## Fast Pyrolysis and Bio-Oil Upgrading

Robert C. Brown Iowa State University and Jennifer Holmgren UOP

## Fast Pyrolysis

- Rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquids, char, and gas
  - Dry feedstock: <10%</li>
  - Small particles: <3 mm</p>
  - Short residence times: 0.5 2 s
  - Moderate temperatures (400-500 °C)
  - Rapid quenching at the end of the process
  - Typical yields
    - Oil: 60 70%
    - Char: 12 -15%
    - Gas: 13 25%

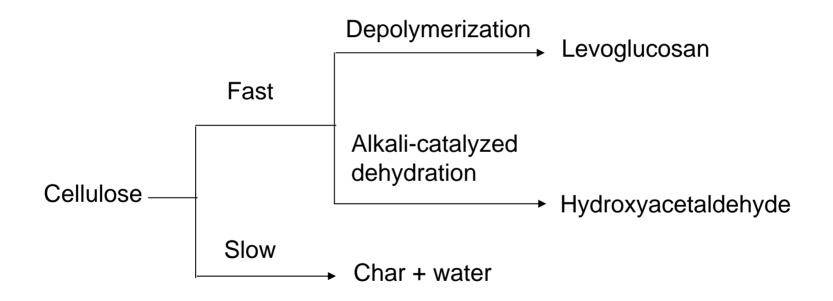
## **Bio-Oil**

Pyrolysis liquid (bio-oil) from flash pyrolysis is a low viscosity, dark-brown fluid with up to 15 to 20% water



Source: Piskorz, J., et al. In Pyrolysis Oils from Biomass, Soltes, E. J., Milne, T. A., Eds., ACS Symposium Series 376, 1988.	White Spruce	Poplar
Moisture content, wt%	7.0	3.3
Particle size, µm (max)	1000	590
Temperature	500	497
Apparent residence time	0.65	0.48
Product Yields, wt %, m.f.		
Water	11.6	12.2
Gas	7.8	10.8
Bio-char	12.2	7.7
Bio-oil	66.5	65.7
Bio-oil composition, wt %, m.f.		
Saccharides	3.3	2.4
Anhydrosugars	6.5	6.8
Aldehydes	10.1	14.0
Furans	0.35	
Ketones	1.24	1.4
Alcohols	2.0	1.2
Carboxylic acids	11.0	8.5
Water-Soluble – Total Above	34.5	34.3
Pyrolytic Lignin	20.6	16.2
Unaccounted fraction	11.4	15.2

## Multiple reaction pathways for pyrolysis of cellulose



## Fast Pyrolysis

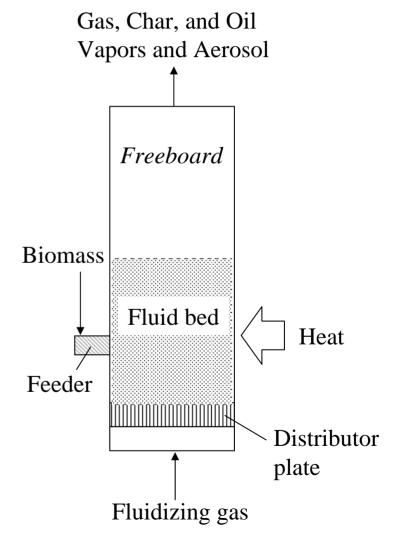
- Advantages
  - Operates at atmospheric pressure and modest temperatures (450 C)
  - Yields of bio-oil can exceed 70 wt-%
- Disadvantages
  - High oxygen and water content of pyrolysis liquids makes them inferior to conventional hydrocarbon fuels
  - Phase-separation and polymerization of the liquids and corrosion of containers make storage of these liquids difficult

## Several Kinds of Fast Pyrolysis Reactors

- Bubbling fluidized bed
- Circulating fluidized beds/transport reactor
- Rotating cone pyrolyzer
- Ablative pyrolyzer
- Vacuum pyrolysis
- Auger reactor

