Thrust 2: Utilization of Petroleum Refinery Technology for Biofuel Production

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Utilization of Petroleum Refining Technologies for Biofuels Production

- To address utilization of petroleum refining technologies for upgrading biomass-derived feedstocks from fast pyrolysis and hydrothermal liquefaction
- For example:
  - hydrotreating
  - hydrocracking
  - catalytic cracking
- Fuel products are the focus, but chemical or chemical feedstock products will also be considered

Objectives of Thrust Area 2

- Identify promising pathways
  - Produce clean liquid biofuels for transportation
  - Use liquid feeds derived from biomass
    - fast pyrolysis
    - hydrothermal liquefaction
  - Use technologies similar in principle to
    - petroleum refining
    - coal liquids upgrading
    - Fischer-Tropsch product refining
  - Not – synthesis gas or aqueous-phase processing

Issues for Thrust Area 2

- Overall process description
- Fuels or products produced from each process
- Feedstocks
- Overview of research done to date
- Economics and potential of technology
- Current technology limitations
- Technical strategy and milestones

Overall Process Description

- Processes to convert liquids derived from lignocellulosic biomass to hydrocarbon-based fuels for transportation
  - Known catalytic processing
    - as applied for deoxygenation
  - Use existing infrastructure
    - processing,
    - market distribution, and
    - utilization
  - TBD

Fuels or Products

- Clean liquid biofuels for transportation
  - gasoline
  - diesel
  - jet fuel
  - TBD
- Organic chemical products
  - Hydrocarbons
  - Oxygenates
  - TBD

Feedstocks

- Liquids derived from lignocellulosic biomass
  - fast pyrolysis
  - hydrothermal liquefaction
  - TBD by Thrust 1

Overview of Research Done to Date

- Biomass-derived Liquids
  - Properties and uses
- Hydroprocessing
  - Hydrothermal liquefaction products
  - Slow/Fast pyrolysis products
- Catalytic cracking
  - Hydrothermal liquefaction products
  - Slow/Fast pyrolysis products

Thermochemical Liquefaction of Biomass

- High-Pressure Liquefaction
  - ~350ºC, 200 atm, biomass slurry in water, minutes
  - Reducing gas, maybe
  - Catalyst, maybe
    - Alkali
    - Metals
- Atmospheric Fast Pyrolysis
  - 500°C, 1 atm, dry, finely divided, < 1 second
  - Inert atmosphere
  - Non-catalytic

Comparison of Bio-oil and Petroleum Fuel

Characteristic	High-Pressure Bio-oil Wet -------- Dry		Fast pyrolysis Bio-oil Wet ------- Dry	Heavy petroleum fuel
Water content, wt%	3-5	0	15-25	0.1
Insoluble solids	1%		0.5-0.8 %	0.01%
Carbon, %	**72.6-74.8**	**76.5-77.5**	39.5-55.8	85.2
Hydrogen, %	**8.0**	**7.8**	7.5-6.1	11.1
Oxygen, %	**16.3-16.6**	**12.5-14.1**	52.6-37.9	1.0
Nitrogen, %	<0.1	<0.1	<0.1	0.3
Sulfur, %	<0.05	<0.05	<0.05	2.3
Ash	0.3-0.5	0.3-0.5	0.2-0.3	--
HHV, MJ/kg			16.5-17.5	40
Density, g/ml	1.10		1.23	0.94
Viscosity, cp	3,000-17,000@ 60ºC		10-150@50ºC	180@50ºC

Unwanted Characteristics of Bio-oil

characteristic	problem	solution
Low pH	corrosion	Adequate Materials
		Neutralization
		Upgrading
High viscosity	Handling	Add water
	Pumping	Add solvent
Instability and temperature sensitivity	Storage	Avoid contact with hot surfaces
	Phase separation	Stabilization or Refining through Catalytic Treatment
	Decomposition and Gum formation	Add Water or Diluents
	Viscosity increase	

