaged.

The project is doing a good job leveraging data from other projects in the platform and external sources, i.e. mining data from publications, universities, national labs, etc. Further, the project is leveraging resources (people and equipment) at other institutions. See remarks in other sections of this review

Feedstock specifications have also to been put into an international context especially with relation to biomass trade nowadays. This would also help to develop international standards and guidelines. Is this database used by industry as well? Do they appreciate it? Exchange with industry for addressing their problems from the applied side would be beneficial to the project.

The database seems like the way to go, i.e., to make this available to a wide audience. DOE should make sure it has the capability to include torrefaction in the cost equation for program goals and in the TEA.

Biomass Resource Library and Relational Database will be excellent tech transfer tools.

Presenter Response

This is correct, there is an important connection to environmental considerations that are a concern all of us. The LCA analysis work supported under the feedstock platform currently accounts for emissions attributed to the harvest, storage, preprocessing steps in the supply chain. The respective gasification and pyrolysis platforms similarly account for the efficiency and by-product emissions on the production side. It seems relevant to this activity to look at the emissions of thermal pre-treatment operations - such as torrefaction. This is not currently funded under the Work Package, but is being taken up by the Feedstock Supply Platform. They believe the system-wide information is coming together. The cost of torrefaction will account for material and energy losses which are relevant both to the technical specifications, and also the transportation logistics/costs. We recognize that torrefaction alone may not reduce transportation costs, unless it is followed with densification. The torrefaction work by ORNL and INL is adding to the body of information also available from Europe and established university programs in the U.S. We agree that a full accounting in the SOT and materials costs must be weighed against the benefits. This subject is becoming an important element of the OBP feedstock supply and assembly chain.

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6. Overall Impressions

Reviewer Comments

Very good work, but very complex to get the needed details. This work builds on the approach developed for the Biochem platform May want to put more emphasis on bench marking the conversion tasks with common feedstocks.
The project is developing a reference database for biomass feedstocks which is valuable resource. The data developed can be used in ways by different conversion technologies. It must be kept in mind that the unique characteristics of different biomass sources present potential opportunities for unique conversion processes. The project should not be too focused on developing a "universal" or uniform feedstock as this may lead to a sub optimum value chain.
See remarks in other sections of this review

Good work for getting a handle on specifications of different feedstocks over the whole process chain.
It looks like all the bases are being covered well. Regarding the Joule milestone of $55/dry ton: would not a better milestone exclude initial procurement costs so the program can focus on value added for pre-processing?

Presenter Response

These are good suggestions. We agree that development of a universal or uniform feedstock is situational. To this end, the development of feedstock specifications needs to be balanced with the flexibility of the thermal conversion platforms, and supply costs. This is a work in progress where an understanding of the barriers to attaining spec-qualified fuels will be weighed against benefits. In summary, the program has been able to show that woody feedstock can be delivered at under $55/ton, but this is for a relatively large particle size (2-inch chip) with higher levels of ash (up to 3%) than may be optimum to the thermal conversion operations. The relational data base will allow cost-benefit tradeoffs to be addressed. The suggestion of focusing on the highest value proposition will resolve with continued effort on the Interface task.

3 - Relevance

Additional Slides

1 – Approach: PNNL
Thermochemical Feedstock Interface

- Overall Technical Approach
  - Process characterized feedstocks in fast pyrolysis reactor to generate bio-oils
  - Develop characterization methods for analyzing bio-oil quality
  - Assess impact of feedstock compositional characteristics on liquid, gas, and solid yield as well as oil quality
- Technical metrics for measuring progress
  - Identification of key relationships between feedstock composition and product yield
  - Fraction of total organic carbon identified and quantified in oils
- Management Approach – Approved Project Management Plan
  - Regular Milestones (1/Quarter) and Deliverables (Annual Reports)

2 – Technical Progress Summary (PNNL)