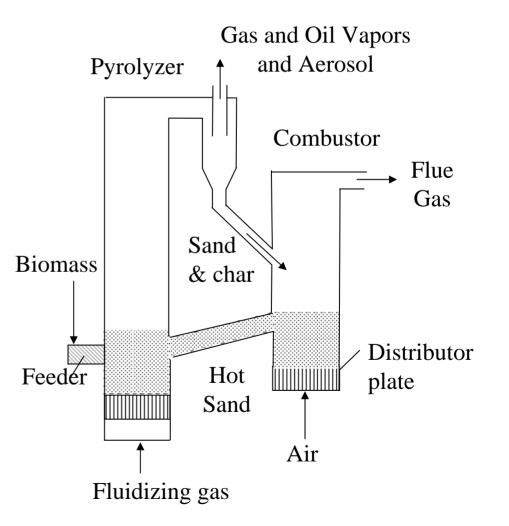
## **Bubbling Fluidized Bed**

- Heat supplied externally to bed
- Good mass & heat transfer
- Requires small biomass particles (2-3 mm)



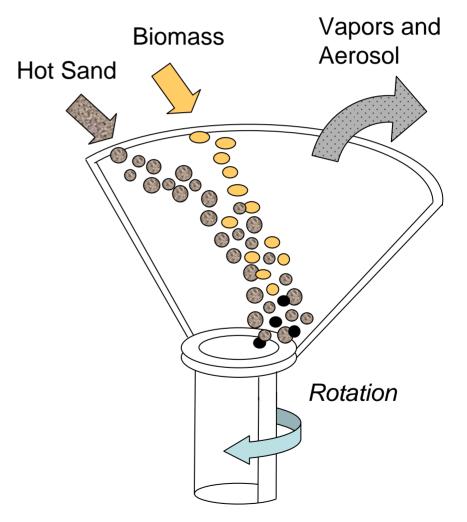
## Circulating Fluidized Bed/Transport Reactor

- Hot sand circulated between combustor and pyrolyzer
- Heat supplied from burning char
- High throughputs but more char attrition



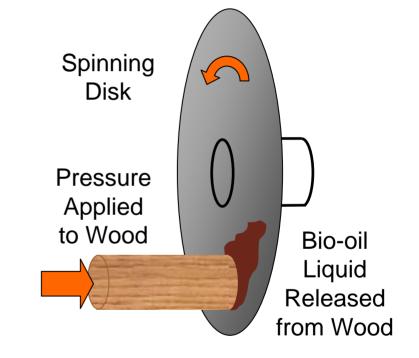
## **Rotating Cone Pyrolyzer**

- Sand and biomass brought into contact within rotating cone
- Compact design and does not need carrier gas
- Requires very small biomass particles and is hard to scale-up



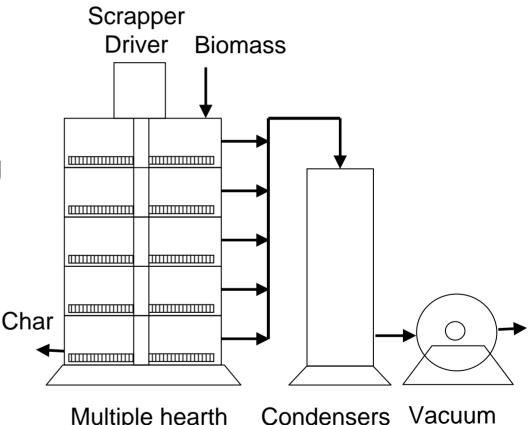
## Ablative Pyrolyzer

- High pressure of particle on hot reactor wall achieved by centrifugal or mechanical motion
- Can use large particles and does not require carrier gas
- Complex and does not scale well



## Vacuum Pyrolysis

- Biomass moved by gravity and rotating scrappers through multiple hearth pyrolyzer with temperature increasing from 200 C to 400 C
- Can use larger particles and employs little carrier gas
- Expensive vacuum pump and difficult to scale-up