Unwanted Characteristics of Bio-oil

characteristic	problem	solution
Char and solids content	Combustion problems	Liquid filtration
	Equipment blockage	Hot gas filtration
	Erosion	
Alkali metals	Deposition of solids in boilers, engines, and turbines	Biomass pretreatment
		Hot gas filtration
		Catalytic upgrading
Water content	Complex effect on heating value, viscosity, pH, homogeneity and other characteristics	Problem recognition
		Optimization and control of water content according to application

Bio-oil Upgrading to Liquid Fuels

Extrapolations from petroleum processing

- Catalytic Hydrotreatment – 49% yield

$$C_{7.5}H_7O_6 + 7H_2 \rightarrow 5H_2O + 0.5CO_2 + C_7H_{11}$$

- Catalytic Cracking – 26% yield

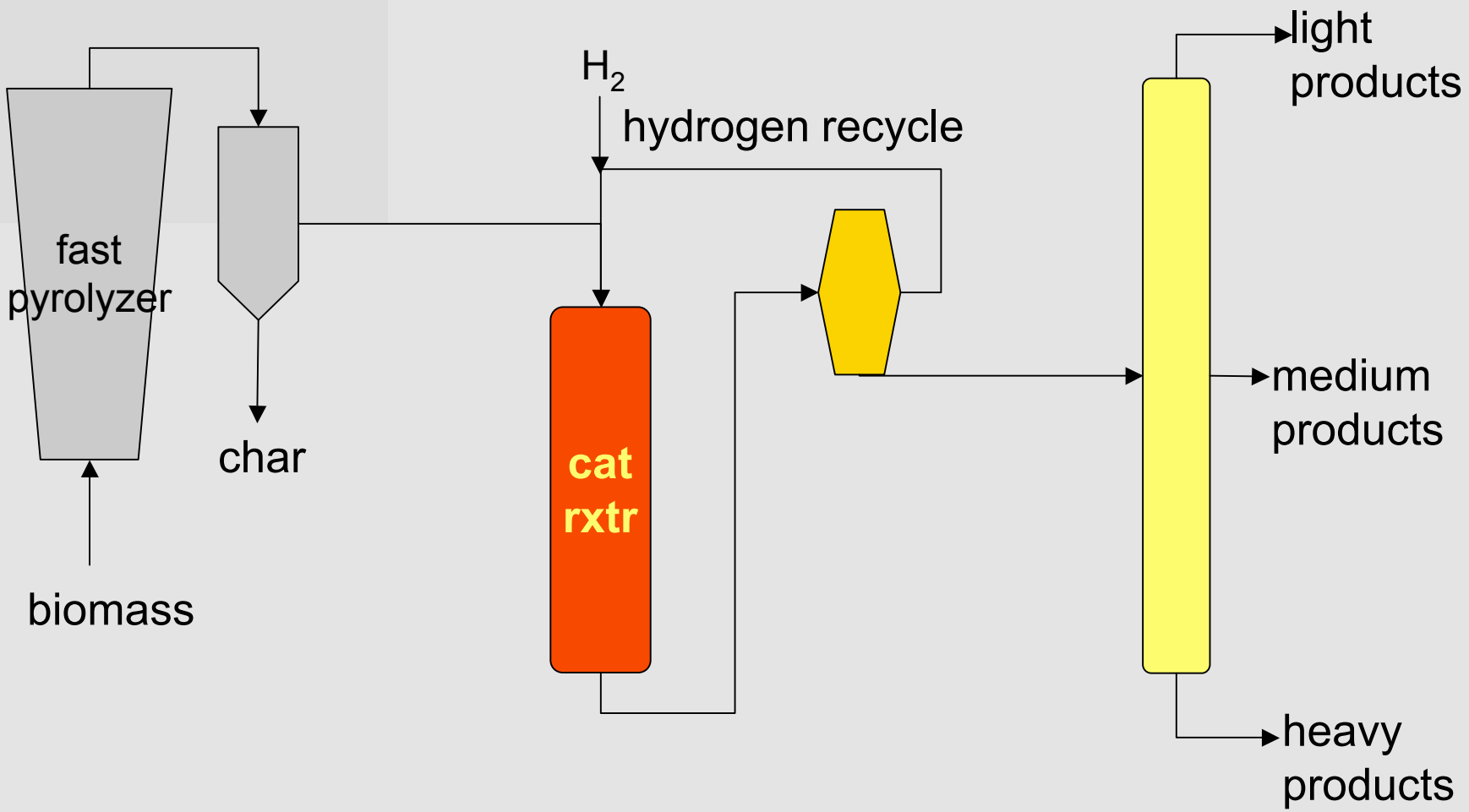
$$C_{7.5}H_7O_6 + O_2 \rightarrow 4CO_2 + 0.6C_6H_{11.7}$$

