Advancement of Bio-oil Utilization for Refinery Feedstock

Presented at the
The Washington Bioenergy Research Symposium
November 8, 2010

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Outline

- Introduction to PNNL
- Bio-oil upgrading by catalytic hydrogenation
- Status of process development

Pacific Northwest National Laboratory

A leader in
Fundamental Science
Energy & Environment
National Security

- $1 billion total revenue
- 4,500 staff
- Environmental Sciences User Facility
- One of seven labs managed by Battelle

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Maximizing the Impact of Biomass in the Pacific Northwest
Bioproducts, Sciences, and Engineering Laboratory

- New 57,000 ft^2 laboratory dedicated May 8, 2008
- Joint effort with Washington State University—about 15 WSU staff including four professors led by Dr. Birgitte Ahring
- 50 PNNL research staff
- $11 million in state-of-the-art equipment
  - Combinatorial catalysis, autoclave reactors, continuous flow reactors
  - Proteomics line, batch and continuous fermentors
  - High bay with pyrolysis and gasification units
  - Complete analytical support

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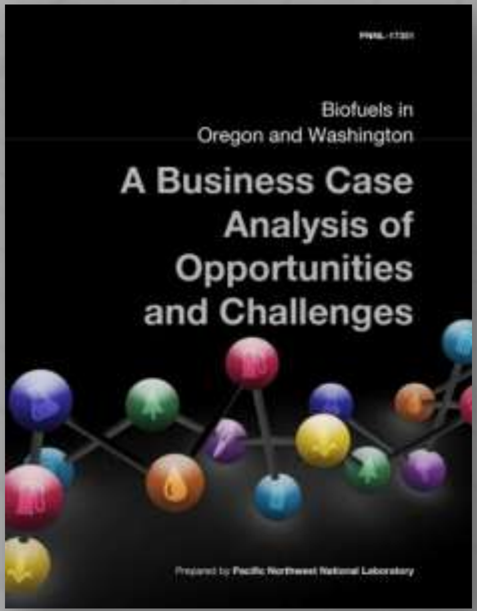
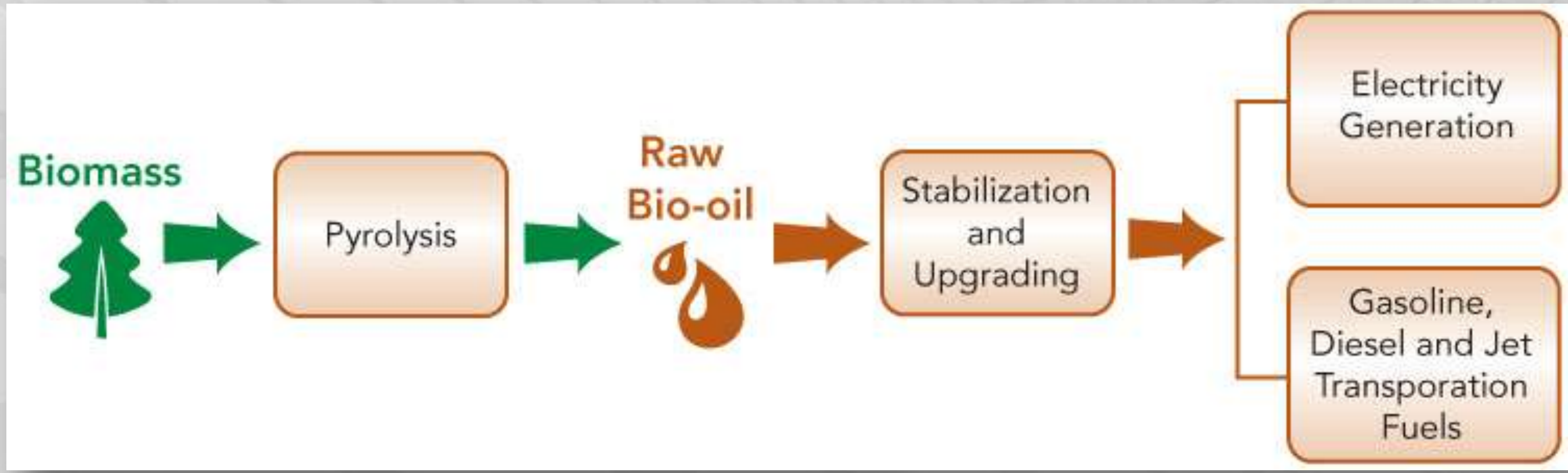
4

