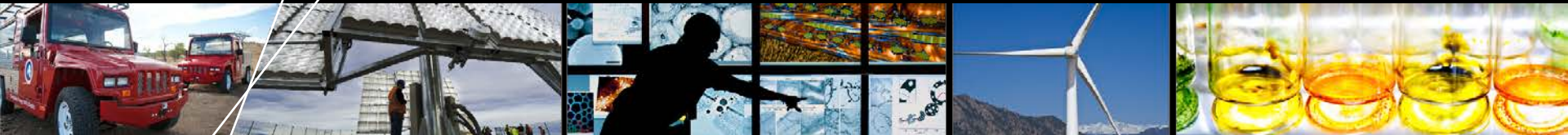


Field-to-fuel Performance Testing of Various Biomass Feedstocks



*Production and catalytic upgrading of bio-oil to refinery
blendstocks*



Daniel Carpenter
Tyler Westover (INL)
Dan Howe (PNNL)
September 4, 2014

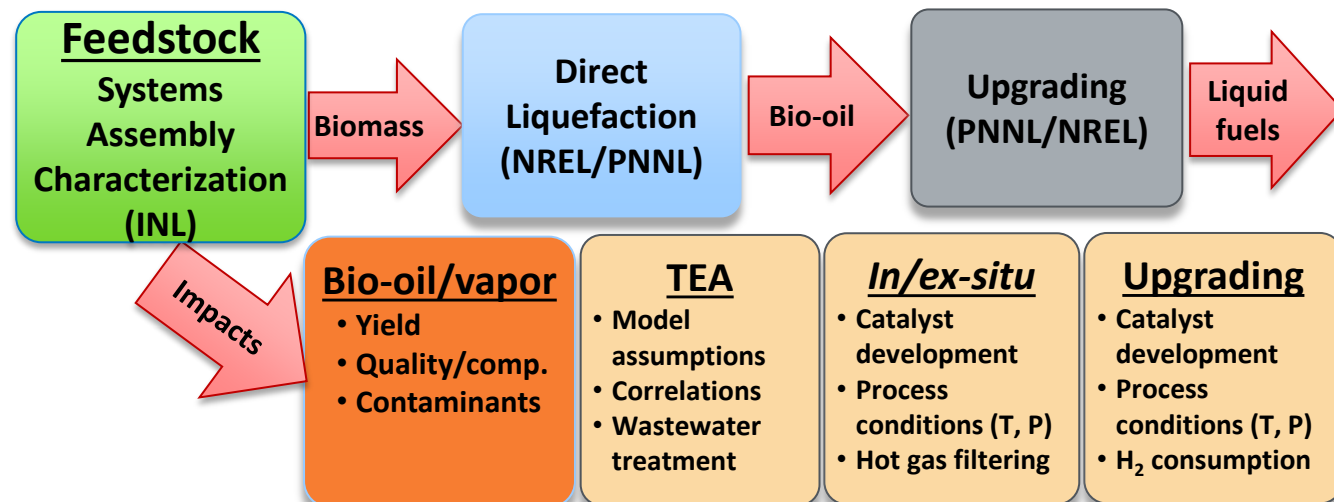
Intra-lab collaboration...



Stuart Black
 Earl Christensen
 Mark Davis
 Steve Deutch
 Robert Evans (MicroChem)
 Rick French
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 Kellene McKinney
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 Alan Zacher

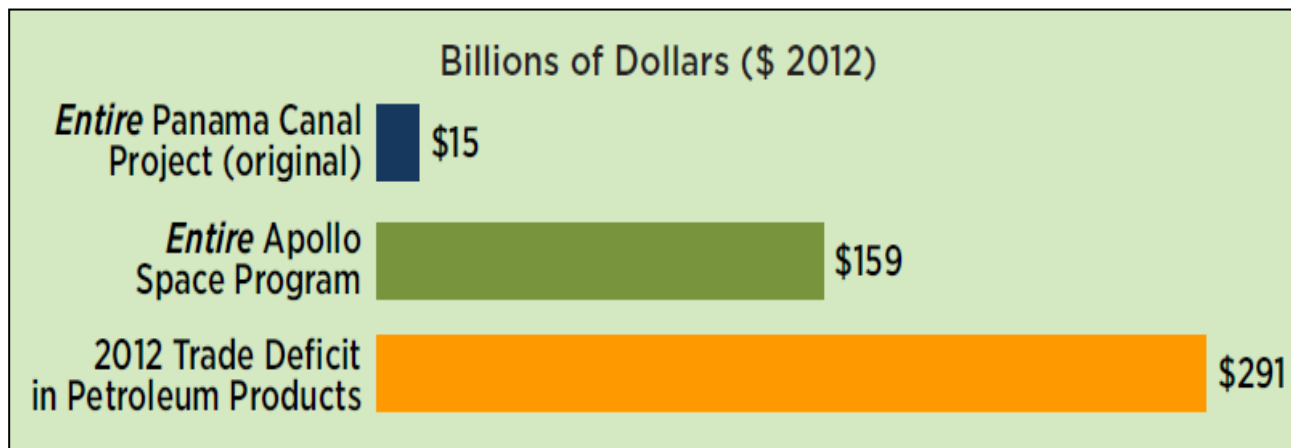


Outline

- **Background and Motivation**
- **Formulated Feedstocks**
- **Feedstock/Conversion Interface**
- **Bench-Scale Experiments**
- **Results**
- **Conclusions and Future Work**

Motivation: EISA 2007

- Reduce greenhouse gas emissions and dependence on foreign fuels
- *Sustainably* produce 36 billion gallons of *infrastructure-compatible*, renewable fuels by 2022
- Minimum fuel selling price: \$3.00/gallon gasoline equivalent (gge), competitive with ~\$95/barrel oil