- Three sets of fast pyrolysis experiments conducted in conjunction with Core Pyrolysis
  - Blended lignocellulosic feedstocks
    - Core Pyrolysis data used to generate specifications for “uniform” feedstocks
      - Report written on results
  - High lignin/high ash feedstock blends
  - “Uniform” feedstocks blended to a specification and obtained from INL
- Liquid, solid, gas yields measured and related to ash, polymer, and extractives content
- Bio-oil characterization method developed to identify and quantify major components of fast pyrolysis oils
  - Based on VTT fractionation method
  - 2D GCxGC TOF-SIMS used for species identification
  - GC-FID calibrated with standards and used to quantify identified species

Approach (NREL)

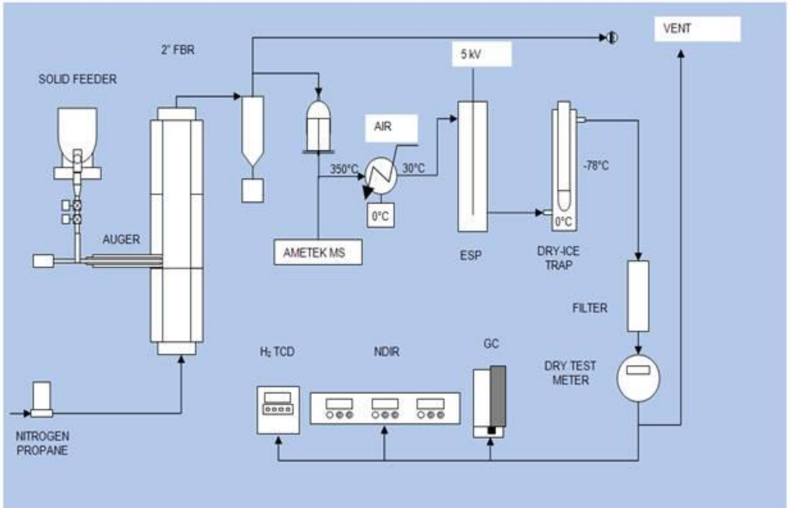
- Overall Technical Approach
  - Rapid analytical pyrolysis screening of feedstocks (molecular-beam mass spectrometry-MBMS, milligram scale)
  - Bench-scale bio-oil production (2" fluid bed reactor, 200 g/h)
  - Develop methods for detailed vapor and oil characterization
  - Develop multivariate data handling methodologies to establish correlations between MS/GC/feedstock data
- Technical metrics for measuring progress
  - Identification and quantitation of key conversion performance indicators that are affected by feedstock
  - Development of mathematical feedstock-conversion correlation functions that can be used in predictive performance models
  - Improved speciation and quantitation of inorganic species volatilized to vapor phase

2 – Technical Progress (NREL)

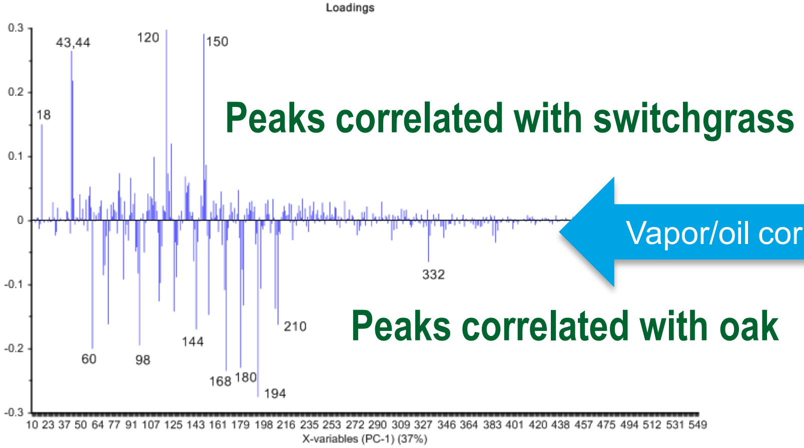
Pyrolysis vapor/oil, 3.1.2.2

Development of feedstock/vapor/oil correlations

- Can we use high throughput py-MBMS screening to tie marker compounds in the vapor to desired oil qualities?
- Generate oil with 2” fluid bed reactor
- Analyze by 2D GC
- Conduct multivariate analysis on *very* complex data sets to uncover latent correlations