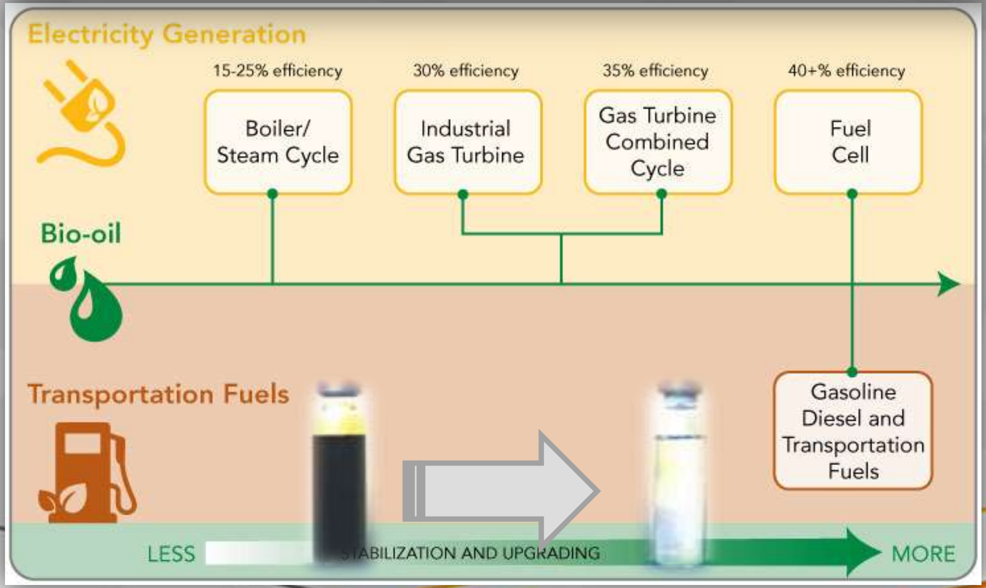
Thesis of our strategy at PNNL

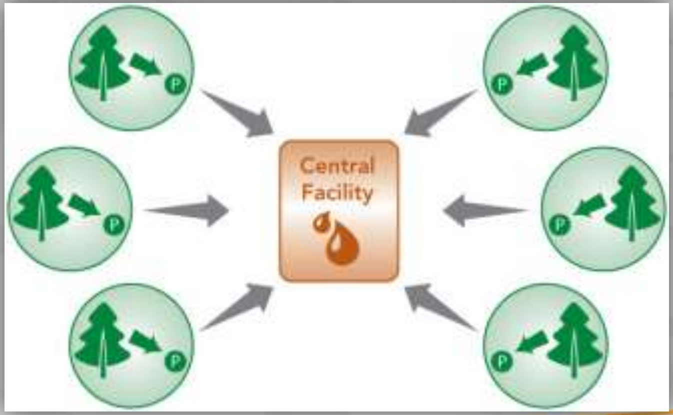
- Take biomass, as it is, and convert it *primarily* to liquid transportation fuels
  - Other renewable technologies produce electrons
  - Even as vehicle fleet are electrified, there will be a need for liquid fuels for heavy trucks and jets
- Focus on fuels that have high energy density and can be used without a blend wall
- Reduce overall cost by converting biomass into refinery ready materials that use today's infrastructure and distribution channels



Pyrolysis Oil Stabilization and Upgrading







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Comparison of Wood-Derived Bio-oils and Petroleum Fuel

Characteristic	Fast pyrolysis Bio-oil Wet --------- Dry		Heavy petroleum fuel
Water content, wt%	15-25		0.1
Insoluble solids, %	0.5-0.8		0.01%
Carbon, %	39.5	55.8	85.2
Hydrogen, %	7.5	6.1	11.1
Oxygen, %	52.6	37.9	1.0
Nitrogen, %	<0.1		0.3
Sulfur, %	<0.05		2.3
Ash	0.2-0.3		<0.1
HHV, MJ/kg	17		40
Density, g/ml	1.23		0.94
Viscosity, cp	10-150@50ºC		180@50ºC