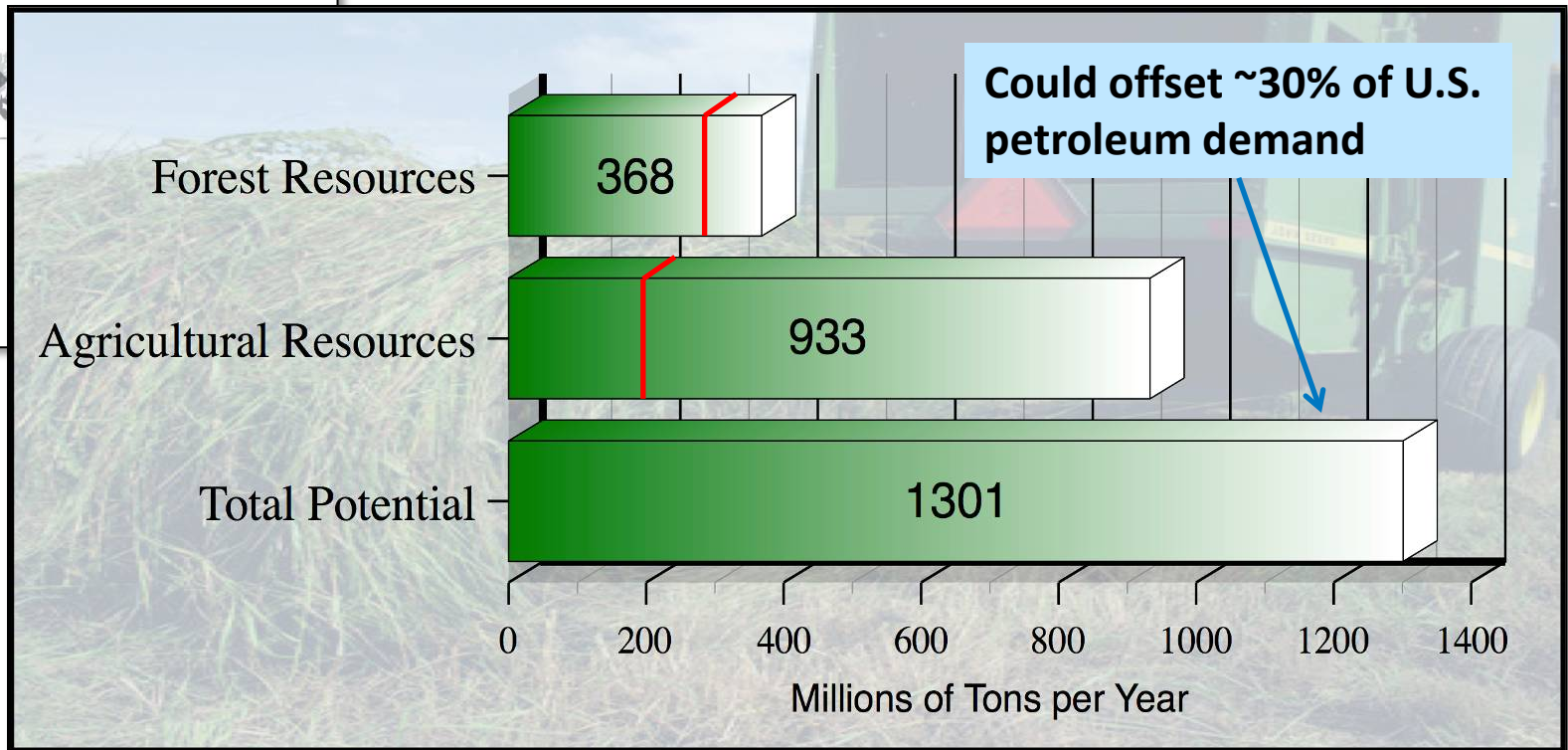


From: *Replacing the Whole Barrel* (BETO, July 2013)

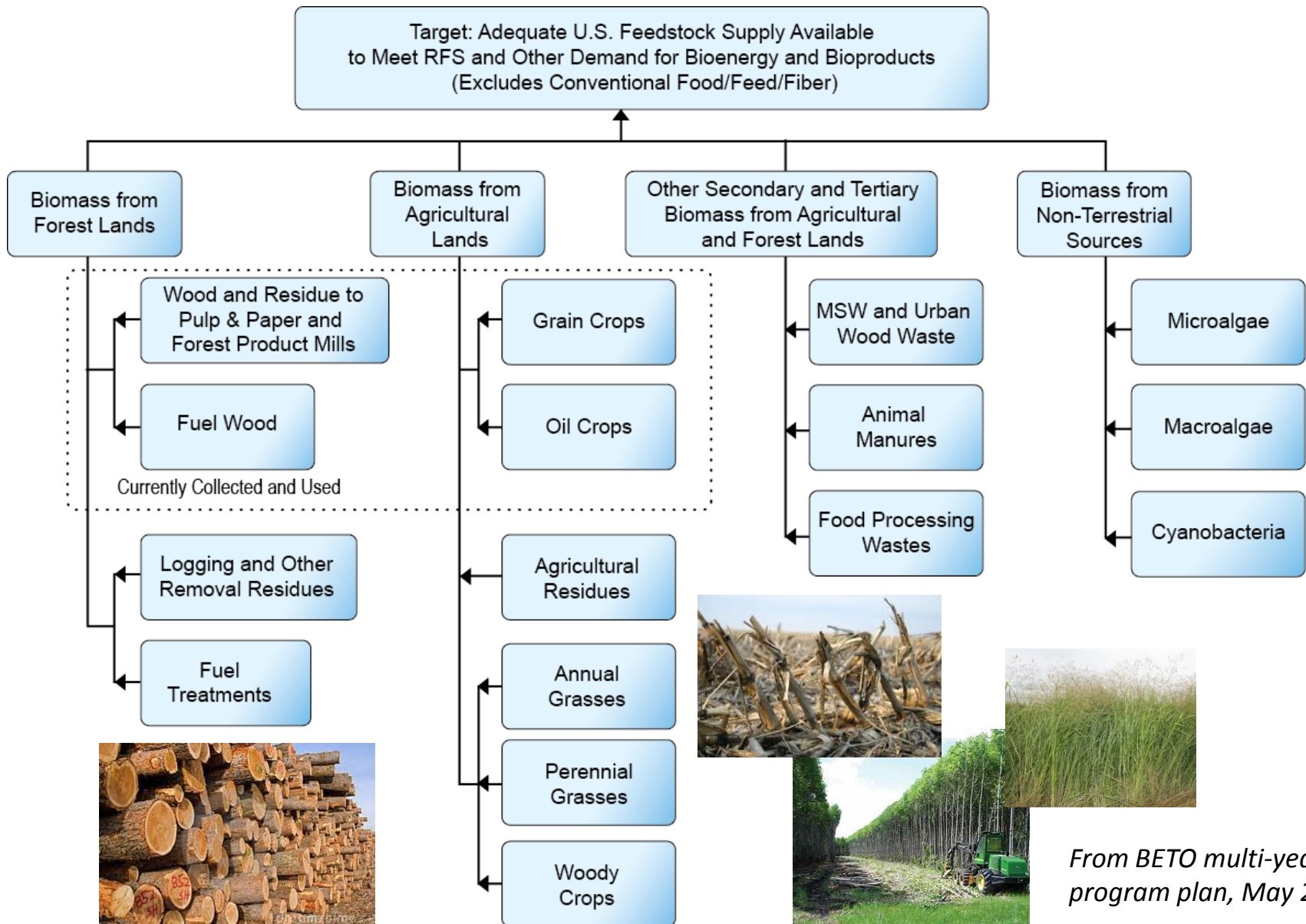
U.S. Biomass Resource Assessment



- BT2: updated August 2011
- Developed jointly by DOE and USDA
- Included supply-cost projections, county level estimates, sustainability

