Fuels and Chemicals from Biomass via Thermochemical Routes

Robert C. Brown
Center for Sustainable Environmental Technologies
Iowa State University

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Opportunities and Obstacles in Large-Scale Biomass Utilization—
The Role of the Chemical Sciences

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• Lipid-rich biomass
• Lignocellulosic biomass
• Waste biomass (all of the above plus more)
Lipid Feedstocks: Almost hydrocarbons

Triglycerides:
three fatty acids
attached to glycerol
backbone; found in
oil seeds and
microalgae

Waxy esters:
fatty acid and fatty
alcohol combination;
found in jojoba seeds

Isoprene:
building block of terpenes;
natural hydrocarbons usually
produced in small quantities in
plants and microorganisms
Lignocellulose: Naturally Recalcitrant

- A three-dimensional polymeric composite that resists biological degradation
- Polymeric constituents:
  - Cellulose: main source of glucose (C6 sugar)
  - Hemicellulose: source of xylose (C5 sugar)
  - Lignin: polymer of monolignols

Glycosidic bonds

Cellulose

Monolignols of lignin

p-coumaryl alcohol
coniferyl alcohol
sinapyl alcohol
Lipids vs Lignocellulose

Which Kind of Plant Should be Used to Deoxygenate Carbohydrate?

Lipid biosynthesis involves biological deoxygenation of carbohydrates, too!

Cellulose to hydrocarbons involves deoxygenation of carbohydrate

Generalized Thermochemical Process

- Feedstock
  - Depolymerization/Decomposition
    - Thermolytic Substrate
      - Upgrading
        - Biofuel
Gasification

Thermal decomposition of organic matter into flammable gases

Low Temperature Gasification (Bubbling Fluidized Bed)

- Biomass
- Fluidized Bed
- Steam/Oxygen
- Syngas
- Ash

High Temperature Gasification (Entrained Flow Gasifier)

- Oxygen
- Biomass
- 1300 °C
- Water cooled radiation screen
- Raw syngas and molten slag
Gasification can be approximated as an equilibrium reaction...

<table>
<thead>
<tr>
<th>Composition of syngas (volume percent)</th>
<th>Hydrogen</th>
<th>Carbon Monoxide</th>
<th>Carbon Dioxide</th>
<th>Methane</th>
<th>Nitrogen</th>
<th>HHV (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>48</td>
<td>15</td>
<td>2</td>
<td>3</td>
<td>10.4</td>
<td></td>
</tr>
</tbody>
</table>

In practice, equilibrium not attained and tar and char are present.

Syngas also contains small amounts of alkali metals, sulfur, nitrogen, and chlorine that must be removed before upgrading to prevent poisoning of catalysts.
Gasification Strengths

• Technical
  – Consumes all of the feedstock (carbohydrate and lignin)
  – Produces uniform intermediate product (syngas)
  – Multiple applications: heat, power, fuels, chemicals

• Commercial
  – Not finicky about feedstock
  – Proven technology for “cracking the lignocellulosic nut”
  – Allows energy integration in biorefinery operations

½ tpd gasification plant at ISU’s BioCentury Research Farm
Gasification Challenges

• Technical
  – Gas cleaning technologies still under development
  – Gasification and fuel synthesis operations must be closely coupled
  – Fuel synthesis occurs at high pressures and exacting stoichiometries

• Commercial
  – Demands large scale operations
  – High capital costs
  – Must complete with steam reforming of natural gas

Pressurized, oxygen-blown entrained flow gasifier at ISU’s Biorenewables Laboratory
Fast Pyrolysis

Thermal decomposition of organic matter in the absence of oxygen to produce:

- **Gas** – non-condensable gases like carbon dioxide, carbon monoxide, hydrogen
- **Solid** – mixture of inorganic compounds (ash) and carbonaceous material (char)
- **Liquid** – mixture of water and organic compounds known as bio-oil recovered from pyrolysis vapors and aerosols (smoke)
## The many faces of pyrolysis