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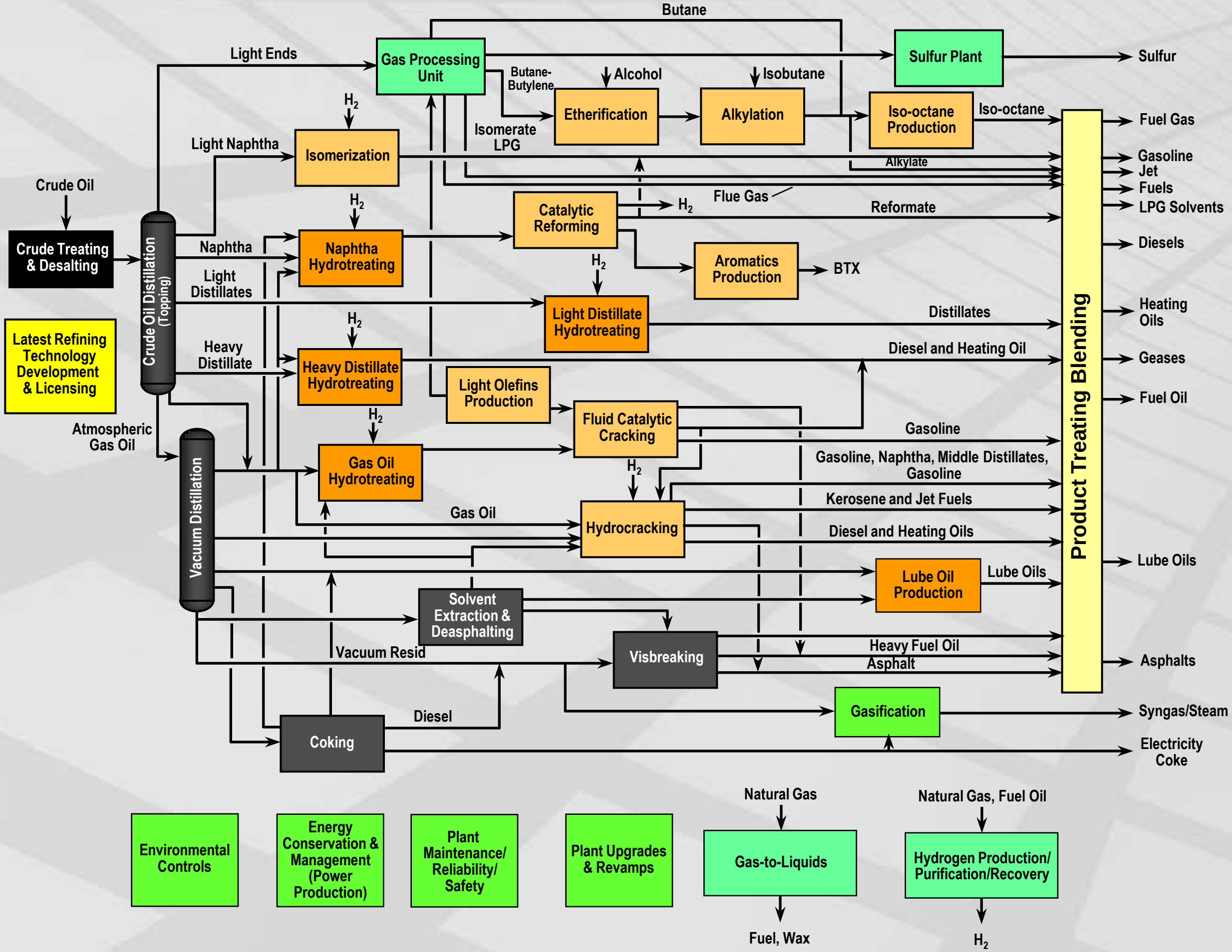
What Kind and Degree of Upgrading?

- First, determine final use …
  - Heavy fuel for boilers
  - Light fuel oil for diesel engine/power generation
  - Light fuel oil for power turbines
  - Refinery feedstock for transportation fuel production
  - Recovery of chemical products
- Determine upgrading requirement …
  - Physical upgrading
    - Solvent addition
    - Filtration
    - Separations
  - Chemical/catalytic upgrading

Petroleum Refining Context



- Refining: ~100 years
- ~750 refineries
- ~85M BBL of crude refined daily
- ~50M BBL transport fuels; ~6M BBL of aviation fuel (~250 M gallons/day; 90 B gallons/year)
- Complex but efficient conversion processes