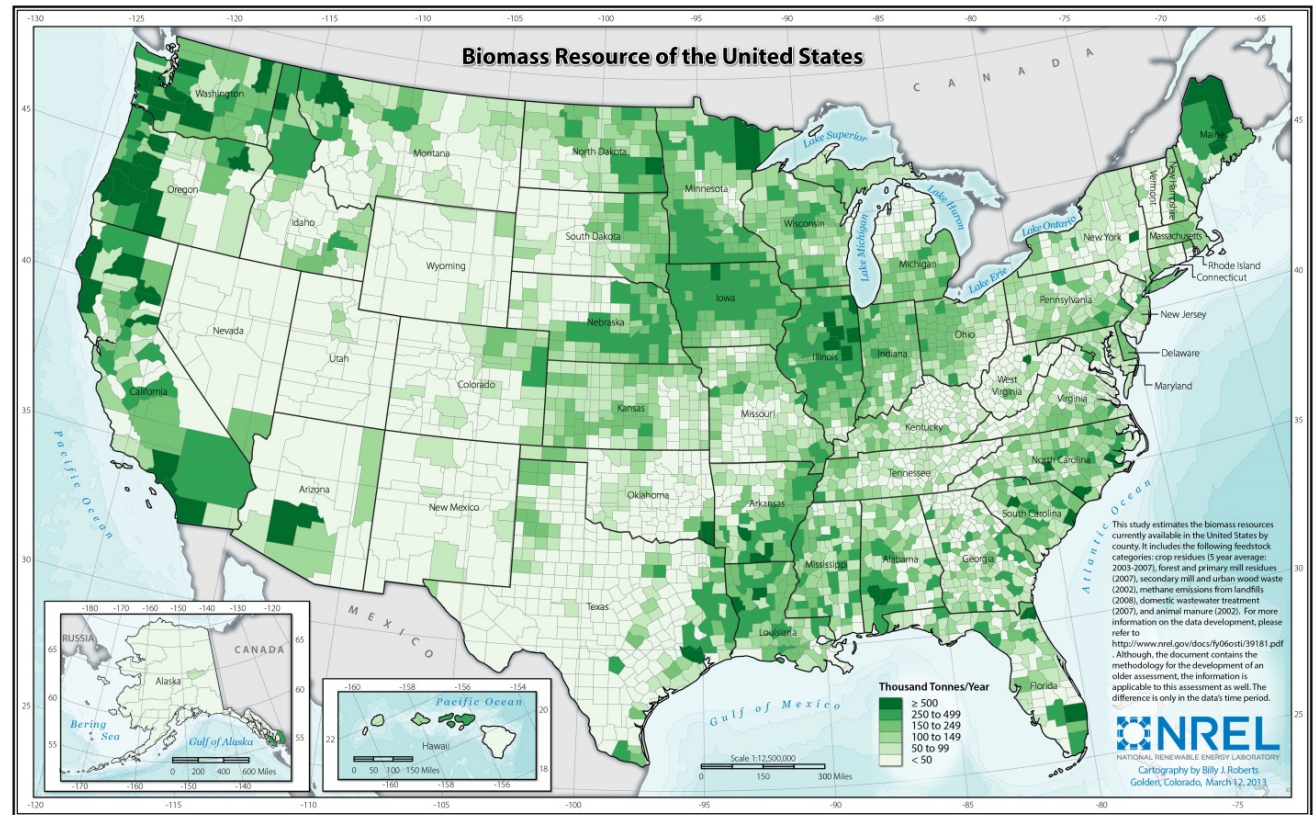


Example resources to meet RFS2



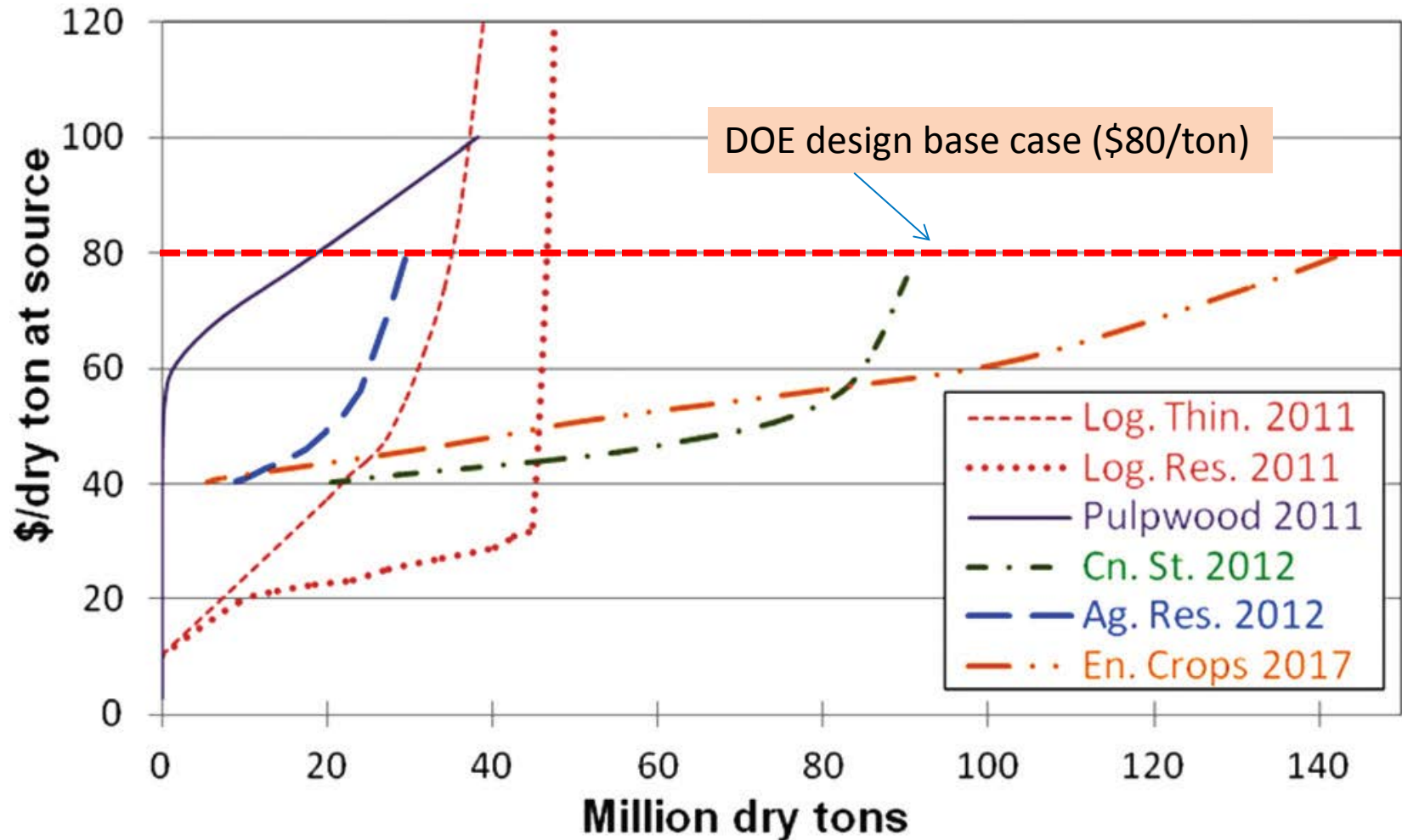
From BETO multi-year program plan, May 2013

Location, location, location



- Need to expand the pool of available biomass
- What about quality?
- Formulated feedstocks?
- Seasonality?

Supply-cost curves for key feedstocks (BT2)



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

TEA design case for FP+HT (one of several pathways)


Pacific Northwest
NATIONAL LABORATORY
Formerly Operated by Battelle Since 1965


NREL
NATIONAL RENEWABLE ENERGY LABORATORY


INL
Idaho National Laboratory

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,
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Pacific Northwest National Laboratory

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National Renewable Energy Laboratory

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Idaho National Laboratory

PNNL-23053
NREL/TP-5100-61178

Prepared for the U.S. Department of Energy Bioenergy Technologies Office

- **Wood** Pyrolysis + Hydrotreating → HC fuels
- Allows sensitivity analysis of technical and market assumptions
- Assumes 64% oil yield and 44% HT product yield (dry basis)
- Yield = 84 gal/ton (gasoline+diesel blendstock)
- MFSP = \$3.39/gge (nth plant)
- **Biomass feedstock is projected to be the largest cost component (~40%) and is known to be one of the largest risk factors for biorefinery commercialization**
 - Need to understand feedstock effects on conversion process
 - Ash (total and elemental)
 - What about blends?

Formulated feedstocks

Move toward formulated feedstocks...to mitigate variability and reduce 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? Process optimization and feedstock development need to be closely-coupled!