<table>
<thead>
<tr>
<th>Technology</th>
<th>Residence Time</th>
<th>Heating Rate</th>
<th>Temperature (°C)</th>
<th>Predominate Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonization</td>
<td>days</td>
<td>very low</td>
<td>400</td>
<td>charcoal</td>
</tr>
<tr>
<td>conventional</td>
<td>5-30 min</td>
<td>low</td>
<td>600</td>
<td>oil, gas, char</td>
</tr>
<tr>
<td>gasification</td>
<td>0.5-5 min</td>
<td>moderate</td>
<td>&gt;700</td>
<td>gas</td>
</tr>
<tr>
<td><strong>fast pyrolysis</strong></td>
<td>0.5-5 s</td>
<td>very high</td>
<td>650</td>
<td>oil</td>
</tr>
<tr>
<td>flash-liquid</td>
<td>&lt;1 s</td>
<td>high</td>
<td>&lt;650</td>
<td>oil</td>
</tr>
<tr>
<td>flash-gas</td>
<td>&lt;1 s</td>
<td>high</td>
<td>&lt;650</td>
<td>chemicals, gas</td>
</tr>
<tr>
<td>ultra</td>
<td>&lt;0.5 s</td>
<td>very high</td>
<td>1000</td>
<td>chemicals, gas</td>
</tr>
<tr>
<td>vacuum</td>
<td>2-30s</td>
<td>high</td>
<td>&lt;500</td>
<td>oil</td>
</tr>
<tr>
<td>hydro-pyrolysis</td>
<td>&lt;10s</td>
<td>high</td>
<td>&lt;500</td>
<td>oil</td>
</tr>
<tr>
<td>methano-pyrolysis</td>
<td>&lt;10s</td>
<td>high</td>
<td>&lt;700</td>
<td>chemicals</td>
</tr>
</tbody>
</table>

Fast Pyrolysis

Rapid thermal decomposition to produce predominately liquid

- Dry feedstock: <10%
- Small particles: <3 mm
- Moderate temperatures (400-500 °C)
- Short residence times: 0.5 - 2 s
- Rapid quenching at the end of the process
- Typical yields
  - Oil: 60 - 70%
  - Char: 12 -15%
  - Gas: 13 - 25%
Research at ISU indicates several stages of competitive processes during cellulose pyrolysis:

- Depolymerization vs. alkali-catalyzed decomposition of cellulose
- Vaporization vs. repolymerization of levoglucosan (LG) to oligomers
- Dehydration of oligomers to light oxygenates or char

Note: LMW (low molecular weight products) include H$_2$O, CO$_2$, 5-HMF, furfural, furan, carboxylic acid, etc.

*Hemicellulose and lignin similarly go through several stages of depolymerization or dehydration
Fast Pyrolysis Strengths

• Technical
  – Rapid (a few seconds)
  – Atmospheric operation
  – Pathway to drop-in fuels
  – Multiple products
  – New technologies emerging (catalytic pyrolysis)

• Commercial
  – Lowest cost option for drop-in biofuels at present
  – Pyrolyzers as small as 200 tpd
  – Opportunities for distributed processing

¼ ton per day fast pyrolysis pilot plant at ISU BioCentury Research Farm
Fast Pyrolysis Challenges

• Technical
  – Bio-oil has high oxygen and water content
  – Bio-oil unstable and corrosive in storage and upgrading
  – Fundamentals of pyrolysis poorly understood

• Commercial
  – No demonstrations of bio-oil production and upgrading
  – Pathway to finished fuels still uncertain

Free fall pyrolyzer for fundamental studies under construction at ISU’s Biorenewables Research Laboratory
Catalytic Pyrolysis

• Definition: Catalysts employed in the pyrolysis reactor or immediately downstream before bio-oil recovery

• Two major approaches:
  – Catalytic cracking (does not require hydrogen)
  – Hydropyrolysis (carbon efficient)

• Advantage: Produces highly reduced molecules

• Challenge: Yields are relatively low due to coking

• Commercialization: Large number of companies are exploring this approach although fundamental chemistry is not well understood
Solvolysis

• Definition: “Pyrolysis in a solvent”
• Two major manifestations:
  – Direct liquefaction (DL) to produce partially deoxygenated “bio-crude”
  – Hydrothermal processing (HTP) to sugars and lignin
• Advantages and challenges are similar to fast pyrolysis with added challenge of operating at high pressures
• Commercialization examples:
  – DL: Catchlight (Chevron-Weyerhauser joint venture)
  – HTP: Renmatix (Kleiner Perkins backed start-up)
Upgrading “Thermolytic Substrates”

- **Syngas**: Mixture of carbon monoxide (CO) and hydrogen ($H_2$) derived from gasification of organic materials

- **Bio-Oil**: Highly oxygenated organic compounds derived from fast pyrolysis

- **Bio-Crude**: Partially deoxygenated organic compounds derived from direct liquefaction or catalytic pyrolysis of biomass.