Massive Scale
Technology Evolution Expected

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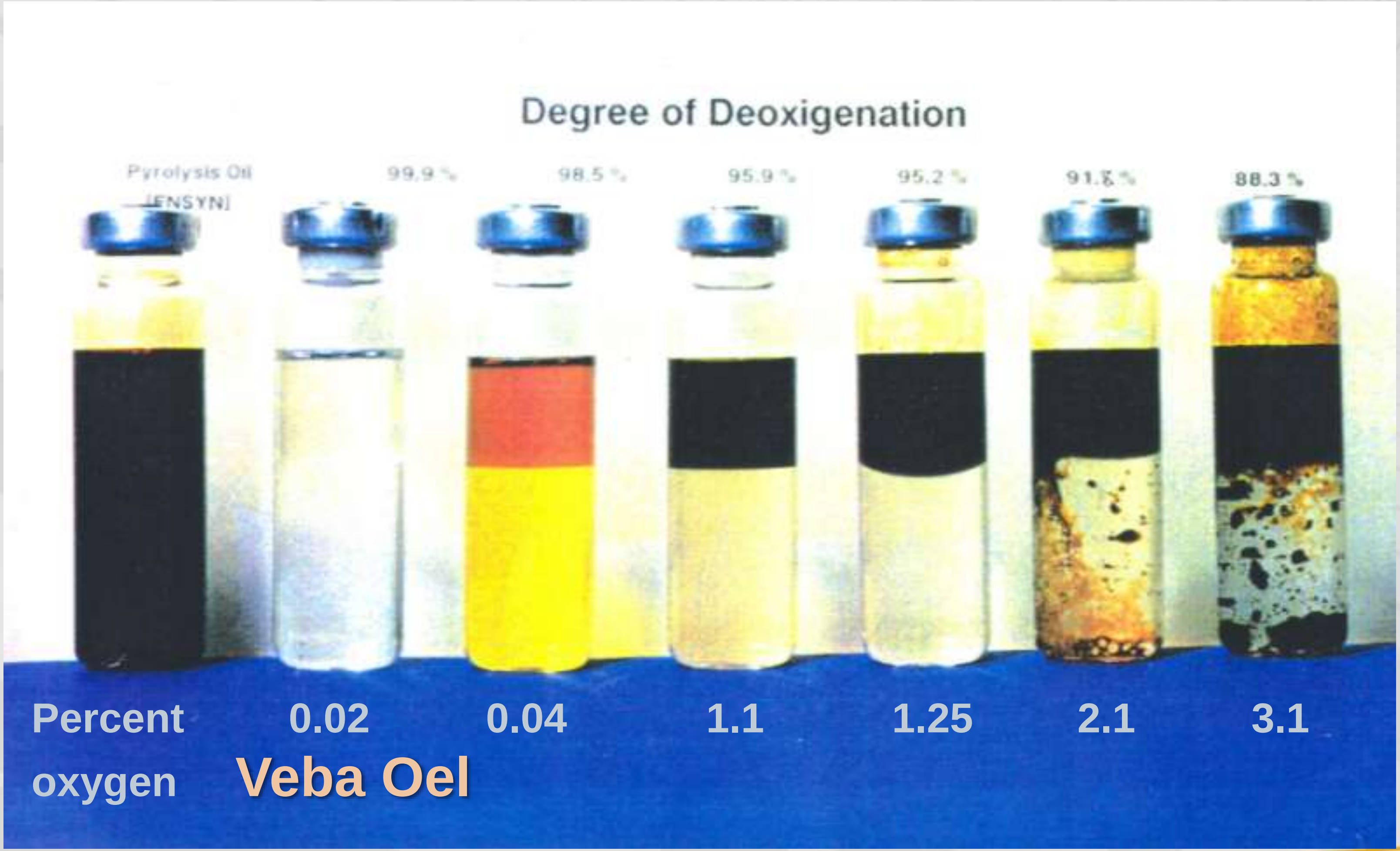
Pyrolysis Bio-oil Upgraded Products