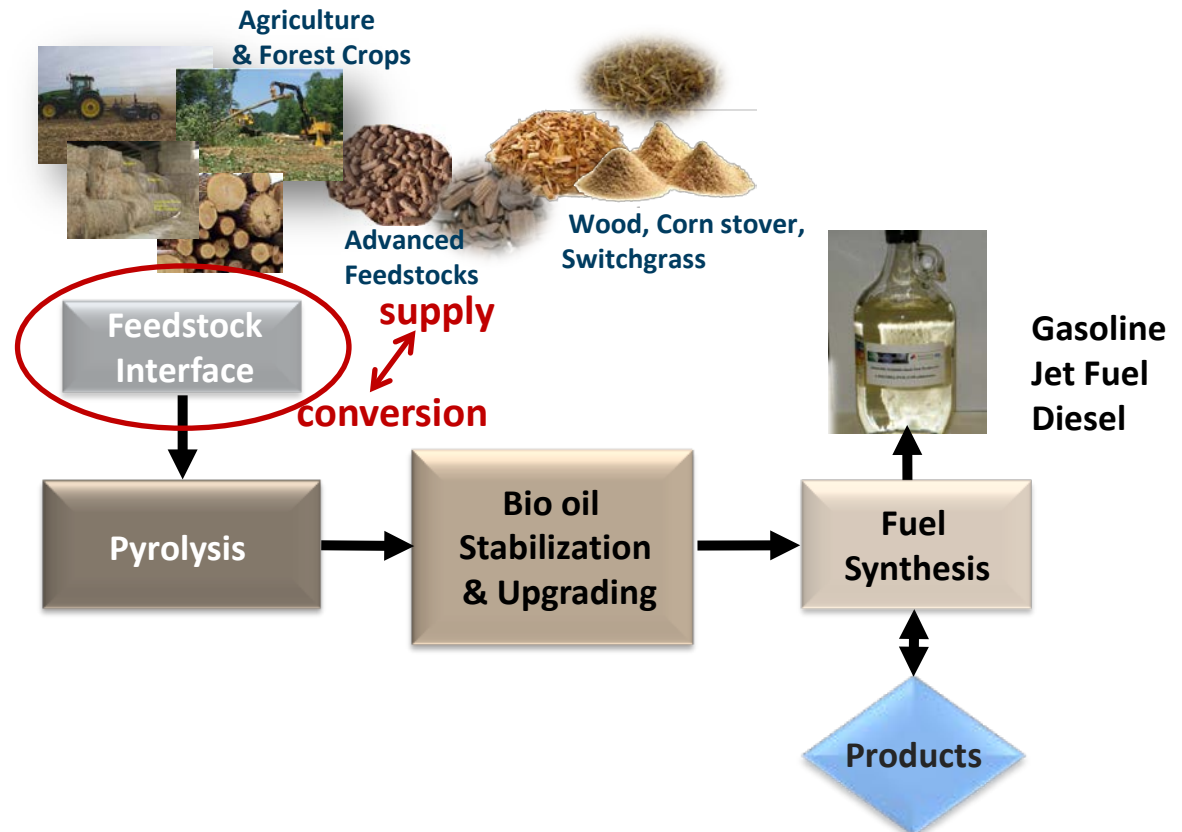
Joint feedstock-process interface project

Process requirements impact feedstock choice ↔ feedstock properties drive R&D decisions

- Goals: **minimize** cost of delivered feedstock, **improve** value and consistency of fuel intermediates, **establish** composition-based specifications

Research Focus/Roles:

- Identify, procure, and characterize feedstock specifications (INL)
- Evaluate TC conversion performance (NREL)
- Input and link data in Biomass Resource Library (INL)
- Develop rapid analysis screening tools (NREL/INL)



Experimental: feedstocks used

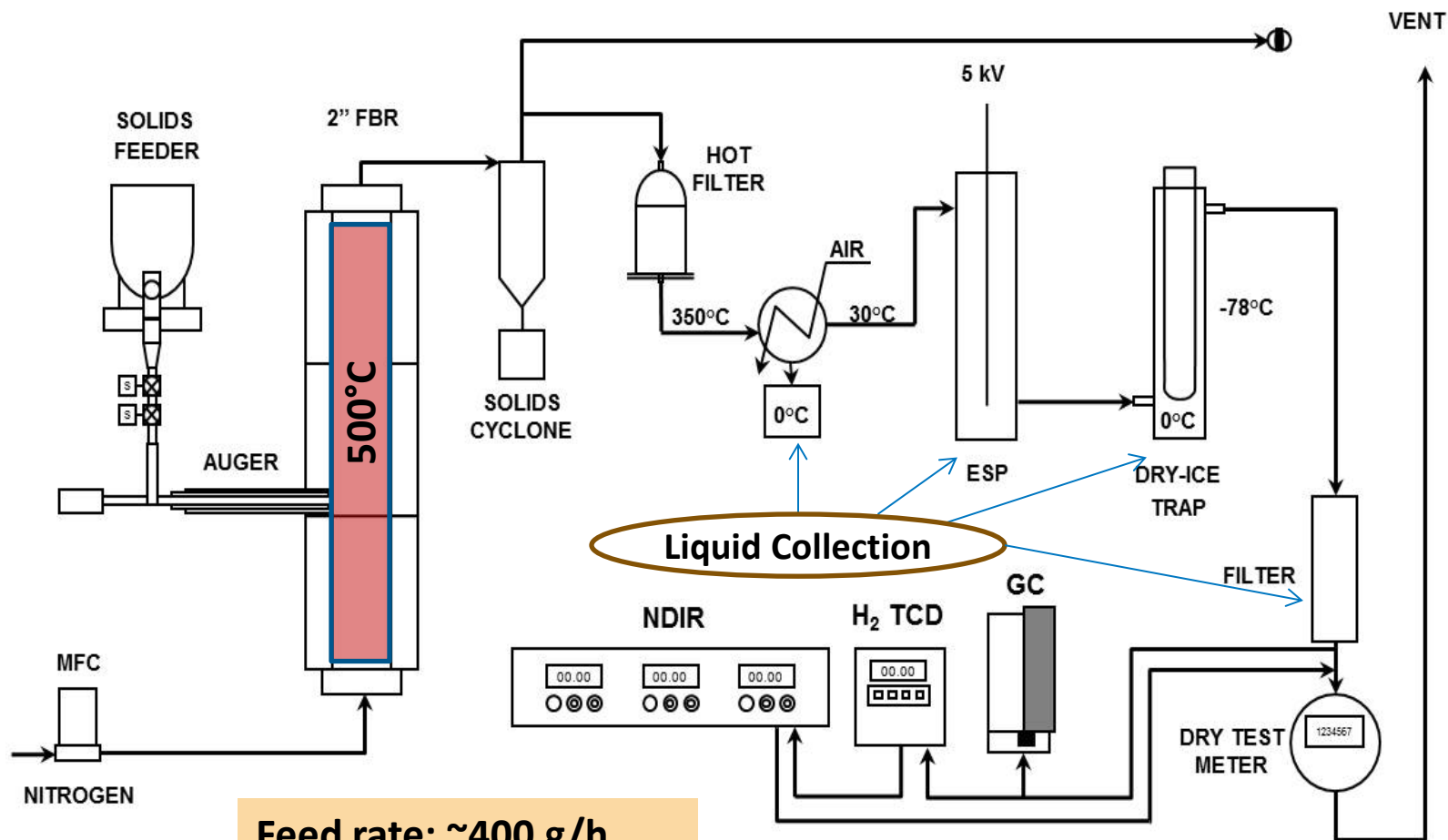
- Could be blended at a projected cost of \$80/ton
- Available at ~50 million tons/year combined
- “Commercial-type” materials used (i.e. harvested & ground in amounts of >1000 kg)
- Blend #1 = 1:1:1 TP:SG:WP
- Blend #2 = 1:1:1 CP:HP:WP

Sample	Proximate (% dry basis)					Ultimate (% dry basis)			
	Moisture	Volatile	Ash	Fixed Carbon	HHV (MJ/kg)	H	C	N	O ^a
Cl. Pine	2.16	79.3	0.7	17.9	8428	5.9	49.6	0.2	44.4
Wh. Pine	1.99	78.4	0.7	18.9	8883	5.9	50.2	0.2	43.4
Hy. Poplar	3.73	79.8	0.9	15.6	8250	6.0	48.1	0.2	45.0
Tu. Poplar	3.79	80.9	0.4	14.9	8202	6.0	47.4	0.2	46.4
Sw. Grass	3.84	73.5	4.0	18.6	7768	5.9	45.4	0.5	44.7
Cn. Stover	5.38	73.0	4.0	17.6	7567	6.0	46.1	0.7	43.5
Blend #1	3.64	77.7	1.7	17.0	8179	6.0	47.5	0.3	45.1
Blend #2	3.73	77.8	0.6	17.9	8551	6.1	48.5	0.2	45.4

Ash composition (ppm in whole biomass, dry basis)

