

U.S. Department of Energy Energy Efficiency and Renewable Energy

# U.S. Department of Energy Biomass Program

# Pyrolysis - A Promising New Path to Liquid Fuels



#### The Future of Forest Biomass in Colorado

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While the growing need for sustainable electric power can be met by other renewables...

Biomass is the only renewable that can meet our demand for carbon-based liquid fuels and chemicals



#### **Biomass Program**

#### **Office of Biomass Programs - Technology Development Drivers**



#### **OBP Vision, Mission and Performance Goals**



## Program Targets Energy Independence Security Act 2007

#### Renewable Fuel Standard (RFS), 2007-2022



#### Source: Hart Energy Consulting, Government Affairs 2007



**Research Focus on the Biorefinery** 





### **Basic Definitions**

#### Combustion

•Thermal conversion in the presence of excess oxygen for production of heat

#### Gasification

- Thermal conversion of organic materials at elevated temperature and reducing conditions to produce primarily permanent gases, with char, water, and condensibles as minor products
- Primary categories are partial oxidation and indirect heating

### **Pyrolysis**

- Thermal conversion (breakdown) of organics in the absence of oxygen
- In the biomass R&D community, this commonly refers to lower temperature thermal processes producing liquids as the primary product



#### **Biomass Constituents**

### Lignin: 15-25%

- \* Complex network of aromatic compounds
- \* High energy content

#### Hemicellulose: 23-32%

Polymer of 5 & 6 carbon sugar

#### Cellulose: 38-50%

\* Polymer of glucose, very good biochemical feedstock





#### **Thermochemical Pathways**





- Rapid heat transfer in the absence of oxygen
- Short residence time at temperature (msec)
- Rapid thermal quenching of vapor products
- Products = Gas (15%), Char (15%), Liquids (70%)





## Fast Pyrolysis Bio-oil

Bio-oil is water miscible and is comprised of many oxygenated organic chemicals.

- Combustible,
- Not miscible with hydrocarbons,
- Heating value ~ 17 MJ/kg,
- Density ~ 1.2 kg/l,
- Acid, pH ~ 2.5,
- Pungent odour,
- "storage stability" viscosity increases with time





Component	Wt% of Bio-oi	
Hydroxyacetaldehyde	5-12	
Acetic acid	3-9	
Formic acid	1-4	
Acetol	3-7	
Glyoxal	1-2	
Levoglucosan	2-5	
Water	15-30	
Pyrolytic lignin	15-30	

Over 300 individual compounds have been identified in bio-oil



## **Bio-oil properties change during storage**

- Increase in viscosity
  - rate = 2.317\*10<sup>13</sup> exp(-9659/T) cP/day

Diebold, J.P.; Czernik, S., *Energy&Fuels* 1997, 11, 1081.

- Decrease volatility
- Phase separation
- Formation of gums and deposits Instability is caused by chemical reactions occurring between certain compounds that lead to molecular growth



## Market Potential for Bio-Oil







# **Different claims for the cost of production:**

- Ensyn \$14-16 / bbl
- **BTG** \$21 / bbl

# Cost = Wood cost/10 + 8.87 \* (Wood throughput)<sup>-0.347</sup> \$/GJ \$/dry ton dry t/h

Source: A.V. Bridgwater, A Guide to Fast Pyrolysis of Biomass for Fuels and Chemicals, PyNe Guide 1, www.pyne.co.uk



#### Estimated Biofuels Cost of Production \$2005, 100% Equity, \$35/dry ton feed





## **Bio-oil as Refinery Feedstock**



Hydrocracking

#### Technical Issues

- Improve storage stability
- Lower acid number

Source: Historical Developments in Hydroprocessing Bio-oils, Energy & Fuels May 2007, 21, 1793-1815



## Yields for Hydroprocessed Bio-oil

Feed	Wgt %
Bio-oil	100
H2	3-4.5
Products	
Naptha Range	21
Diesel Range	21
CO2, H2O, Light Hydrocarbons	62

Source: UOP Presentation to National Petroleum Refiners Association, February 2008



## Hydroprocessed Bio-oil Product Composition

Hydroprocessed bio-oil (from mixed wood)			Gasoline
	Min	Max	Typical
Paraffin, wt%	5.2	9.5	44.2
Iso-Paraffin, wt%	16.7	24.9	
Olefin, wt%	0.6	0.9	4.1
Naphthene, wt%	39.6	55.0	6.9
Aromatic, wt%	9.9	34.6	37.7
Oxygenate, wt%		0.8	



## **Bio-oil Hydrocarbon Product Cost Estimates**

	From Wood	From Corn Stover
Production Cost \$/gal	2.01	1.80
Production Cost ethanol equivalent \$/gal	1.27	1.13
Gal ethanol equivalent / ton	148	126
% carbon recovery	~45	~45



# Terra Preta (Dark Earth)



Addition of char to soil



- Bio-char is highly stable in soil and can persist thousands of years.
- Enhanced nutrient retention mechanism (water retention, microbial & fungus habitat, minerals)
- May offer potential for significant carbon sequestration (~3 tons CO2/ton char)
- Positive effects inconclusive in some geographical regions (needs further study)



Terra Preta Soil



"Normal" Soil

Source:2007 Grossman J.M., Farmers' understanding of soil processes. Low External Input and Sustainable Agriculture (LEISA). Issue title: "Ecological Processes at Work" 22(4):24.



- Long term access to forest resources on public lands (stewardship contracts)
- Payments to lignocellulosic biomass suppliers for residues and energy crops
- Alternative Fuel Subsidies applied equally to all fuels (incentivise biomass content-not the product fuel)
- Valuation of sequestered carbon



Ramp-up of biofuels production will require innovative and focused policies for infrastructure and biomass feedstocks



#### Multiple Benefits of Bio-oil to Hydrocarbon Fuel Technology

- Biomass domestic fuel production can displace significant amounts of petroleum based fuel
- Commercial viability appears favorable for the near term (5-10 years)
- CO2 sequestration with biomass pyrolysis and char incorporation in soil can potentially be a net <u>negative</u> carbon sink
- Terra Preta soil enhancement can potentially improve forest health and agricultural productivity
- Emerging industry for domestic jobs in rural economies
- Appropriate forest management can benefit long term forest health and minimize fire risk