Baldauf, W.; Balfanz, U. Veba Oel AG,
Final Report JOUB-0015, 1992

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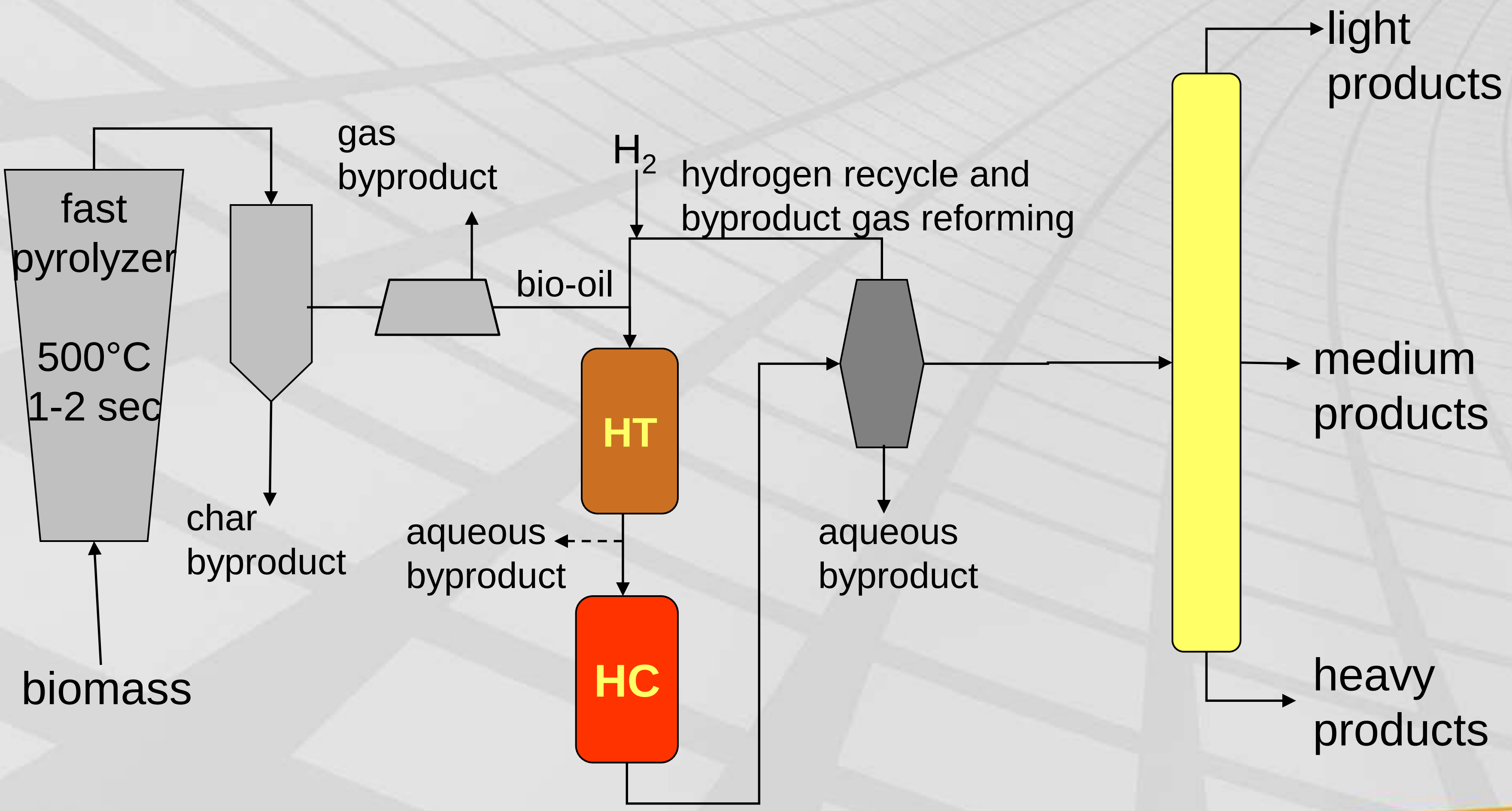
Hydrotreating of Pyrolysis Bio-oils



PNNL Contributions

- Chemical and physical analysis of wood and peat fast and slow pyrolysis oil

- 2-stage hydrotreating of pyrolysis oil for gasoline
  - Elliott, D. C. and E. G. Baker. "Process For Upgrading Biomass Pyrolyzates." U.S. Patent Number 4,795,841, issued January 3, 1989
  - Baker, E. G., and D. C. Elliott. "Method of Upgrading Oils Containing Hydroxyaromatic Hydrocarbon Compounds to Highly Aromatic Gasoline." U.S. Patent Number 5,180,868, issued January 19, 1993