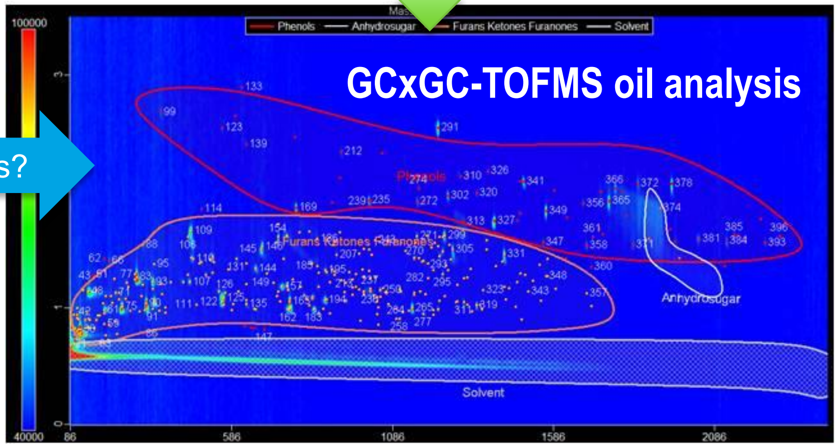


2” Fluidized Bed Reactor system (~2 kg/day)

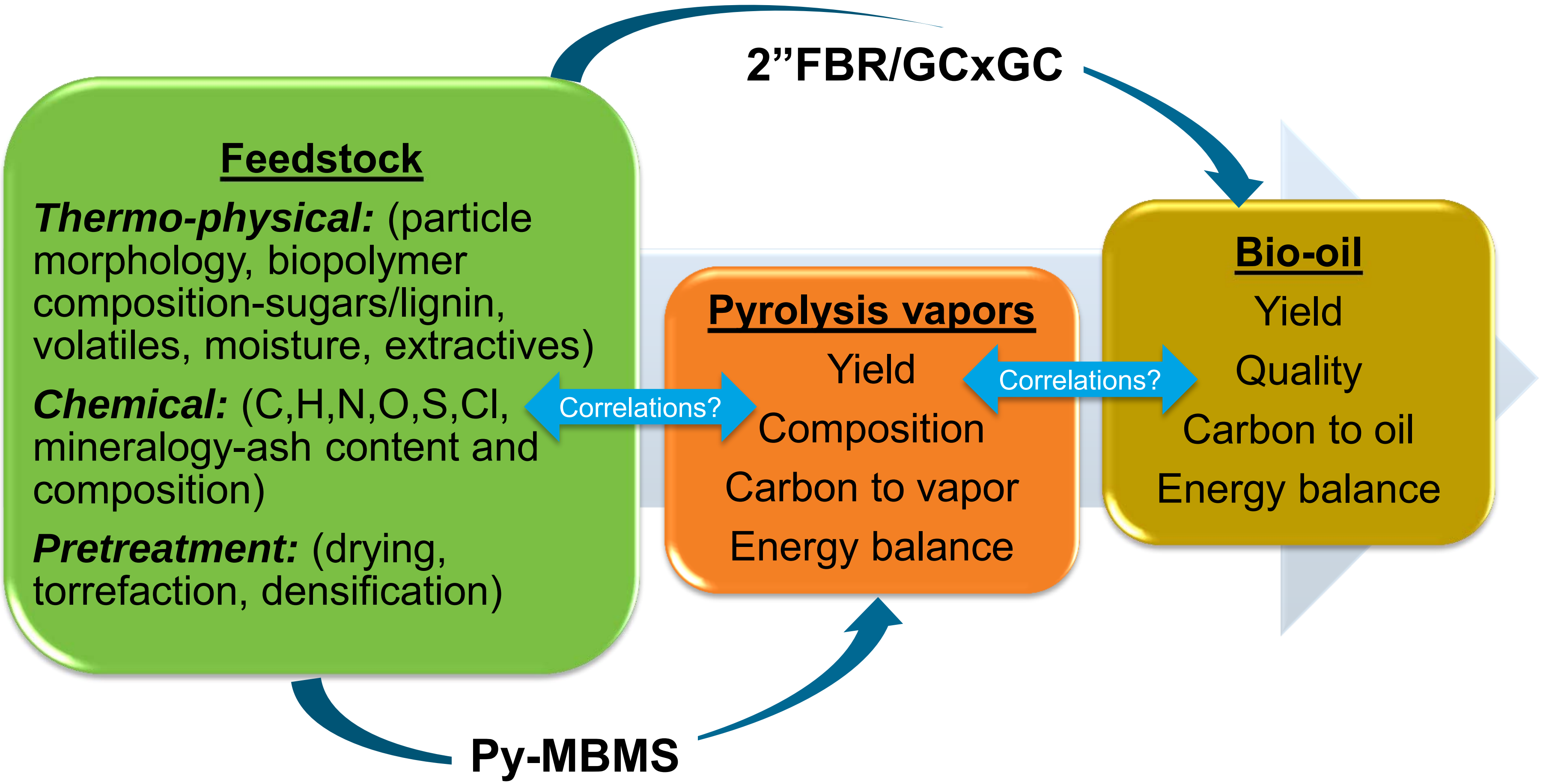


Principal component analysis of py-MBMS data

Vapor/oil correlations?



Approach cont. (NREL)



2"FBR/GCxGC

Feedstock

Thermo-physical: (particle morphology, biopolymer composition-sugars/lignin, volatiles, moisture, extractives)

Chemical: (C,H,N,O,S,Cl, mineralogy-ash content and composition)

Pretreatment: (drying, torrefaction, densification)