- **Solubilized carbohydrate**: Aqueous solution of monosaccharides, anhydrosugars, and other water-soluble compounds derived from plant carbohydrates using a variety of processes including acid or enzymatic hydrolysis, fast pyrolysis, and hydrothermal processing
An important part of all biomass upgrading

• Idealization: \( C_6H_{12}O_6 + H_2 \rightarrow C_6H_{14} + 3O_2 \)

• In practice, oxygen removed as CO\(_2\) or H\(_2\)O

• Examples:
  – Ethanol fermentation (biocatalytic upgrading)
    \( C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \)
  – Gasification/Fischer-Tropsch Synthesis
    \( C_6H_{12}O_6 + 3H_2O \rightarrow 6H_2 + 3CO + 3CO_2 \)
    \((2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O\)
Syngas Upgrading to Fuels

• Catalytic – performed at moderate temperatures and high pressures using metal catalysts
  – Fischer-Tropsch synthesis to hydrocarbons suitable for fuels
  – Methanol synthesis followed by upgrading to gasoline
  – Ethanol synthesis

• Syngas fermentation – performed at ambient temperature and pressure using biocatalysts
Carbohydrate Derived Compounds

- Light oxygenates (ring breaking): carboxylic acids, aldehydes, ketones, alcohols.

\[
\begin{align*}
\text{Formic acid} & \quad \text{Acetol} & \quad \text{Glycolaldehyde} \\
\ & \quad \text{HOH}_2 \text{C}-\text{CHO} & \quad \text{HO}\text{-CHO} \\
\ & \quad 5\text{-hydroxymethyl furfural} & \quad 2\text{-Furaldehyde} \\
\end{align*}
\]

- Furans (products of carbohydrate dehydration)

- Sugars (depolymerization): Monosaccharides, anhydrosugars, oligosaccharides.

\[
\text{Levogluicosan}
\]
Upgrading Bio-oil: What’s in It?

Lignin Derived Compounds

- **Depolymerization of lignin:** Substituted phenolic monomers
- **Repolymerized monomers:** Phenolic oligomers
  - Consisting of 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
• **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)
• Sugars can be catalytically converted to hydrocarbons via aqueous phase processing if cheap feedstock available
• Commercially available feedstocks: Sugar cane and corn starch
  – Constrained by cost and food vs. fuel concerns
• Promising feedstock: Lignocellulose
  – Requires deconstruction to sugar monomers
  – Can be accomplished via acid hydrolysis, enzymatic hydrolysis, or thermal depolymerization

“Pyrolytic dextrin” (>20 wt% sugars)
Secure a source of clean straw (or other lignocellulose)

Infuse biomass with a dilute acid solution

Bake it in a hot oven (set the timer for 2 seconds)

Sugar

Gasoline or ethanol

Phenolics

Bio-asphalt, chemicals, fuels

Wash out the sugars
## Future Innovations?

### Gasification Challenge

<table>
<thead>
<tr>
<th>Challenge</th>
<th>Innovation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport, storage, and pressurized feeding of biomass</td>
<td>Preprocessing of biomass into torrefied bio-coal, pelletized feedstock, or bio-oil</td>
</tr>
<tr>
<td>Demanding operating conditions for catalytic synthesis to fuel</td>
<td>Substitute biocatalyst (syngas fermentation)</td>
</tr>
<tr>
<td>High capital costs</td>
<td>Operation at atmospheric pressure and with fewer unit operations for gas cleaning</td>
</tr>
</tbody>
</table>

### Fast Pyrolysis Challenge

<table>
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<tr>
<th>Challenge</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Complex chemical composition of bio-oil makes upgrading difficult</td>
<td>Recover bio-oil as fractions with similar physical and chemical properties</td>
</tr>
<tr>
<td>Bio-oil is highly oxygenated</td>
<td>Catalytic pyrolysis for in-situ deoxygenation of pyrolysis products</td>
</tr>
<tr>
<td>Goldilock’s dilemma: Molecules are either too big or too small for ideal upgrading</td>
<td>Thermal depolymerization to monomers (monosaccharides and phenolic monomers)</td>
</tr>
</tbody>
</table>