- Non-isothermal hydrotreating for upgrading of pyrolysis oil to stable fuels

Catalytic Hydrogenation Development

- Early Work
  - Based on petroleum processing technology
  - Sulfided catalysts
  - Liquid hydrocarbon fuel products
  - Highly aromatic product
  - High hydrogen consumption
- Present Work
  - Optimized for bio-oil products
  - Non-sulfided catalysts
  - Liquid fuel and chemical products
  - Mixed hydrocarbon products
  - Targeted hydrogen consumption

Batch Reactor Testing

- Improved catalysts for bio-oil hydrogenation
  - ruthenium
  - palladium

- Small batch testing of model compounds
  - acetic acid
  - guaiacol (2-methoxyphenol)
  - furfural

Elliott, D.C. & Hart, T.R.
Energy & Fuels, *23,* 631-637, 2009.

Elliott, D.C. et al. U.S. Patent #7,425,657, September 16, 2008.

Recent Research Activities

- Continuous-flow bench-scale reactor tests have been performed to test catalysts and processing conditions.
  - 99 HT
  - 49 HC

- Recovered products are analyzed at PNNL and UOP to determine composition and value

Composition of Hydrotreated Bio-oils

340°C, 2000 psig, 0.25 LHSV

bio-oil source	H/C (dry)	C	H	O	N	S	H_2O	TAN
mixed wood	1.43	75.5	9.4	12.3	0.6	0.02	2.7	49
oak	1.35	74.2	9.0	14.5	0.1	0.01	5.7	NA
poplar (hot-filtered)	1.33	73.1	8.6	17.9	0.2	0.16	3.5	NA
corn stover	1.53	77.1	10.2	11.9	2.3	NA	2.9	60
corn stover light phase	1.28	76.2	8.5	15.5	2.4	NA	2.6	54
corn stover heavy phase	1.40	76.2	9.4	12.7	2.0	0.06	3.5	46

How much refining is required before pyrolysis oil can enter the refinery?

Elliott, et al. Environmental Progress & Sustainable Energy
28(3), 441-449; 2009

Hydrocracking Product Oil Chemical Components Determined by GC-MS/FID

Component Groups	O1	O2	O3	O4	Feed 1
unsaturated ketones	0.00%	0.00%	0.00%	0.00%	0.00%
carbonyls (hydroxyketones)	0.00%	0.00%	0.00%	0.00%	0.00%
naphthenes	70.77%	67.88%	69.67%	71.63%	4.22%
phenol and alkyl phenols	0.00%	0.00%	0.00%	0.00%	15.68%
alcohols & diols	0.00%	0.00%	0.00%	0.00%	22.67%
HDO aromatics	12.02%	14.05%	11.53%	12.82%	10.51%
Total saturated ketones	0.00%	0.00%	0.00%	0.00%	12.84%
Total acids & esters	0.00%	0.00%	0.00%	0.00%	11.89%
Total furans & furanones	0.00%	0.00%	0.00%	0.00%	0.00%
Total tetrahydrofurans	0.00%	0.00%	0.00%	0.00%	3.28%
guaiacols/syringols	0.00%	0.00%	0.00%	0.00%	18.91%
straight-chain/branched alkanes	11.72%	13.62%	13.18%	10.32%	0.00%
unknowns	5.49%	4.45%	5.62%	5.24%	0.00%
TOTAL	100.00%	100.00%	100.00%	100.00%	100.00%

