Generation of Thermochemical Intermediates Suitable for Catalytic Upgrading

Robert C. Brown
Iowa State University
Ames, IA
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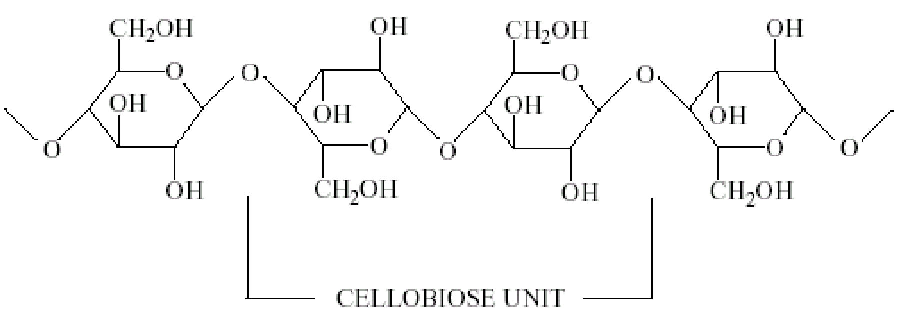
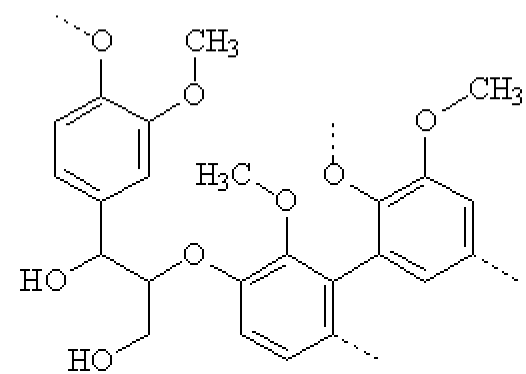
The Problem With Biomass
(Actually Two Problems)

- Lignocellulosic biomass consists of polymers (polysaccharide and lignin) unsuitable as fuel molecules
- Lignocellulose is highly oxygenated, which detracts from its use as fuel



Cellulose



Lignin

Deoxygenation is an important element of all biomass upgrading

- Idealized: $C_6H_{12}O_6 \rightarrow C_6H_{12} + O_2$
- In practice, oxygen removed as CO_2 or H_2O
- Examples:
  - Ethanol fermentation (biocatalytic upgrading)

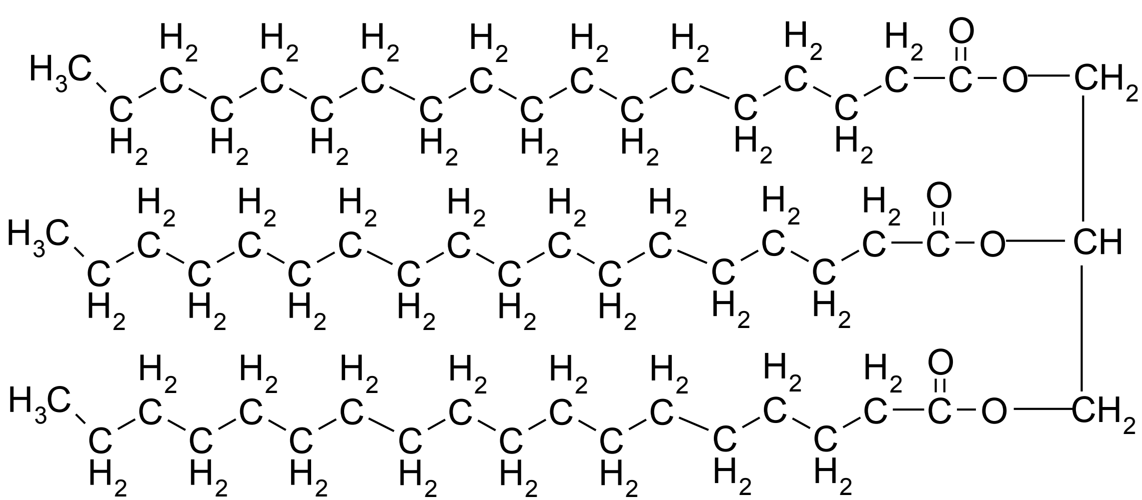
    $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
  - Gasification/Fischer-Tropsch Synthesis