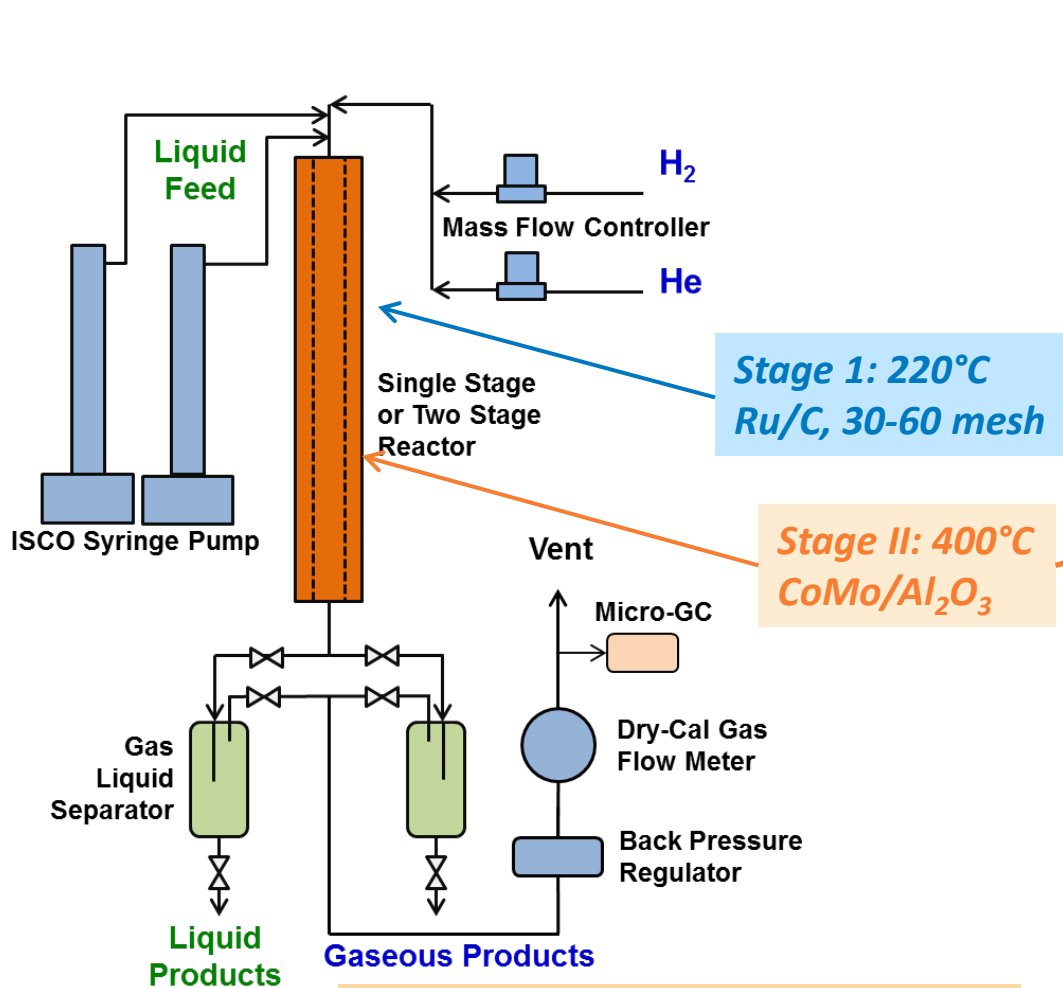
	Ash%	Al	Ca	Fe	Mg	Mn	P	K	Si	Na	S	Ti
Cl. Pine	0.73	199	942	290	265	68	75	758	1,557	51	68	13
Wh. Pine	0.74	184	1,096	415	291	72	93	756	1,300	54	73	9
Hy. Poplar	0.86	76	1,702	143	377	7	252	1,956	523	79	107	7
Tu. Poplar	0.47	39	944	62	261	35	70	822	568	23	70	3
Sw. Grass	4.29	59	2,312	537	2,579	66	831	6,097	10,843	506	466	5
Cn. Stover	4.24	63	2,815	356	1,601	33	551	9,338	10,055	25	387	3
Blend #1	0.62	107	1,162	144	295	48	134	1,137	673	49	79	6
Blend #2	1.66	90	1,366	383	934	58	319	2,505	3,632	182	181	6

Experimental: Fast pyrolysis reactor

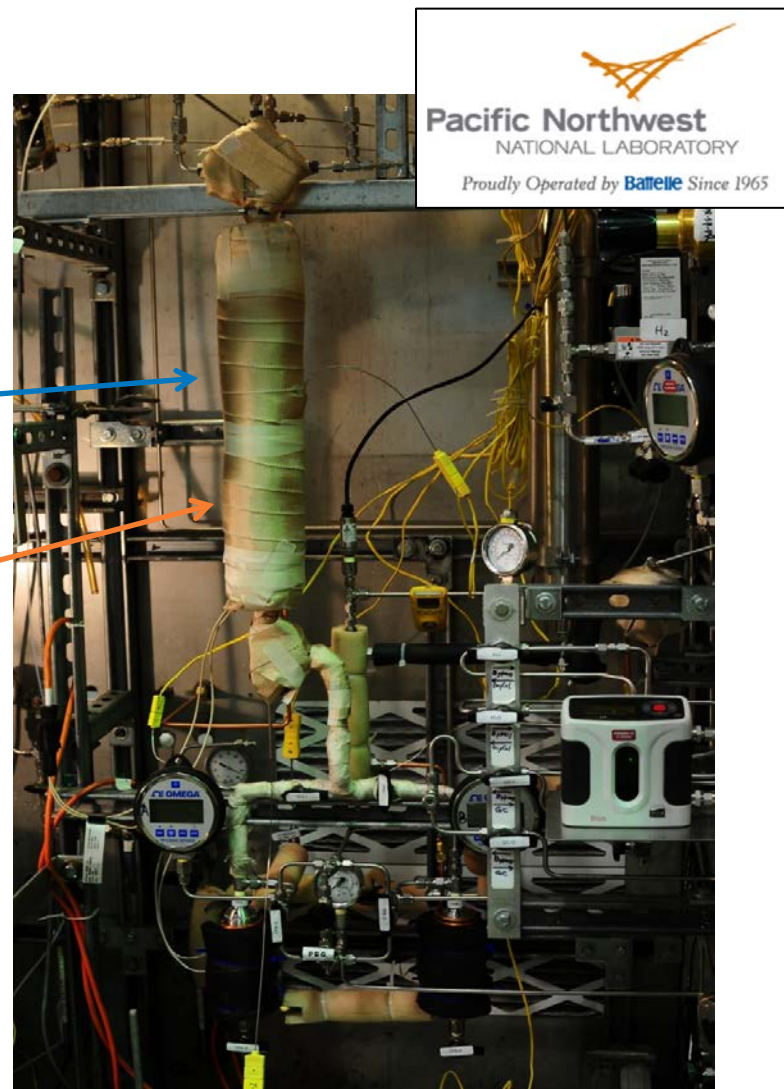


Feed rate: ~400 g/h
Reactor: 5.0 cm ID
Fluidizing N₂: 14 slm
Residence time: ~2 sec.