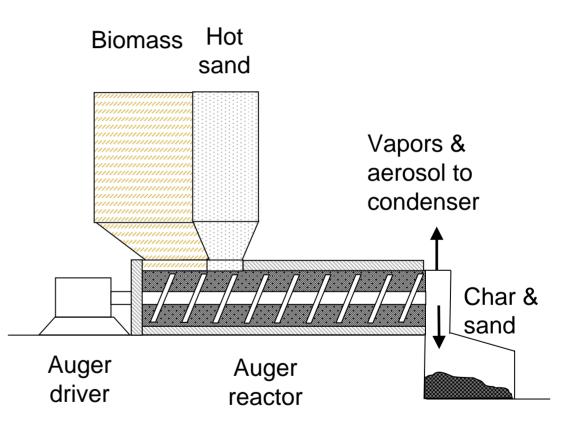


pump

Multiple hearth vacuum pyrolysis reactor

## Auger Reactor

- Hot sand and biomass mixed by auger
- Suitable for small scale
- Requires hot sand heating and circulation system

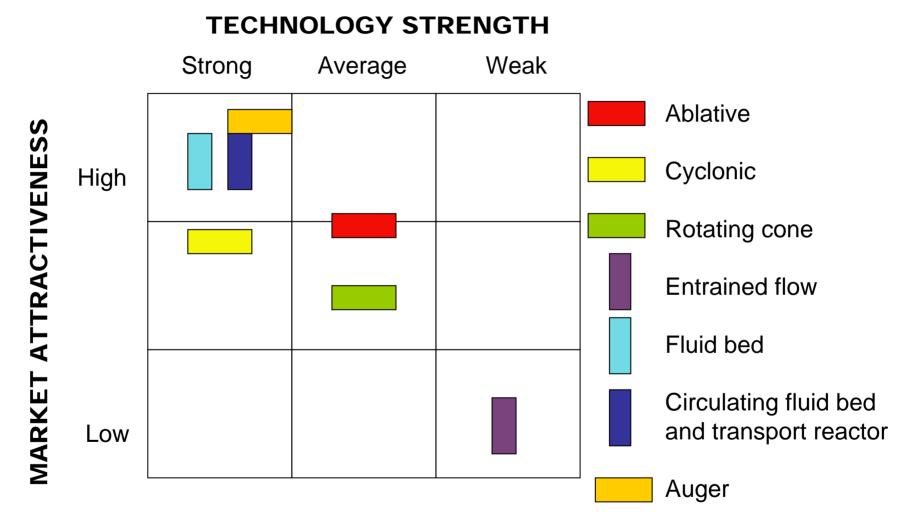


## **Relative Merits of Various Reactors**

Property	Status	Bio- oil wt%	Comp- lexity	Feed size	l nert gas need	Specific size	Scale up
Fluid bed	Demo	75	Medium	Small	High	Medium	Easy
CFB	Pilot	75	High	Medium	High	Large	Easy
Entrained	None	65	High	Small	High	Large	Easy
Rotating cone	Pilot	65	High	V small	Low	Small	Hard
Ablative	Lab	75	High	Large	Low	Small	Hard
Auger	Lab	65	Low	Small	Low	Medium	Easy
Vacuum	Demo	60	High	Large	Low	Large	Hard
The darker th desirable the		or, the le	F	_ab: 1 – 20 Pilot: 20 – 2 Demo: 200	200 kg ł		

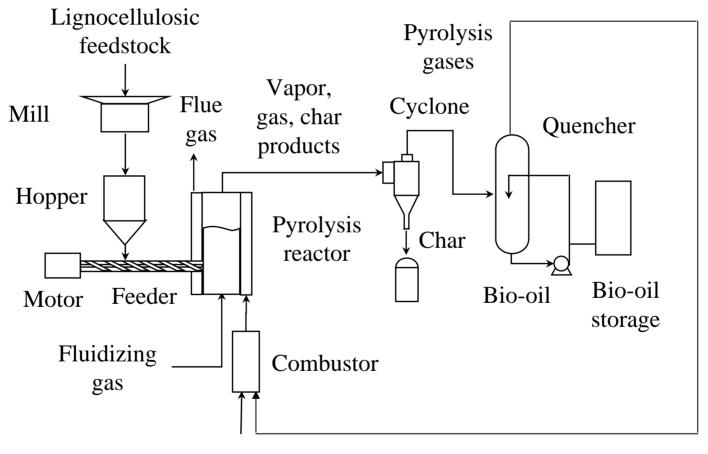
Adapted from PYNE IEA Bioenergy http://www.pyne.co.uk