    $C_6H_{12}O_6 + 3H_2O \rightarrow 6H_2 + 3CO + 3CO_2$

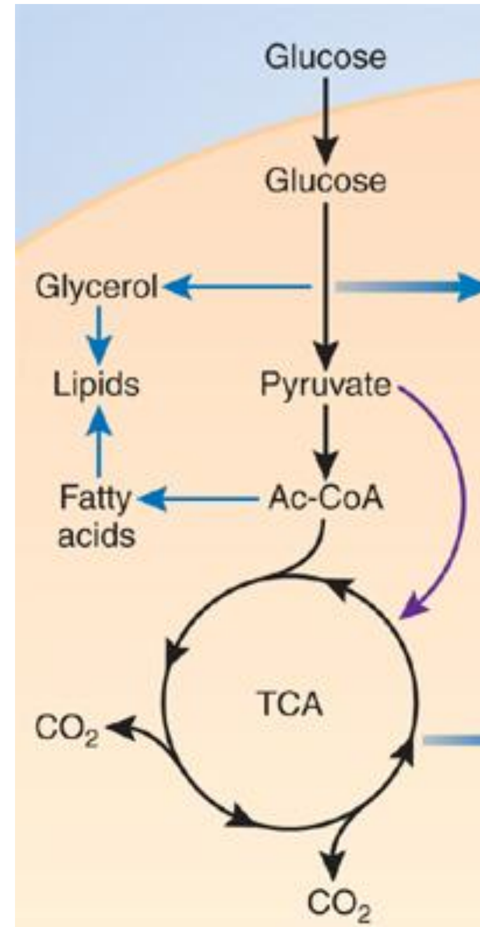
    $(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$

Even Lipid Biosynthesis is Decarboxylation of Biomass

Lipid biosynthesis involves the decarboxylation of glucose to form triglycerides with the rejection of two CO_2 molecules



Triglyceride is a plant molecule already deoxygenated by Nature



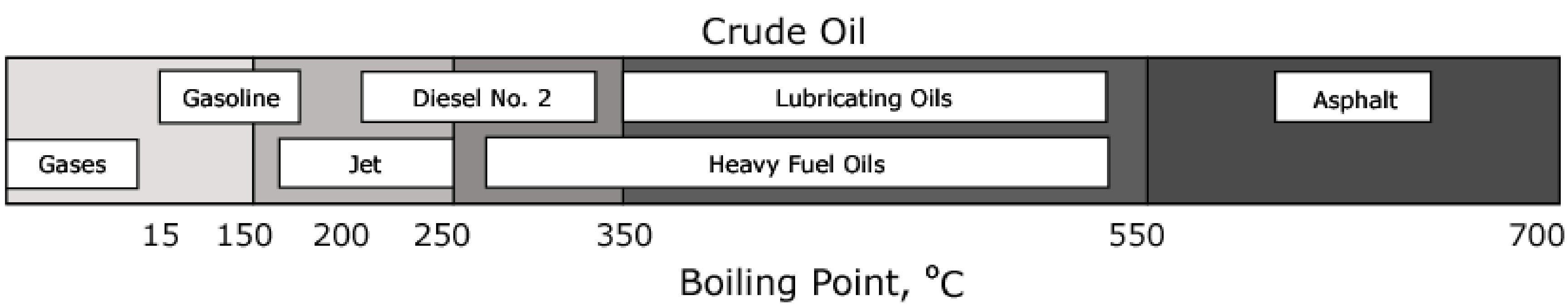
Source: Nature Medicine 11, 599 – 600, 2005)

Other Upgrading Processes

- Hydrotreating (removal of heteroatoms): Deoxygenation, desulfurization, denitrification, and demetalization
- Cracking: Reduction in size of large molecules to fuel range
- Condensation: Reaction of two molecules to produce a larger (fuel range) molecule and a small molecule
- Oligomerization: Reaction of monomer with another monomer, dimer, etc. to produce larger molecules (oligomers)