Experimental: Hydrotreating reactor

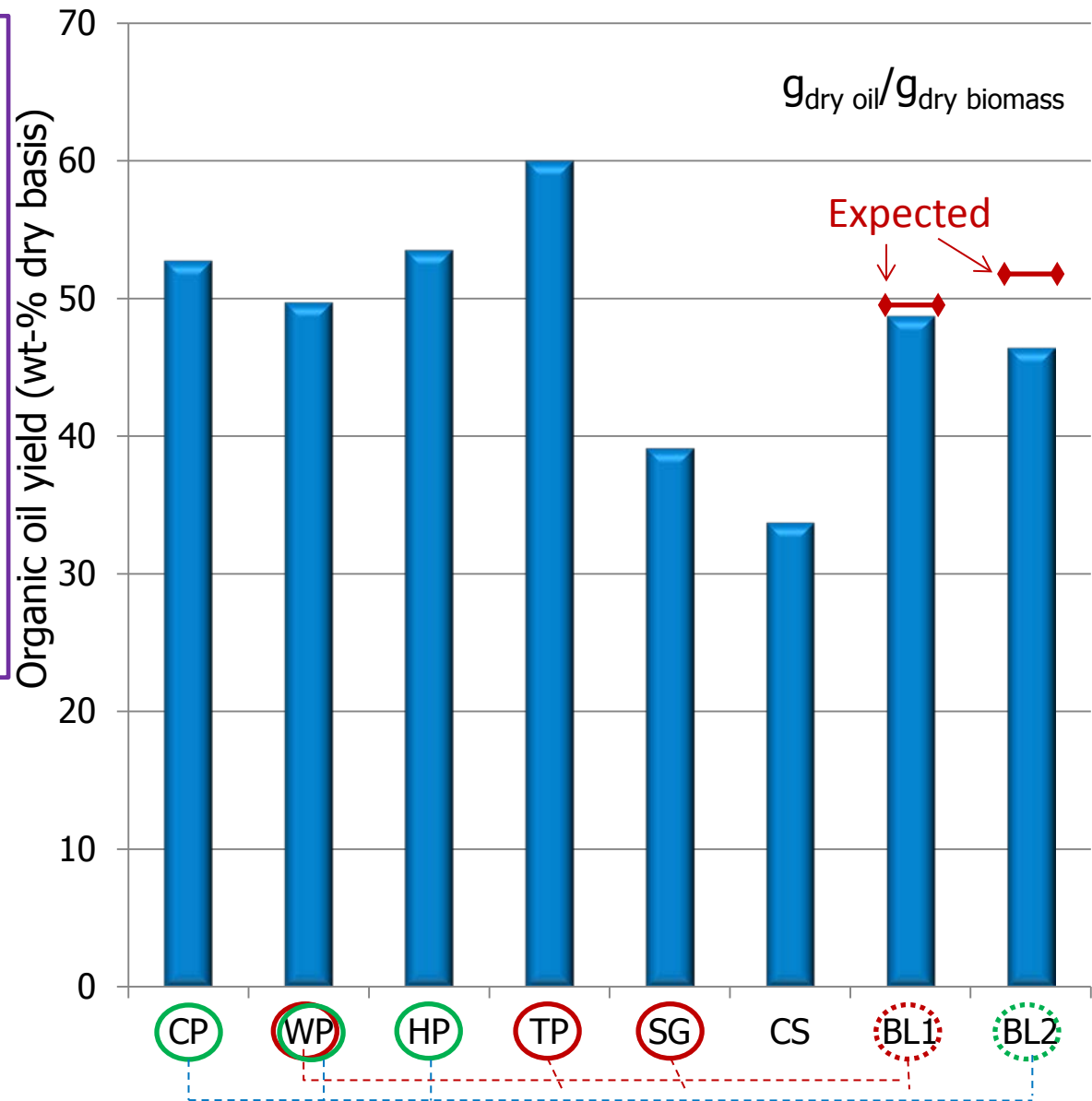


Reactor: 1.3 cm ID, 63.5 cm long
Feed rate: 48 mL/hr
Pressure: 1550 psi



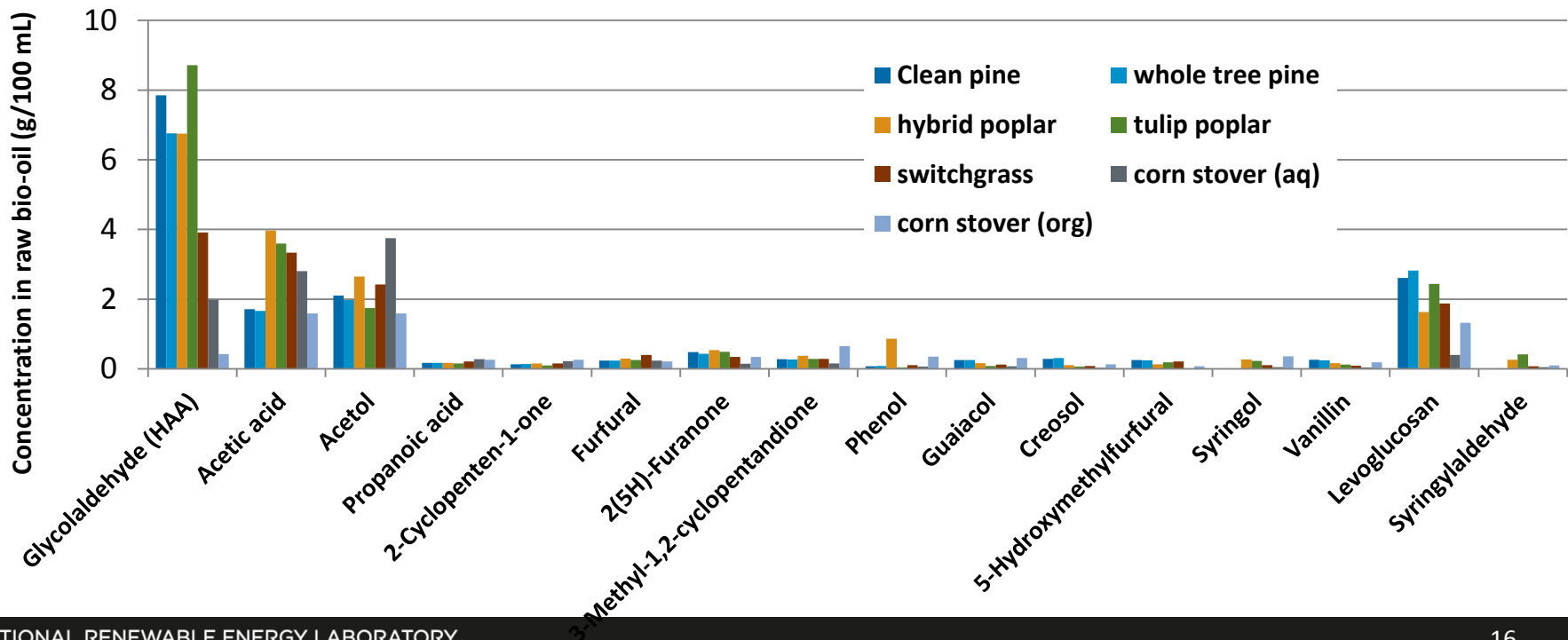
Fast pyrolysis results: product distributions

- Total liquid yields **52-71 wt%**
- Water in bio-oil **18-37 wt%**
- Char yields **9-19 wt%**
- Gas yields **14-22 wt%**
- Carbon conversion **45(CS)-70(TP) wt% of feed**
- Average mass balance **94% (87% for C)**