## Which will dominate?



Adapted from PYNE IEA Bioenergy http://www.pyne.co.uk

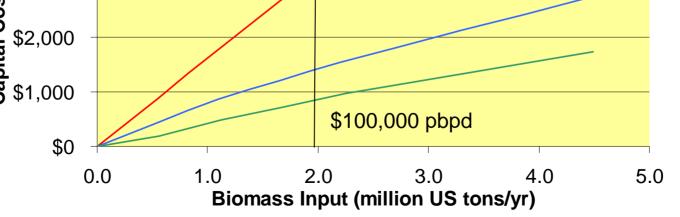
## Fast Pyrolysis System





#### Scale

Diesel Output (million US gallons/yr) 0 50 100 150 200 250 \$8,000 Small gasification (multiple units 110,000 US ton/yr) + small FT multiple units **Capital Cost (million 2005 US dollars)** (million 2005 US dollars) (m Small pyrolysis (multiple units 110,000 US ton/yr) + large FT Large gasification + large FT \$400,000 pbpd



Adapted from: Bridgwater, ACS Meeting, Washington, D.C., 2005

## Suitable Feedstocks

- Wide variety of feedstocks can be used
- Fibrous biomass usually employed
- Wood higher yielding than herbaceous biomass

## Storage & Transportation

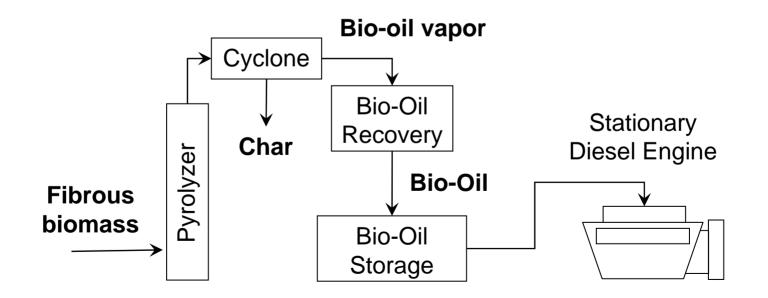
- Distributed preprocessing allows transport and storage as liquid
- High acidity requires storage in stainless steel or plastic
- Stability problems need to be solved

## Post Processing to Motor Fuels

- Direct application of bio-oil
- Hydrocracking of bio-oil
- Gasification of bio-oil
- Fermentation of Bio-oil

### **Bio-Oil Burned in Diesel Engines**

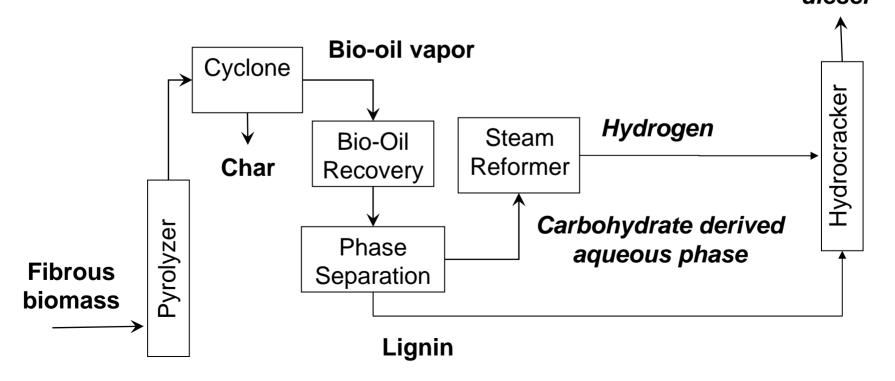
- Bio-oil used as directly as diesel fuel substitute
- Only suitable for stationary power applications