Pyrolysis vapors

Yield

Composition

Carbon to vapor

Energy balance

Bio-oil

Yield

Quality

Carbon to oil

Energy balance

Py-MBMS

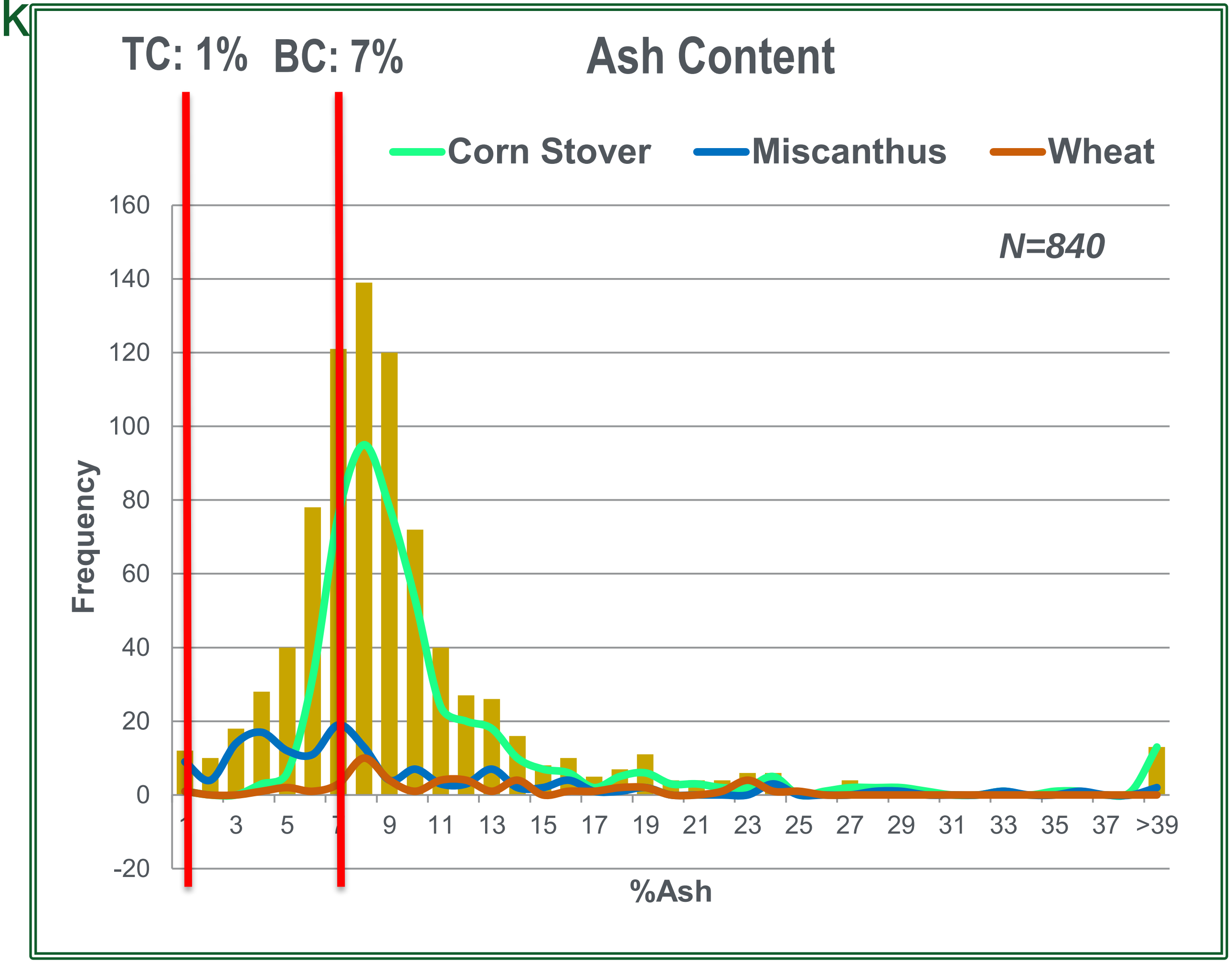
5. Future Work: PNNL

Thermochemical Feedstock Interface

ML, DL or Go/No Go	Description	FY13 Q3	FY13 Q4	FY14 Q1	FY14 Q2	FY14 Q3	FY14 Q4
ML	Conduct torrefied feedstock testing	🟩					
ML	Conduct testing on high yield feedstock		🟩				
DL	Annual progress report		🟩				
ML	Conduct pyrolysis testing on round robin feedstocks			🟩	🟩		
ML	Conduct hydrotreating testing on round robin feedstocks				🟩	🟩	
ML	Conduct analysis of round robin oils				🟩	🟩	
ML	Perform multi-variate analysis						🟩