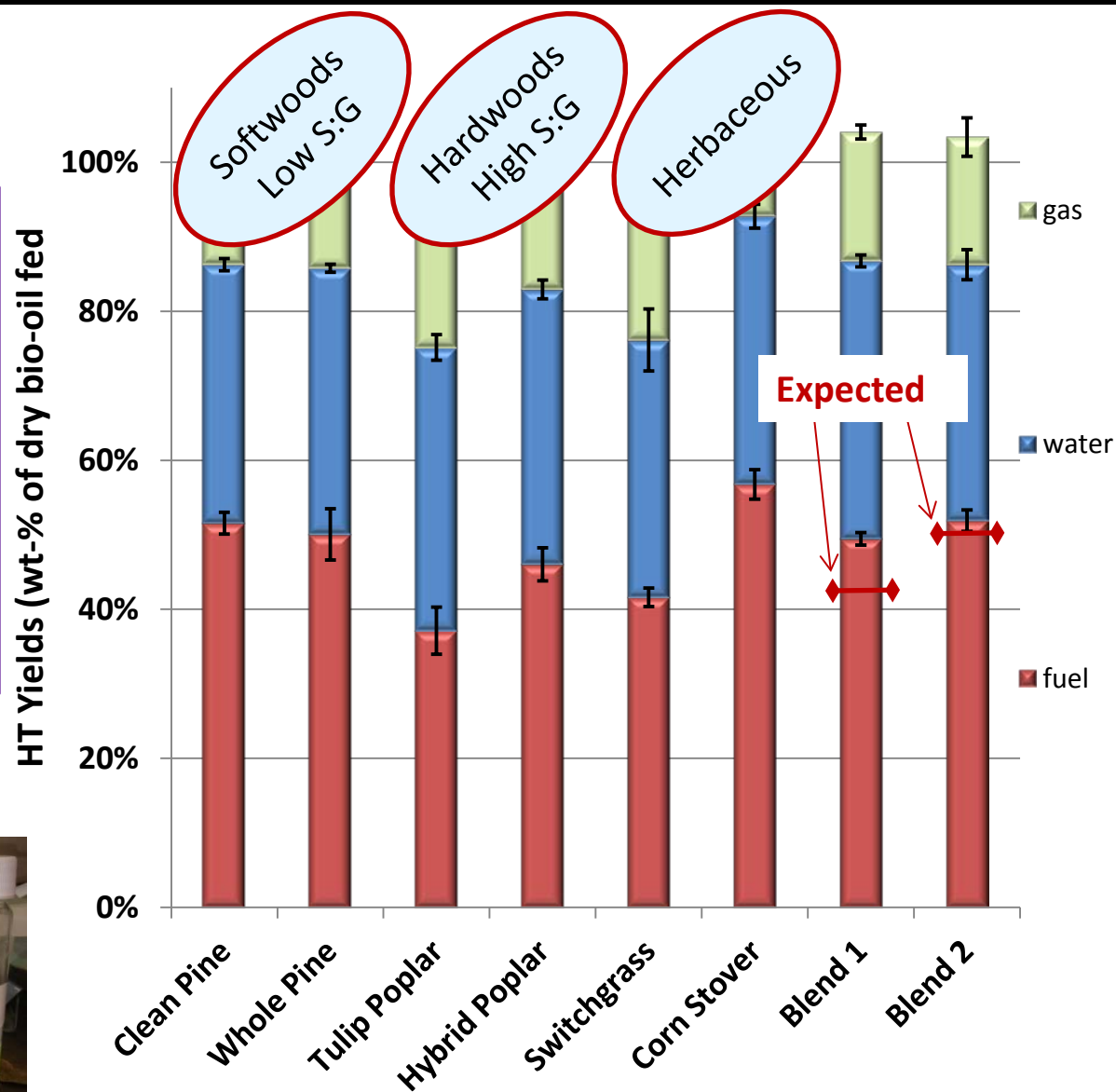
Fast pyrolysis results: bio-oil properties

	Clean pine	Whole tree pine	Hybrid poplar	Switchgrass	Corn stover (48 _{aq} /52 _{org})	Tulip poplar	Blend #1	Blend #2
C (wt% as rec'd)	45	45	46	35	14/59	45	40	43
H (wt% as rec'd)	8	8	8	9	11/8	7.7	8.5	8
N (wt% as rec'd)	0.08	0.09	0.08	0.36	0.16/1.29	0.08	0.19	0.09
O (by diff.)	47	47	46	55	76/32	47	50	48
S (wt% as rec'd)	0.06	0.06	0.06	0.1	0.08/0.12	0.06	0.08	0.07
Water (KF-wt%)	21	23	21	37	72/10	19	27	26
TAN (mg/g KOH)	40	38	66	104	41/46	71	72	47
Viscosity (cP, 25°C)	83	92	60	17	2/773	101	39	44

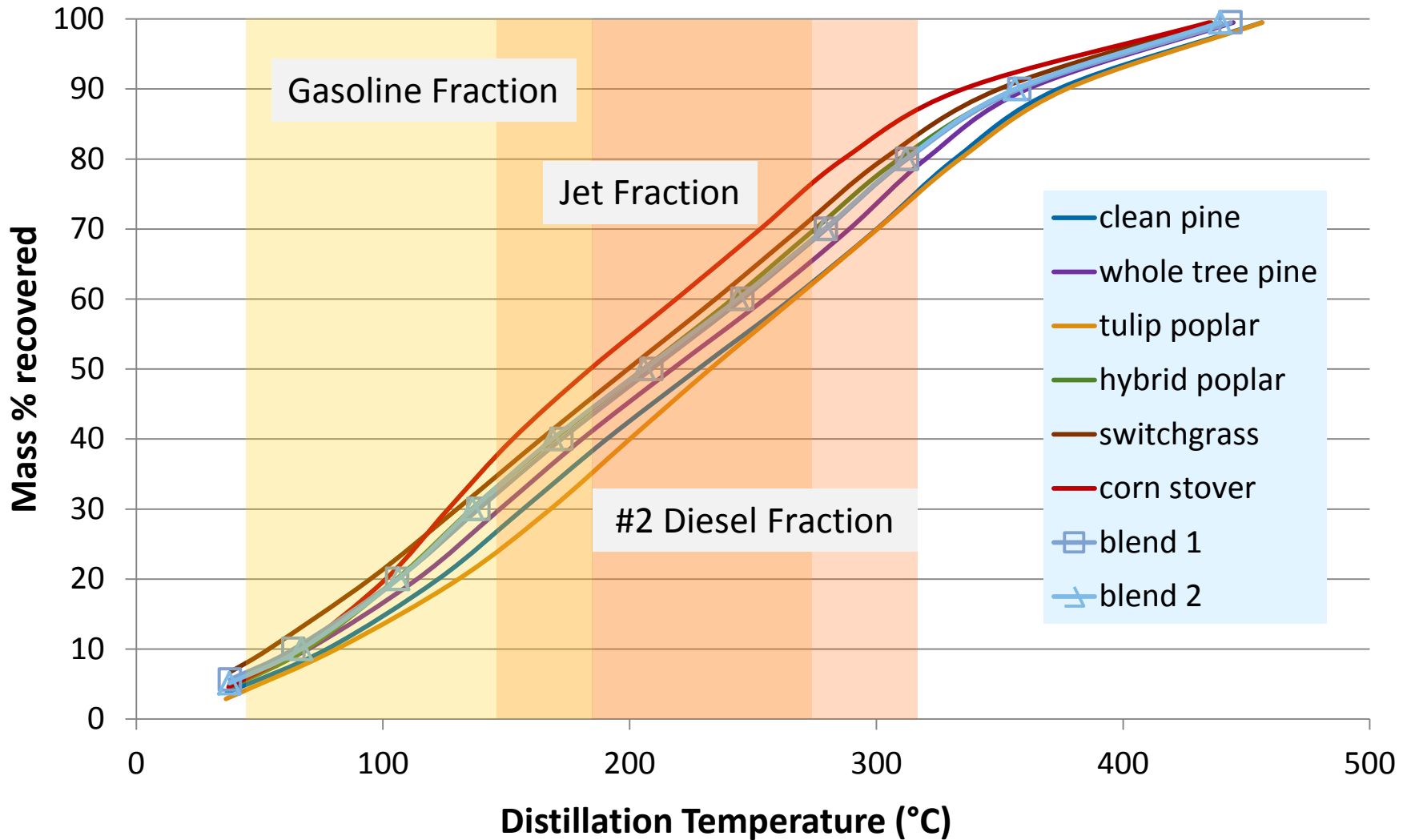


Catalytic hydrotreating results

- Fuel yields
37.2-56.8 (g/g dry oil)
- Water produced
34.3-39.8 g/g dry oil
- Gas yield
14.1-21.0 g/g dry oil
- H₂ consumption
53(CS)-70(CP) mg/g dry oil