### **Bio-Oil Hydrocracking**

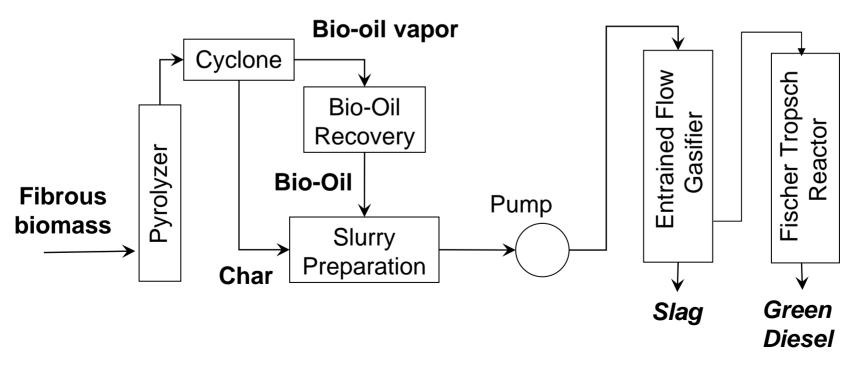
- Directly converts biomass into liquid bio-oil (lignin, carbohydrate derivatives, and water) and char
- Bio-oil catalytically converted into hydrocarbon fuel (green diesel)

Green diesel

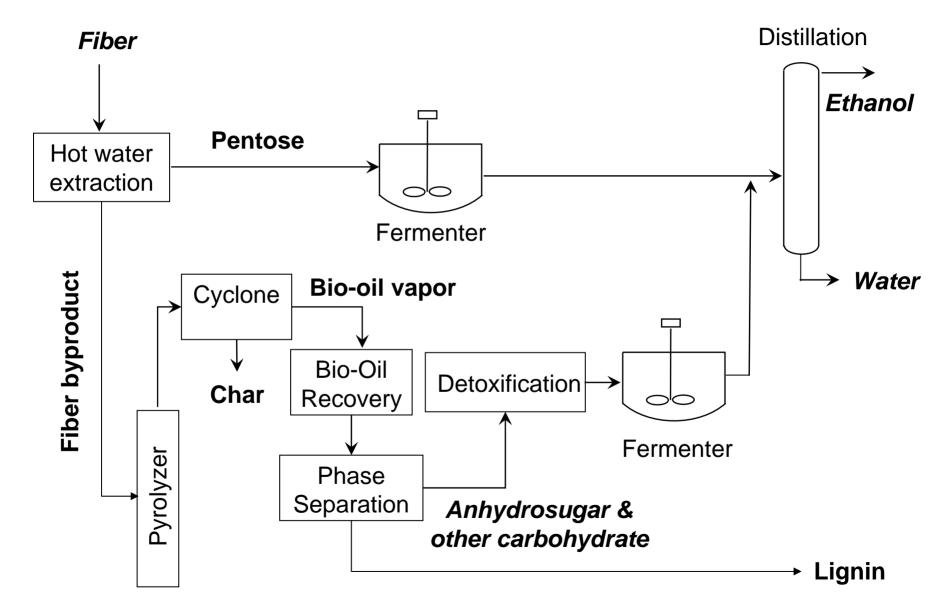


### **Bio-Oil Gasification**

- Bio-oil and char slurried together to recover 90% of the original biomass energy
- Slurry transported to central processing site where it is gasified in an entrained flow gasifier to syngas
- Syngas is catalytic processed into green diesel (F-T liquids)



#### **Bio-Oil Fermentation**

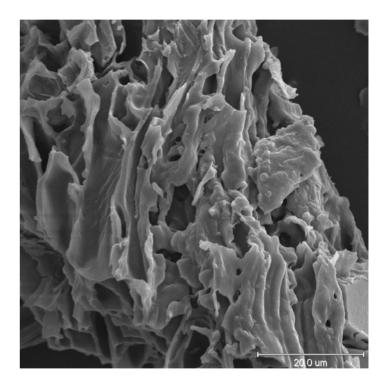


## Energy Efficiency

- Conversion to 75 wt-% bio-oil translates to energy efficiency of 70%
- If carbon used for energy source (process heat or slurried with liquid) then efficiency approaches 94%

## **Co-Products**

- Gas (CO, H2, light hydrocarbons)
  - Can be used to heat pyrolysis reactor
- Char: Several potential applications
  - Process heat
  - Activated carbon
  - Soil amendment



## Potential Co-Products from Bio-Oil

Products of pyrolysis for several different pretreatments of cornstover (Brown et al. 2001)