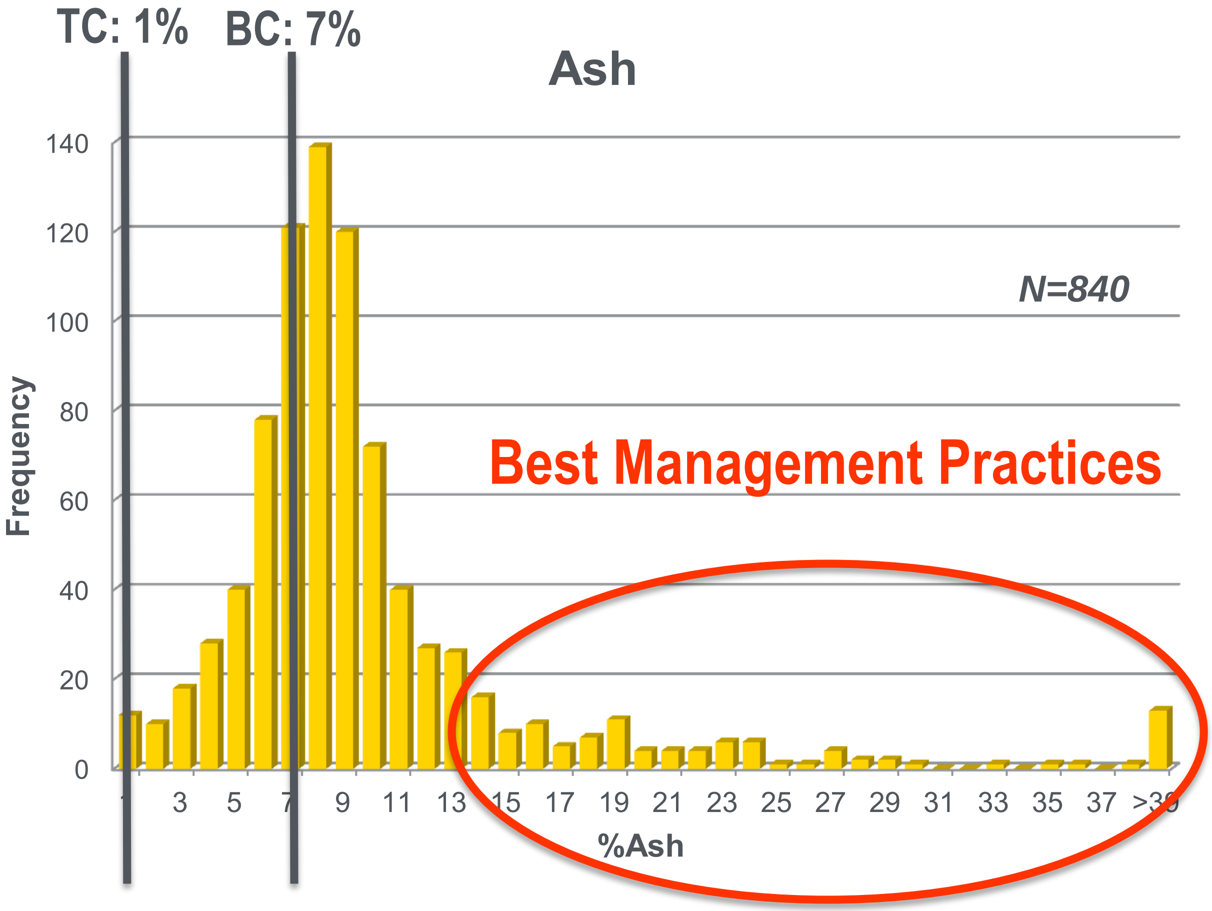
2 – Technical Progress (INL)

- Step 1: Feedstock Selection
  - Selection of optimum feedstock
  - Risk: reliance on specific biomass resources
  - Results in boutique feedstocks



2 – Technical Progress (INL)