Comparison

- Catalytic Hydrotreatment
  - High pressure
  - Requires H_2
  - Coking of catalyst may be a problem
  - Produces aliphatic and aromatic hydrocarbons

- Catalytic Cracking
  - Atmospheric pressure
  - No H_2 required
  - Produces mostly aromatic hydrocarbons (and coke!)

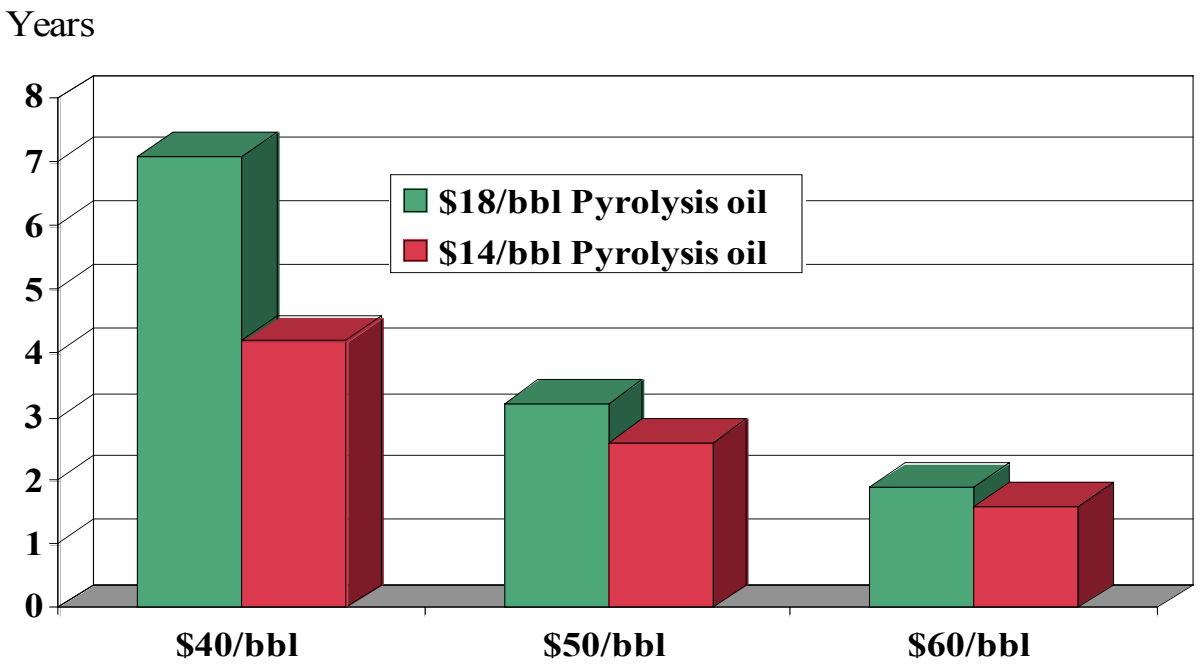
Hydrotreating of Biomass Pyrolysis Oils



Catalytic Hydrogenation Development

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

Year to Simple Payback for Conversion of Pyrolytic Lignin to Gasoline



Based on Capital Cost of $30MM for HT/HCK Unit

Technical Barriers

- Improve utility of bio-oil
  - Increase energy density
  - Improve chemical stability
  - Reduce corrosivity
- Improve process economics
  - Reduce hydrogen requirements
  - Demonstrate catalyst stability
  - Increase product value
- Develop process economic model

Bio-oil Upgrading Research Is Needed!

- Key value-added processing step
  - Reduces negative aspects of bio-oil
    - instability
    - corrosivity
  - Produces valuable chemical products
- Major cost center in overall economics
  - High-yield performance at low cost essential for economic feasibility