Drop-In Biofuels: Emulating Conventional Transportation Fuels

- **Gasoline:** hydrocarbons containing between 5 and 12 carbon atoms with boiling points in the range of 25-225 °C (mostly alkanes with aromatics added to boost octane)
- **Diesel fuel:** lower volatility mixture of hydrocarbons containing 12 to 22 carbon atoms with boiling points in the range of 180-360°C (aromatics limited to less than 35 vol% to avoid sooting)
- **Aviation fuel:** mixture of straight-chain alkane molecules containing 9 to 20 carbon atoms giving it a moderately high boiling range of 165-290°C, similar to diesel fuel (aromatics are added up to 25 vol% for thermal stability)



Renewable Crude

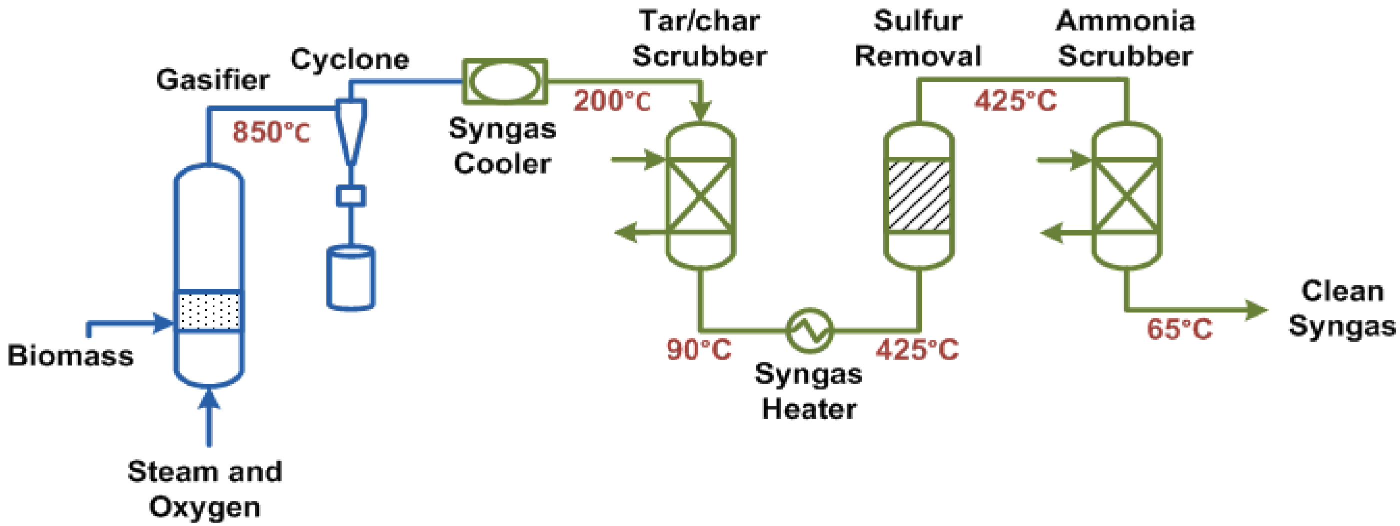
- Intermediate (liquid or gas) generated from raw biomass and suitable for catalytic upgrading
- Desired properties
  - Plant polymers reduced to monomers or manageable oligomers (both carbohydrate and lignin)
  - Removal of as much oxygen as possible before catalytic upgrading to reduce hydrogen demand and improve carbon efficiency

Renewable Crudes

- **Syngas:** Mixture of carbon monoxide (CO) and hydrogen (H_2) derived from gasification of carbonaceous feedstocks
- **Bio-Oil:** Wide variety of oxygenated organic compounds derived from both carbohydrate and lignin in biomass (also biocrude) from pyrolysis
- **Solubilized carbohydrate:** Aqueous solution of monosaccharides, sugar alcohols, and other water-soluble compounds derived from holocellulose (cellulose + hemicellulose) using a variety of processes including acid or enzymatic hydrolysis, fast pyrolysis, and hydrothermal processing

Renewable Crude: Syngas

- Advantages
  - Uniform gaseous feedstock for catalytic upgrading
  - Gas production, cleaning, and upgrading technologies are well known



Gasification/gas cleaning pilot plant at Iowa State University's BioCentury Research Farm

Renewable Crude: Syngas

- Disadvantages
  - Large, centralized facility poorly adapted to dispersed biomass supply
  - High capital and operating costs