- Step #2: Eliminate soil contamination

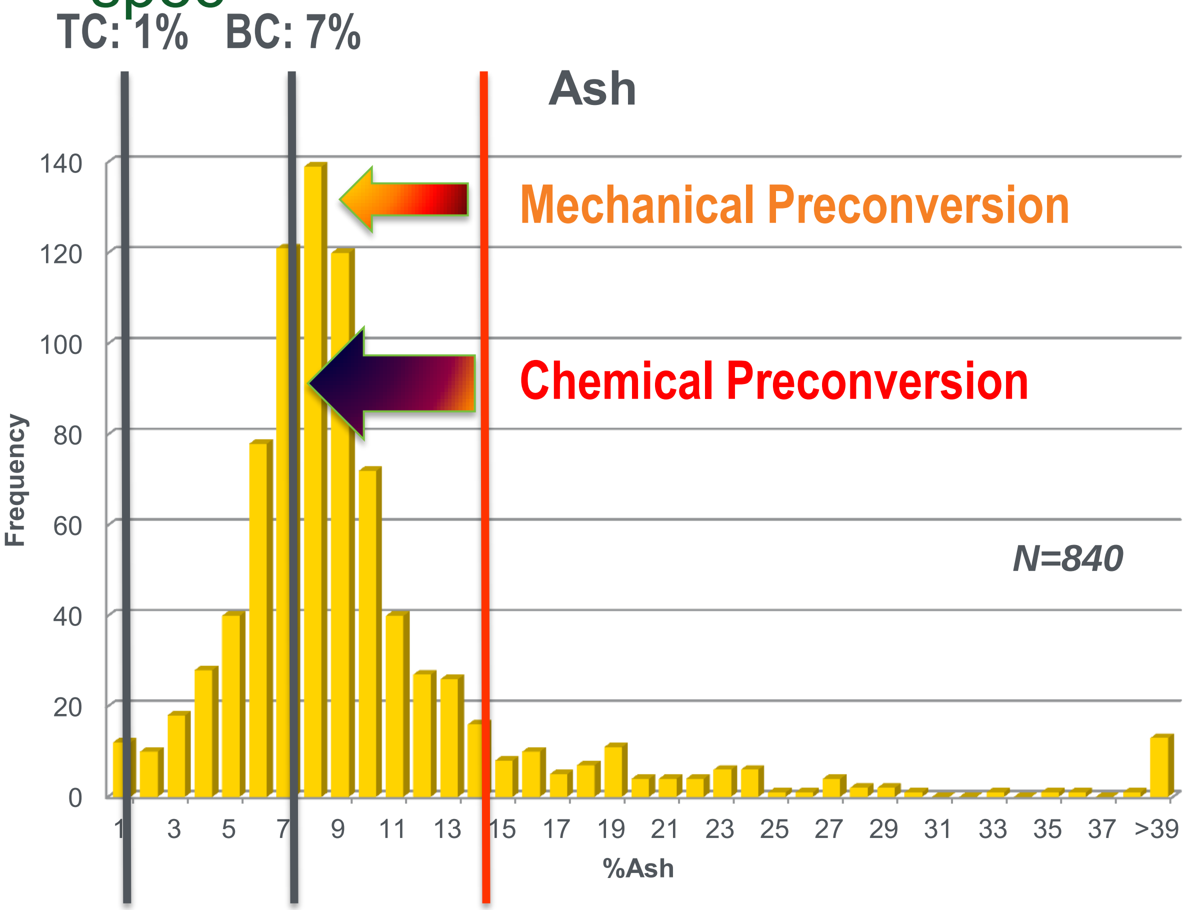


Reduce ash content to physiological levels (5-7 wt%) by minimizing soil contamination

- Biomass-specific methods
- Feedstock-specific equipment

2 – Technical Progress (INL)