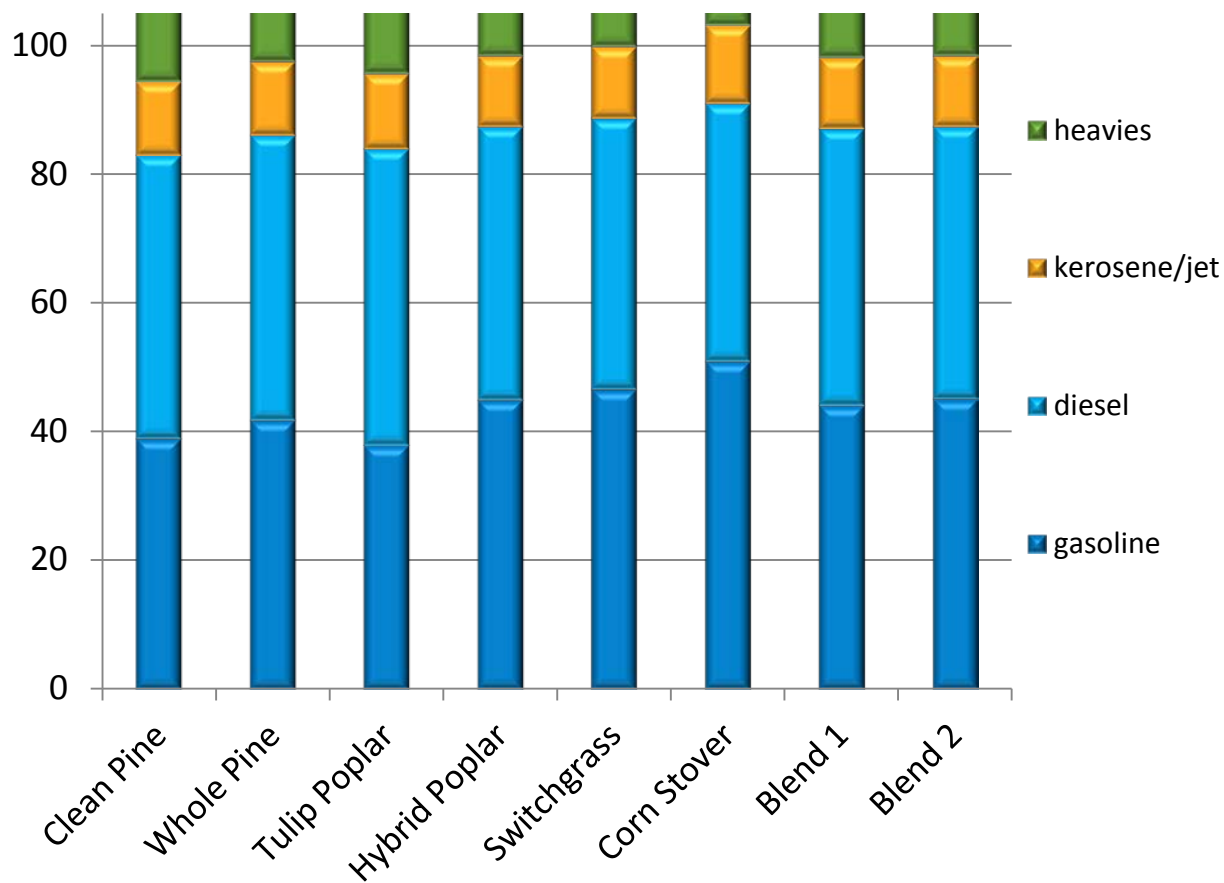
SimDis of final fuel blendstocks



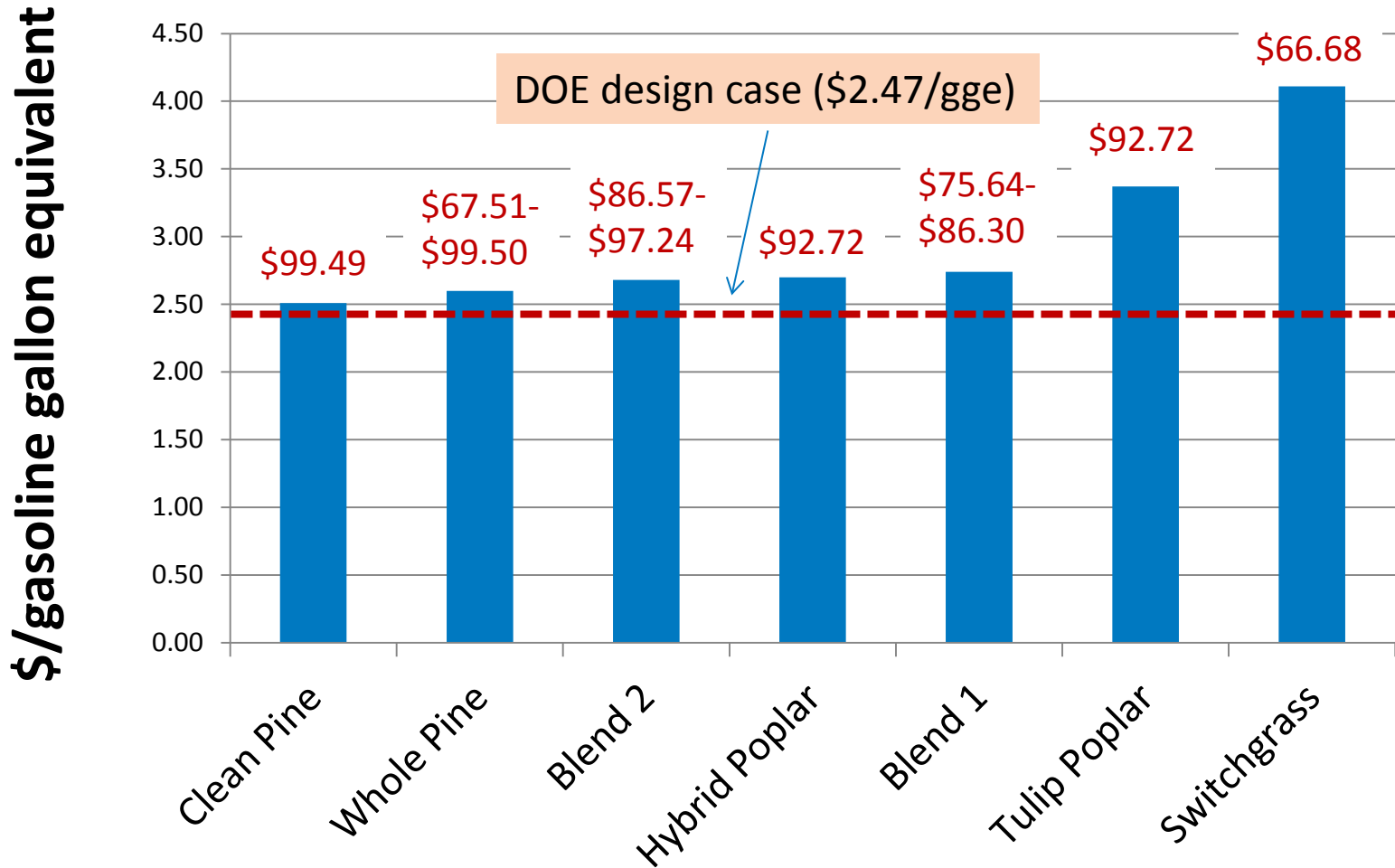
Hydrotreating summary

Fuel composition

Biomass Feedstock	Field-to-Fleet Yield (g fuel oil/ g biomass)
Clean Pine	27.2%
Whole Pine	24.9%
Tulip Poplar	22.3%
Hybrid Poplar	24.6%
Switchgrass	16.3%
Corn stover	19.3%
Blend 1	24.1%
Blend 2	24.1%



Preliminary Modeled Conversion Costs (excludes feedstock cost)



Summary

- **Feedstock affects everything downstream:**
 - **FP yields**
 - **Bio-oil composition**
 - **HT yields**
 - **Selectivity to fuel products**
- **S:G ratio may have negative effect on hydrotreating**
- **Blends aren't bad, demonstrated same performance for less \$**

Future work

- **Develop PLS model to predict bio-oil/fuel yields based on feedstock composition (INL)**
- **Test more blended materials (include other high-volume feedstocks: MSW, C&D waste, yard waste)**

Thank you for your attention!

Acknowledgements:



Stuart Black

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