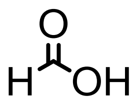
2000 tpd plant capacity gge=gallons gasoline equivlalent capital cost is based on annual capacity	Capital Cost ($/gge)	Production Cost ($/gge)	Feedstock Cost
Grain Ethanol[1]	0.94	1.74	$3.00/bu
Lignocellulosic Ethanol[2]	7.52	5.50	$75/ton
LT gasification Fischer-Tropsch liquids[3]	15.43	4.75	$75/ton
HT gasification Fischer-Tropsch liquids[4]	14.52	4.25	$75/ton
Motor fuels from bio-oil[5]	7.82	3.04	$75/ton
Motor fuels from bio-oil + merchant H_2[5]	3.30	2.09	$75/ton

See slide notes for references

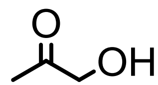
Renewable Crude: Bio-Oil

Aqueous Phase

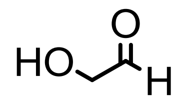
- High: Light oxygenates (carboxylic aids, aldehydes, ketones, alcohols)



Formic acid

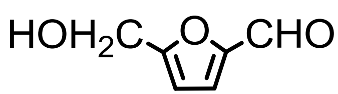


Acetol

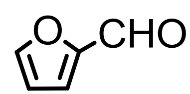


Glycolaldehyde

- Moderate: Furans (dehydration of carbohydrate)

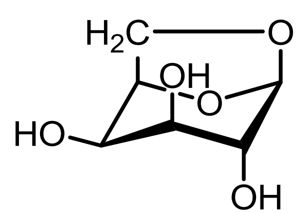


5-hydroxymethyl furfural

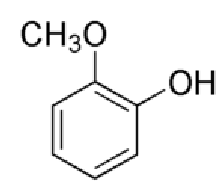


2-Furaldehyde

- Low: Monosaccharides, anhydrosugars, oligosaccharides



Levoglucosan

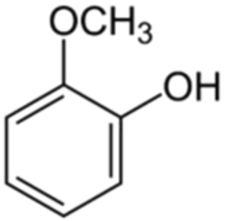


Guaiacol

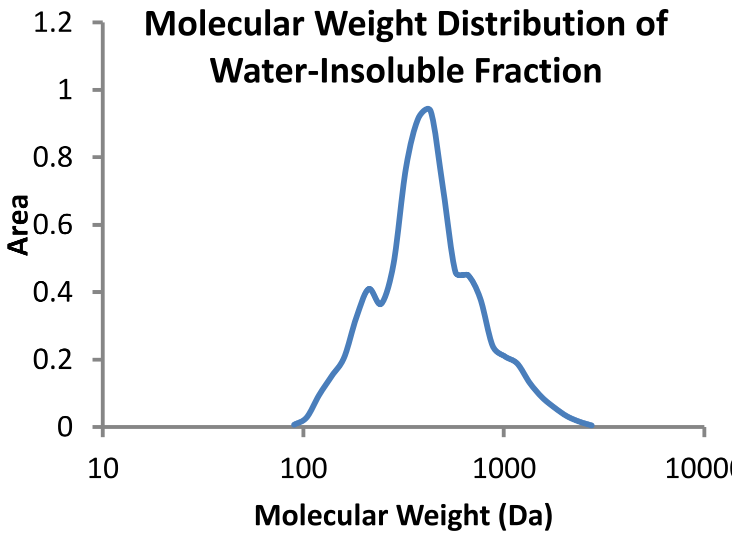
Renewable Crude: Bio-Oil

Water Insoluble Phase

- Low: Substituted phenolic monomers (approximated by 2-methoxy phenol which weighs 124 Da



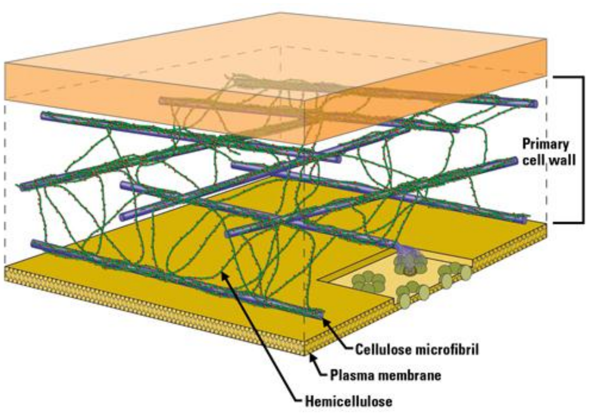
- High: Phenolic oligomers
  - Can as many as 50 to 80 monomeric units
- To produce diesel fuel (C_{10}-C_{24}), the phenolic oligomers should occur as dimers (C_{14}) or trimers (C_{21}) of 2-methoxy phenol