	No Pretreatment	Acid Hydrolysis	Acid Wash	Acid Wash with catalyst
Products (Wt% maf)				
Char	15.8	13.2	13.2	15.9
Water	2.57	10.6	10.4	7.96
Organics	59.1	67.2	68.5	67.7
Gases	22.6	9.02	7.88	8.44
Organics (Wt %)				
Cellobiosan	trace	4.55	3.34	4.97
Levoglucosan	2.75	17.69	20.12	23.10
Hydroxy-acetaldehyde	11.57	5.97	3.73	3.93
Formic acid	2.61	Trace	Trace	0.73
Acetic acid	3.40	1.51	1.26	0.40
Acetol	4.53	trace	trace	trace
Formaldehyde	2.75	1.63	trace	0.70
Pyrolytic lignin	33.40	16.89	17.74	20.08

## **Quality Assurance**

- Bio-oil quality issues:
  - Moisture content
  - Particulate content
  - Sulfur and nitrogen content
  - Stability

## **Equipment Maintenance**

- Potential problems with pyrolysis equipment
  - Bed agglomeration
  - Clogging of condensers
  - ESP performance
- Catalytic reactors
  - Poisoning by sulfur and chlorine
  - Coking

## Waste Streams

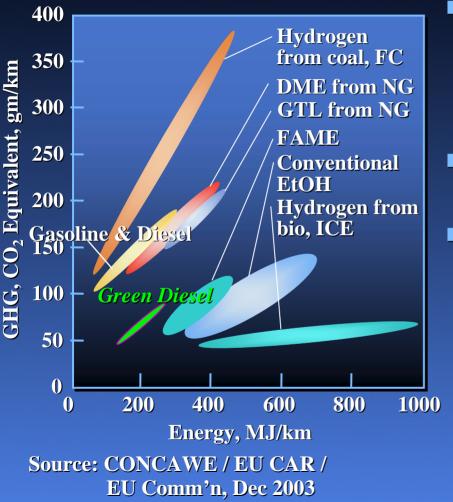
 Main products (gas, char, bio-oil) account for all mass of biomass feedstock

## **Technical Barriers**

- Preparing dry, finely divided biomass particles
- Maintaining high bio-oil yields
- Improving bio-oil stability
- Determining optimal scale of facility

### Alternative Fuels: Targets

#### WTW Energy /GHG Emissions Clusters



Alternative fuels may need to target:

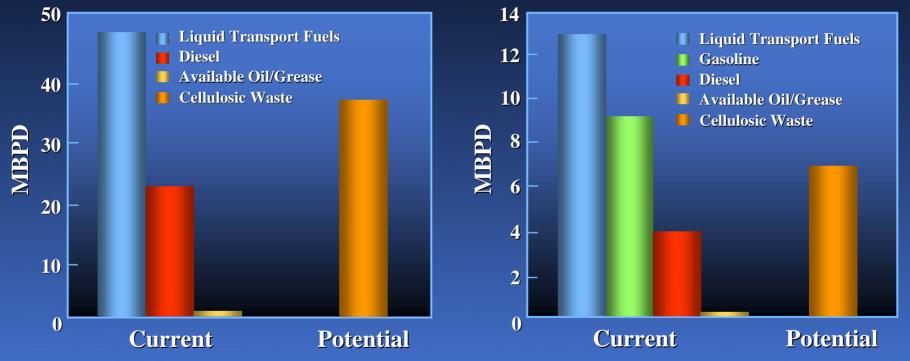
- $< 100 \text{ gm CO}_2/\text{km WTW}$
- GTL, DME from gas close, but not there yet
- Several other alternatives in study (not shown for simplicity)
- Engine manufacturers developing more efficient advanced ICE's in addition to hybrids and FC's
  - Variable DI gasoline
  - "Part Homogeneous" diesel combustion
  - "Combined Combustion" systems
  - Improve fuel efficiency

Gasoline & Diesel in Advanced ICE's Set Tough Targets!