390°C, 1500 psig, 0.12-0.23 LHSV

Elliott, et al. Environmental Progress & Sustainable Energy 28(3), 441-449; 2009

Composition of Non-isothermal Hydroprocessed Products

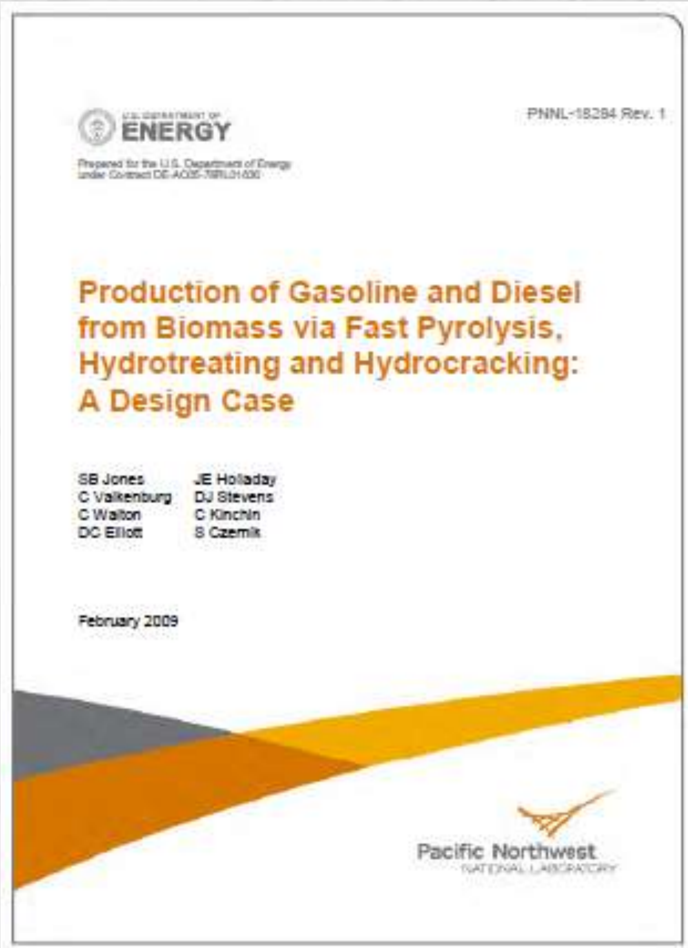
bio-oil source	C	H	O	N	S	moisture	density	TAN
mixed wood	87.7	11.6	0.6	<0.05	0.01	0.07	0.84	1.6
oak	87.7	11.7	0.3	0.05	0.06	0.04	0.84	0.8
corn stover	87.4	11.9	0.4	0.40	0.005	0.06	0.84	2.5
poplar	85.2	10.2	4.9	0.14	0.19	0.51	0.92	6.1

250-410°C, 2000 psig, 0.15 LHSV

Elliott, et al. Environmental Progress & Sustainable Energy 28(3), 441-449; 2009

Efficiencies

- 121 gallon of fuel/tonne of dry wood (requires 81 kg NG)
- 34 wt% yield from biomass to hydrocarbon fuel
- 61% thermal efficiency (Btu content of fuel out vs Btu of all inputs)
- 55% carbon yield (most of the "remainder" used for heat and power)


ENERGY

PNNL-18284 Rev. 1

Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case

SB Jones, C Valkenburg, C Walton, DC Elliott, JE Holladay, DJ Stevens, C Kinchin, S Czernik