Renewable Crude: Solubilized Carbohydrate

- Ideal feedstocks: Sugar and starch
  - Constrained by cost and food vs. fuel concerns
- Plentiful feedstock: Lignocellulose
  - Requires deconstruction to produce sugar monomers and separate them from lignin (acid or enzymatic hydrolysis but also pyrolysis)

Lignocellulose



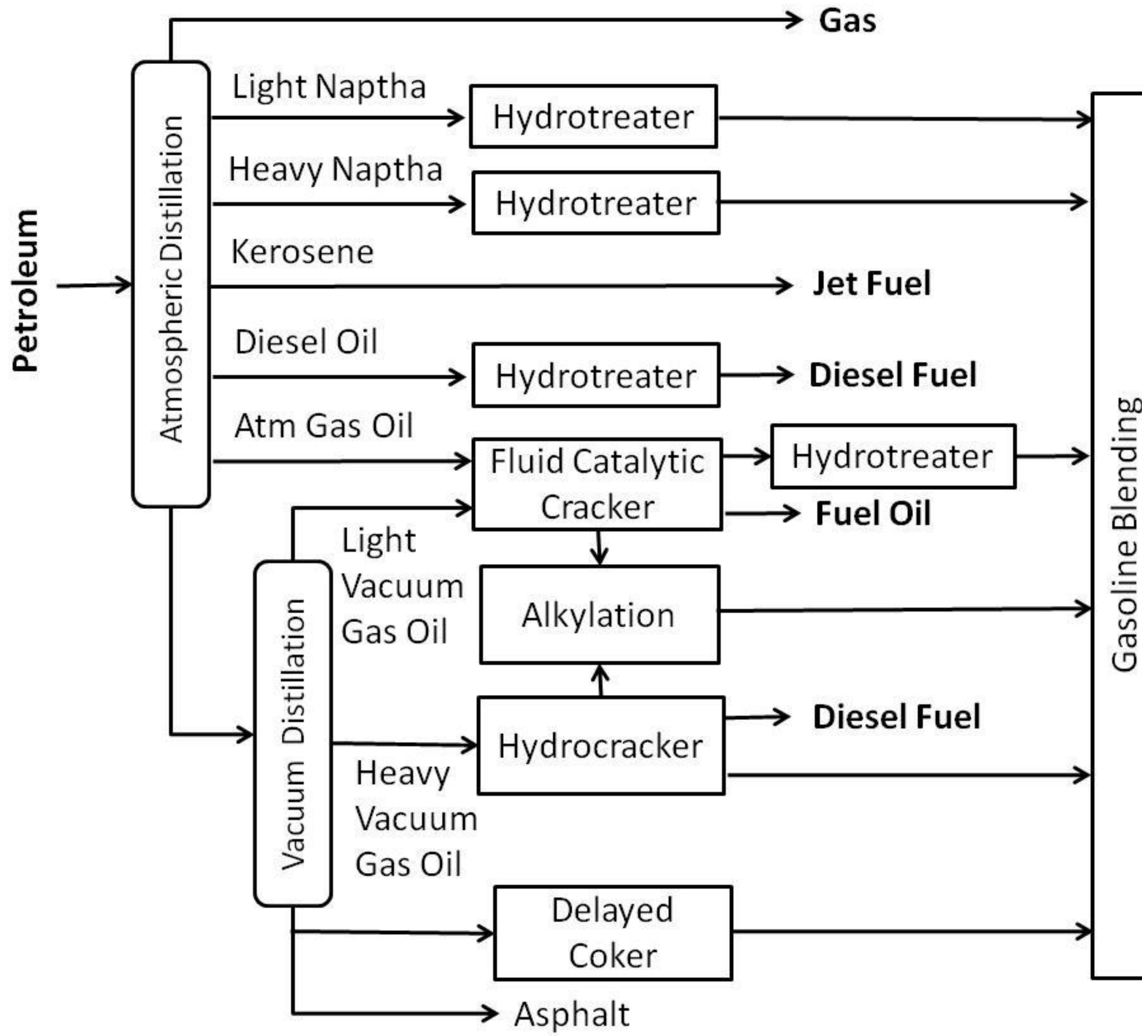
Pyrolytic Molasses (ISU)