### Biorenewables and Petroleum Feeds: Relative Availability

#### Global

#### US



Available Cellulosic Biomass Could Make a Significant Impact in Fuels Pool

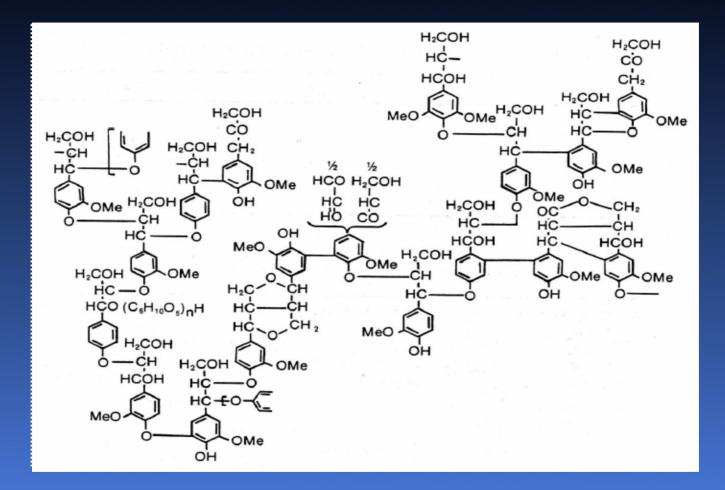


Py Oil Portfolio





#### **Lignin Molecular Structure**





### Treating Technologies Hydrotreating

- Hydrotreating is the key process to meet quality specifications for refinery fuel products
- Removes sulfur, nitrogen, olefins, and metals using hydrogen
- Hydrogen addition also improves the quality of distillate fuels (poly aromatics, cetane, smoke point)
- Treating feedstocks for other processing units





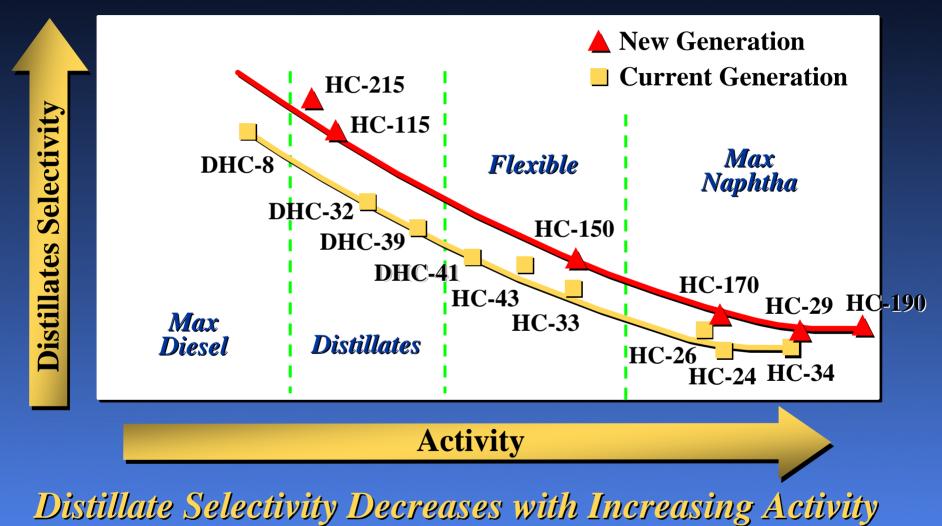
#### Conversion Technologies Hydrocracking

- Hydrocracking upgrades heavy feeds including gas oils and cycle oils into lighter, higher value, low sulfur products
- High pressure is used to add hydrogen and produce premium distillate products
- Naphtha products normally are low octane and are upgraded in a reformer
- Product volume is 10-20% higher than the feedstock





## Hydrocracking Catalyst Portfolio





### YE for Hydrocracking Pyrolysis Oil

Feed	Wt%	bpd
Pyrolysis Oil	100	2,250
H <sub>2</sub>	4-5	
Products		
Lt ends	15	
Gasoline	30	1,010
Diesel	8	250
Water, CO <sub>2</sub>	51-52	



#### Gasoline Production from Py Oil (\$40/bbl crude)

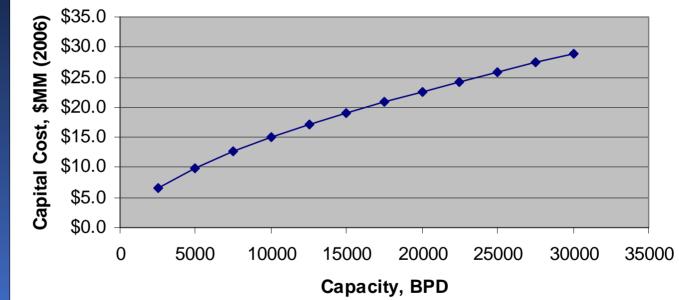
Feed	\$/D	bpd
Pyrolysis Oil	40,500	2,250
$H_2$	25,680	21.4 T
Products		
Lt Hydrocarbons	19,303	64T/D
Gasoline	52,520	1,010
Diesel	12,000	250
Utilities	-4,800	
Net	12,843	