- Step #3: Preprocessing to achieve final ash spec



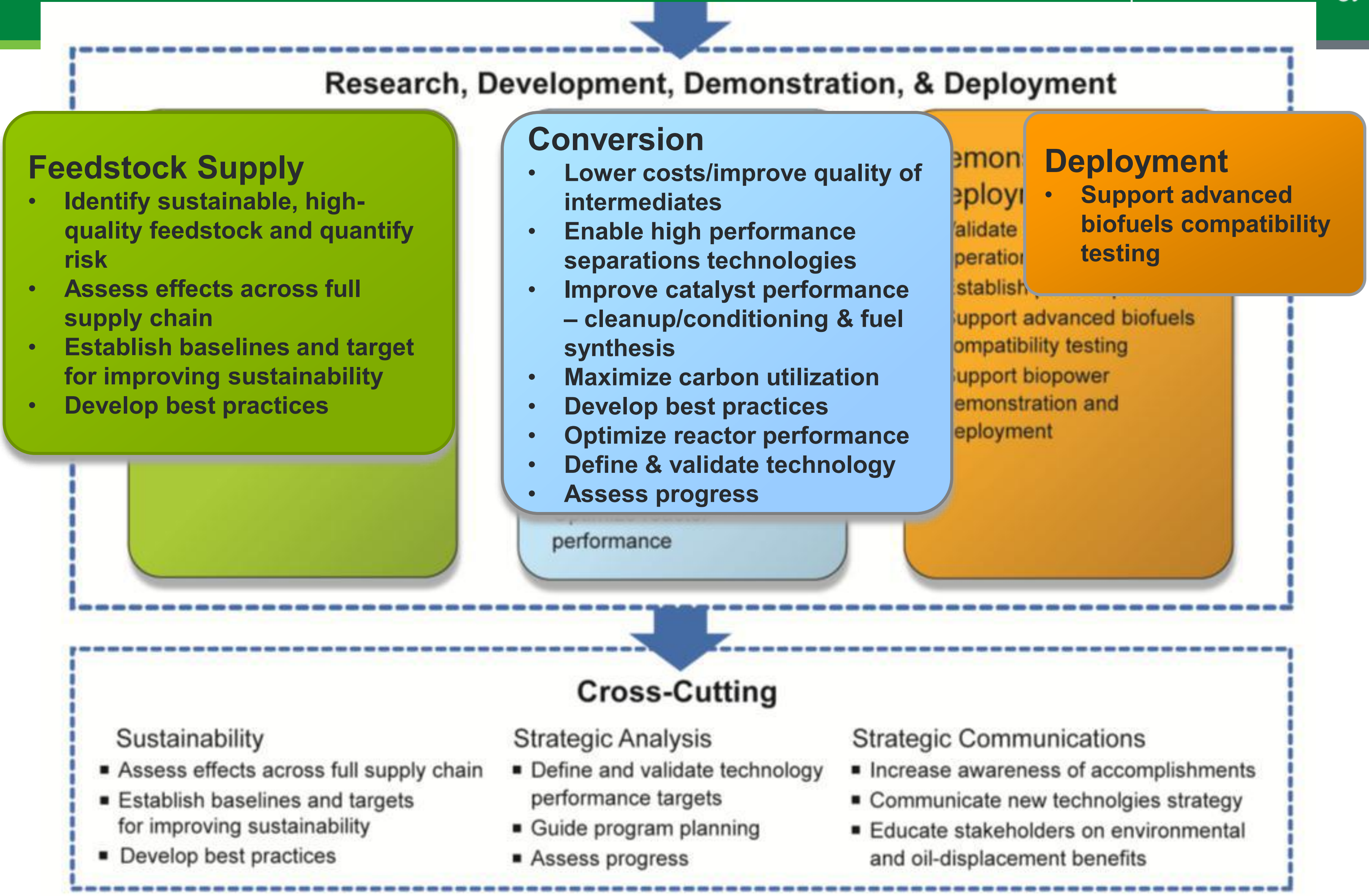
Mechanical Preconversion

- Removal of non-structural ash (soil)
  - Fractionation & separation of high ash anatomical fractions
  - Sieving operations

Chemical Preconversion

- Removal of structural ash
  - Hydrothermal treatment
  - Hot water
  - Acidic
  - Alkaline

3 - Relevance



Research, Development, Demonstration, & Deployment

Feedstock Supply

- Identify sustainable, high-quality feedstock and quantify risk
- Assess effects across full supply chain
- Establish baselines and target for improving sustainability
- Develop best practices

Conversion

- Lower costs/improve quality of intermediates
- Enable high performance separations technologies
- Improve catalyst performance – cleanup/conditioning & fuel synthesis
- Maximize carbon utilization
- Develop best practices
- Optimize reactor performance
- Define & validate technology
- Assess progress

Deployment

- Support advanced biofuels compatibility testing

Cross-Cutting

Sustainability

- Assess effects across full supply chain
- Establish baselines and targets for improving sustainability
- Develop best practices

Strategic Analysis

- Define and validate technology performance targets
- Guide program planning
- Assess progress

Strategic Communications

- Increase awareness of accomplishments
- Communicate new technolgies strategy
- Educate stakeholders on environmental and oil-displacement benefits

3 - Extra

Biomass Characteristics That Pose Challenges to Thermochemical (Pyrolysis) Conversion

Property	**Impact**
Mass & energy densities	Heating value; transportation and storage costs
Oxygen & volatiles content	Material heating rate in reactor; increases fuel acidity; affects upgradeability and long and short term fuel stability; emissions during conversion and upgrading
Moisture/ hydrophobicity	Transportation costs; pyrolysis heating rate and requirement; moisture level in fuel; char production; feedstock reactivity/storability
Ash/ash composition	Soluble ash affects fuel acidity/quality; char composition and disposal; transportation costs
Particle size/shape distributions and grindability	Material heating rate in reactor; feed system performance; dust & explosivity; grinding costs and energy requirements
Flowability	In-plant processing costs; conversion reliability