Refining of Liquid Renewable Crude

- Highly desirable to utilize existing petroleum refining infrastructure but renewable crudes cannot be distilled
  - Bio-oil: Lignin oligomers further polymerize
  - Solubilized carbohydrate: Sugars non-volatile
- Limitations to co-refining renewable crudes downstream of distillation columns
  - High water content incompatible with catalysts
  - High oxygen content requires large hydrogen demand
  - Many molecules smaller than fuel range
- Additional limitations specific to bio-oil
  - Corrosive
  - Alkali metal content

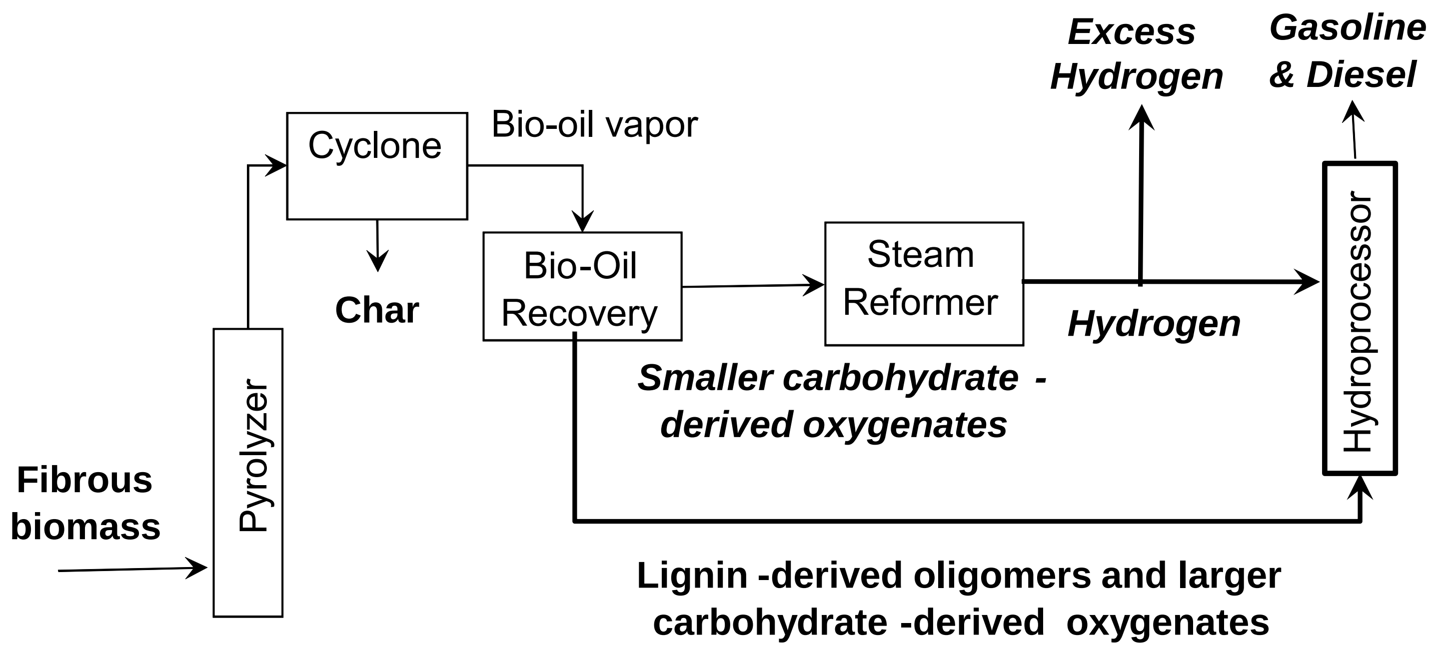
Refining Liquid Renewable Crude

- Near-term strategy: Renewable crude enters downstream of distillation process
- Far-term strategy: Renewable crude and petroleum crude blended and co-distilled and refined