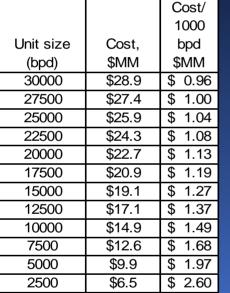




#### Hydroprocessing costs: Effect of Scale

**HDT Capital Cost vs Capacity** 







## Size of Hydroprocessing Units

#### 2000 bpd HC units

#### Dynamotive's Planned 200 tpd Plant

Dynamotive's 200 tonne/day facility (planned production)			
200	tonne/day	biomass processed	
200000	kg/day		
	% conversion		
	biomass to pyrolysis		
65%	oil		
130000	kg/day	biooil	
1.2	kg/liter	density of pyrolysis oil	
108333	liter/day		
28622	gal/day		
681	bbl/day	Hydroprocessing unit	

2500	bbl/day	
38.3	M gal/year	pyrolysis oil processed
174072	tonnes/yr	pyrolysis oil processed
65%		Conv. to biooil
267803	tonnes/yr	biomass
734	tonne/day plant	

## **30,000 bpd HC unit** (typical refinery size)

30000	bbl/day	
459.9	M gal/year	pyrolysis oil processed
2088866	tonnes/yr	pyrolysis oil processed
65%		Conv. to biooil
3213640	tonnes/yr	biomass
8804	tonne/day plant	



### **Example: Potential from logging residues**

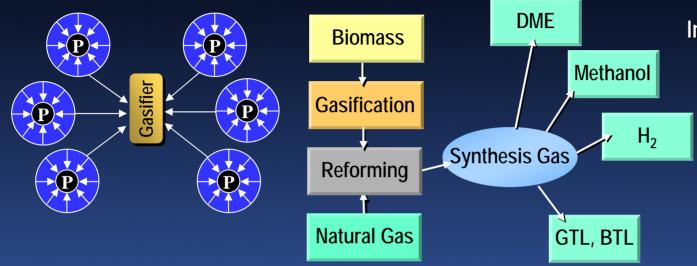
41	Million dry tons logging residue available (Billion ton annual study)
10%	% water of biomass for pyrolysis unit
46	Million tons of logging residue feed
65%	% conversion to pyrolysis oil
29.6	million tons of pyrolysis oil
6519	M gallons of pyrolysis oil from logging residue
425271	bbl/day

~14 30,000 bpd hydroprocessing units
 – Estimated cost: \$405 MM

~170 2500 bpd hydroprocessing units
 – Estimated cost: \$1105 MM



#### Distributed Pyrolysis Plants; Centralized Refining



Integrated into traditional natural gas conversion process or refinery

# Key Decision: What are we planning to transport?



### **Technical Barriers**

- Securing a consistent py Oil feedstock
  Logistics
  Balance of distributed vs. centralized
  Catalyst and process
  - invention/development/commercialization



### Summary

- Vegetable oils, grease and pyrolysis oil could be feasible feedstocks for conventional petroleum refineries
  - Other feedstocks and processing options also look promising
  - Increased volumes of biobased feedstocks required
    - Consistent source of pyrolysis oil or other lignocellulosic biomass

Biorenewable processing options identified are not limited to refinery integration – Stand alone units possible

- Biorefineries; Biofeedstock source
- Portable H<sub>2</sub>



### Acknowledgements

#### DOE, Project DE-FG36-05GO15085

#### **Contributors**

- MTU
  - David Shonnard
- NREL
  - Stefan Czernik
  - Richard Bain

#### **Contributors**

- PNNL
  - Doug Elliott
  - Don Stevens

#### UOP

- Tom Kalnes
- Terry Marker
- Dave Mackowiak
- Mike McCall
- John Petri

Project Manager: Rich Marinangeli