February 2009

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Gasoline/Diesel Prospects

Bioderived fuel from corn stover
spinning band distillation

54% in gasoline range
IBP-193°C

35% in diesel range
193-325°C

10-20% heavies
>325°C

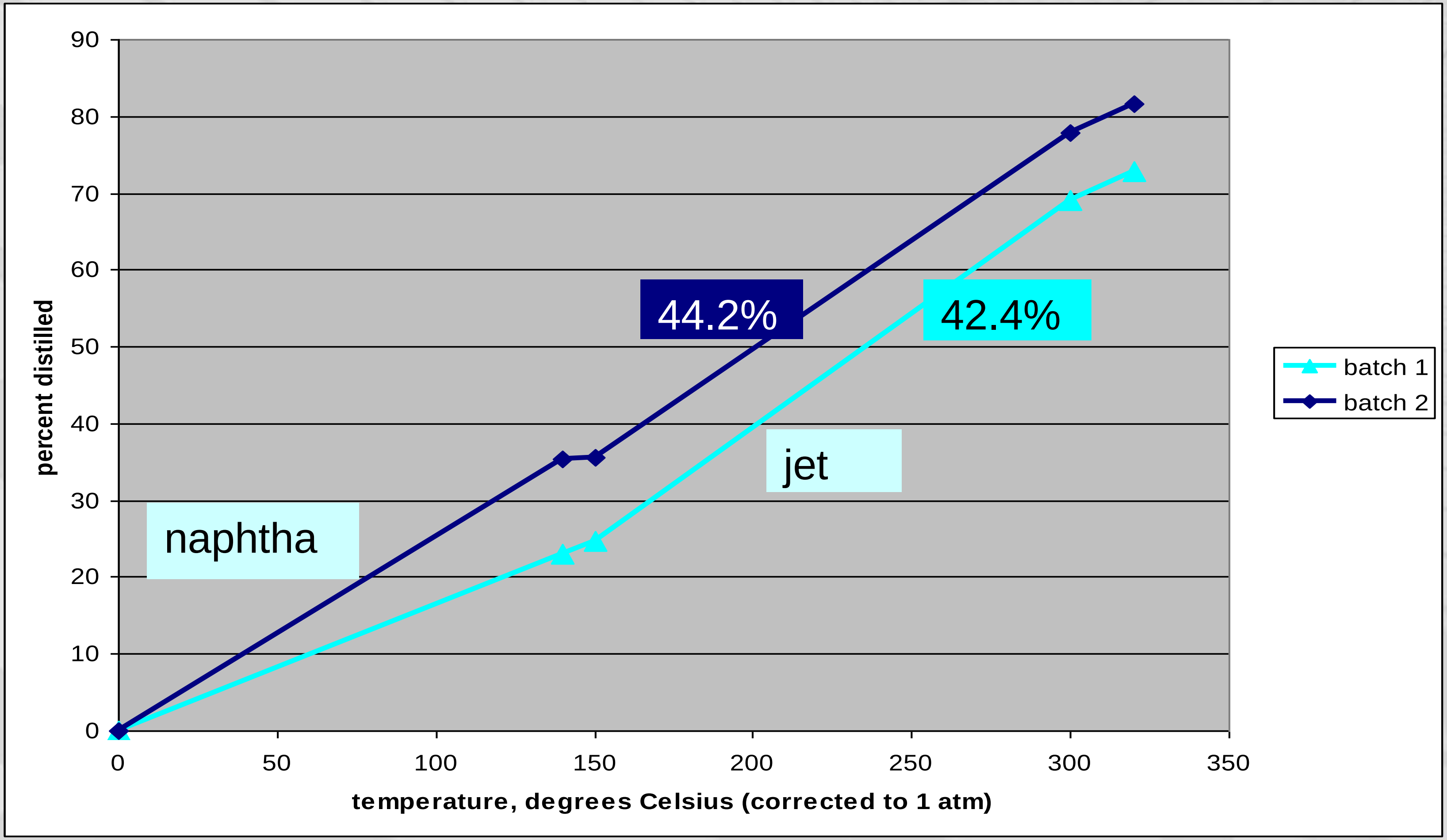
Gasoline Octane number
RON+MON/2=89

Cetane number
31.5

likely partially
converted feed

from: Timothy Brandvold, UOP LLC, “Pyrolysis Oil to Gasoline”
presented at the Thermochemical Portfolio Alignment and Peer Review
April 15, 2009, Denver, CO
http://obpreview2009.govtools.us/thermochem/documents/UOP_Project.PyOilGasoline.Final.pdf

Vacuum Distillation Curves for Hydroprocessed Bio-oil



The Future: 100% Renewable Jet

UOP A Honeywell Company

Pacific Northwest National Laboratory

The hydroplane ran on 98% Bio-SPK and 2% renewable aromatics

	Jet A1 Spec	***Starting SPK***	***Woody Pyrolysis Oil Aromatics***
Freeze Point (^{o}C)	**-47**	**-63**	**-53**
Flash Point (^{o}C)	**39**	**42**	**52**
Density (g/mL)	**0.775**	**0.753**	**0.863**

Integrated Biorefinery Demonstration Kapolei, Hawaii

- $25 M DOE funded with industrial cost share
- UOP LLC, Ensyn, PNNL, Tesoro, and many others
- Integrated pyrolysis and hydroconversion
- Demonstrate fungibility within the petroleum refinery and determine fuel properties
- 1 ton/day = 4 bpd renewable gasoline, diesel, jet fuel
- Accelerate liquid transportation fuel production
- Detailed life cycle assessment and growth potential
- Commercialization plan includes 4 RTP units and 1 upgrading unit to produce 50 million gallons of fuels annually

Conclusions

- Biomass conversion to liquid fuels via pyrolytic processes and catalytic hydroprocessing is under development.
- Interesting yields of hydrocarbon liquid products have been demonstrated at the bench-scale.
- Improved understanding of process steps and product properties is developing.
- Process economics are promising in the current economic environment.
- Scale-up is envisioned in the near term.

Thank You!

Acknowledgement:

Pyrolysis
Todd Hart
Gary Neuenschwander
DM Santosa
LJ Rotness
Alan Zacher

Technoeconomic Analysis
Sue Jones
Corinne Valkenburg

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