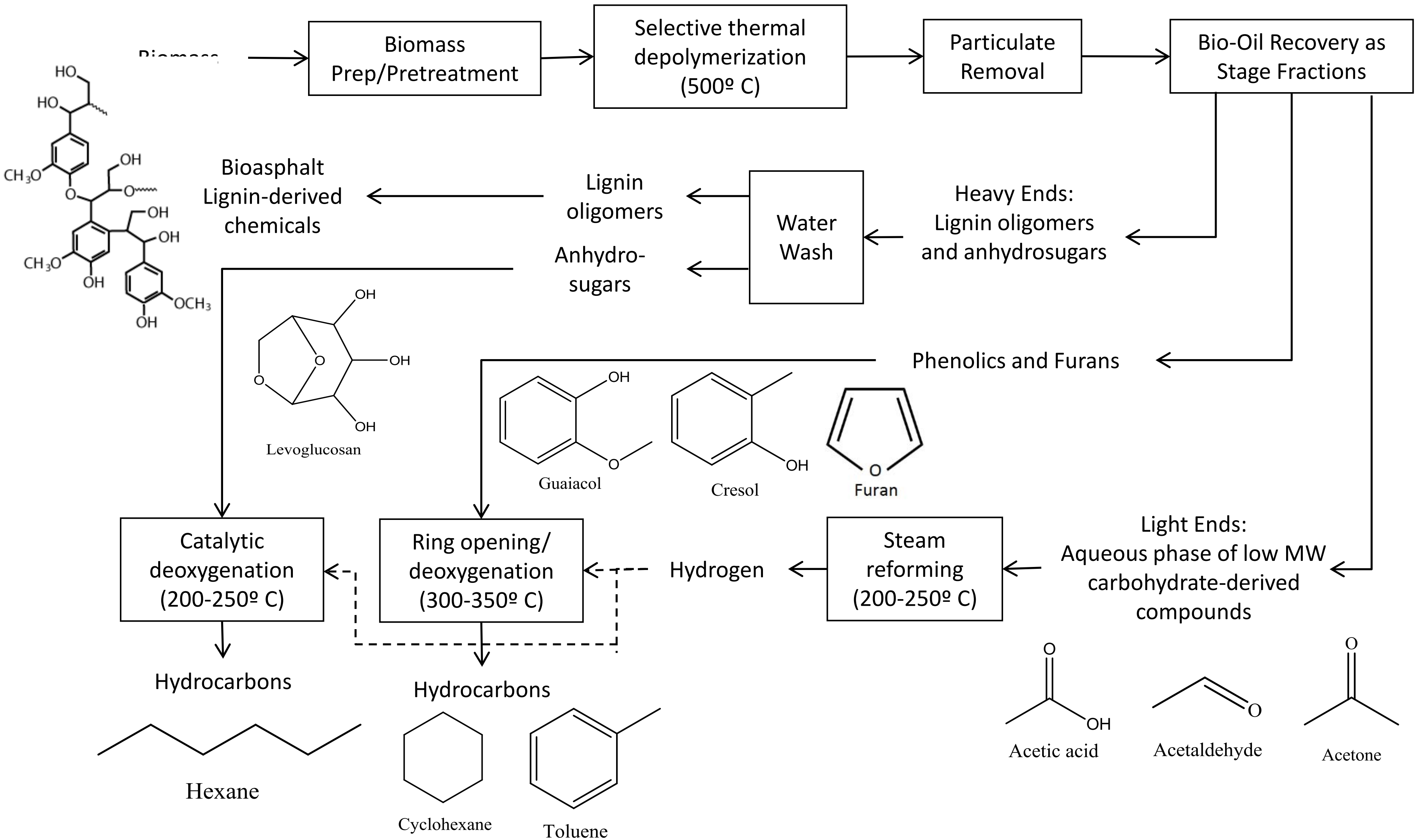


Upgrading Bio-Oil: Current Approach

- Aqueous phase (mostly carbohydrate derived)
  - Steam reformed to produce hydrogen for hydroprocessing of water insoluble fraction
  - Appropriate for small molecules in aqueous phase
- Water insoluble fraction (mostly lignin derived)
  - Attractive for its low oxygen content
  - Problematic for its high viscosity, low volatility, and tendency to coke



Upgrading Bio-Oil: Future Vision



Upgrading Solubilized Carbohydrate: Aqueous Phase Processing

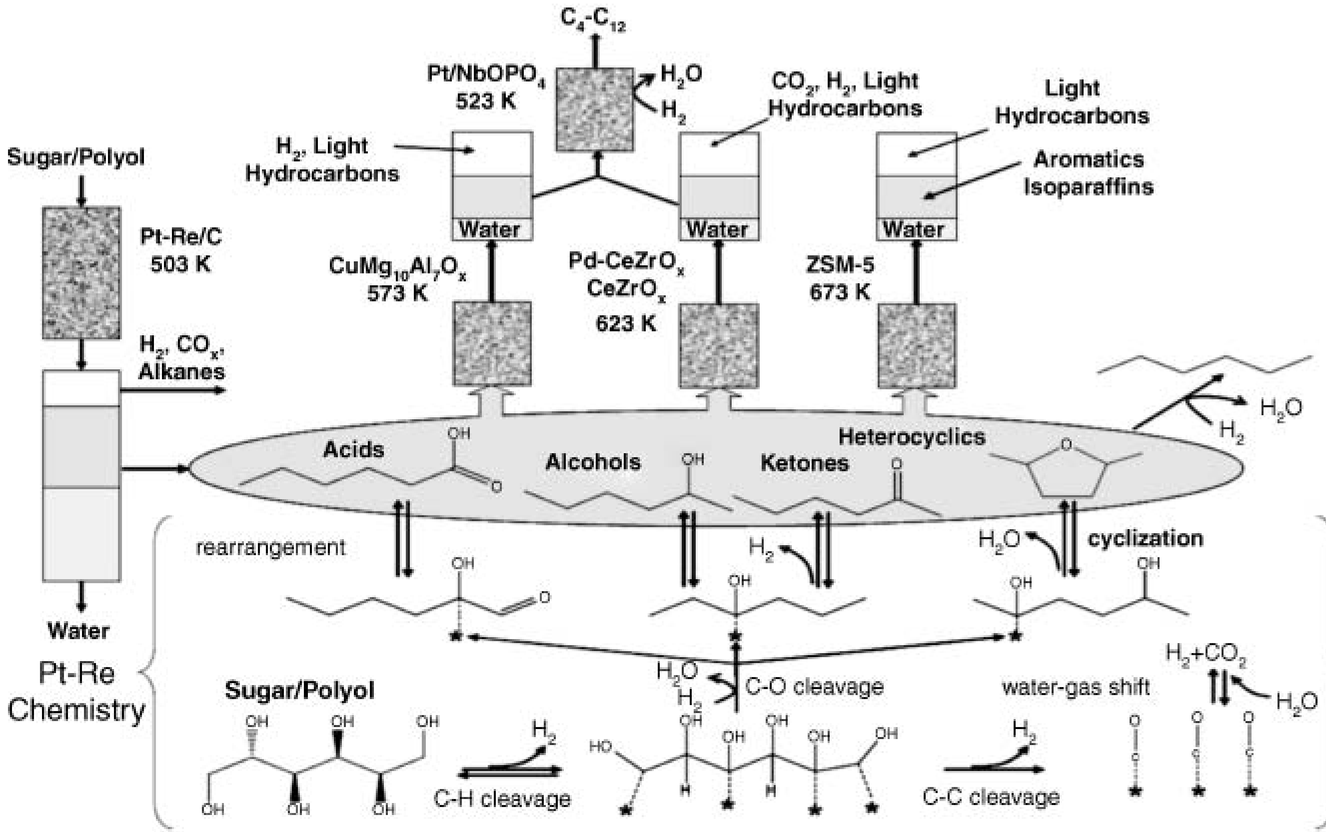


Figure 8.21 Schematic representation of reactor sequence used to generate monofunctional organic compounds from catalytic processing of sorbitol or glucose, providing a platform for the production of liquid transport fuels [95]. (From E.L. Kunkes, et al., Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes, Science, 2008, ***322****, 417. Reprinted with permission from AAAS)*

Thank You