The Use of Renewable Feedstocks for the Production of Chemicals and Materials - A Brief Overview of Concepts

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“The U.S. is the Saudi Arabia of carbohydrates.”
David Morris, Institute for Local Self Reliance

“Moving from an economy based on geology to one based on biology.”
USDA

“Changes that will have effects comparable to those of the Industrial Revolution... are now beginning.”
Phillip Abelson, Science
DOE Strategic Goals for the Use of Renewable Feedstocks

- Dramatically reduce, or even end, dependence on foreign oil (a displacement and energy component)

- Spur the creation of a domestic bioindustry (an enabling and economic component)

- Integration of chemicals with fuels will simultaneously address both goals.
The Biorefinery is Flexible

Inputs (Supply)

- Corn
- Potatoes
- Sorghum
- Soybeans
- Apple pomace
- Jerusalem artichoke
- Guayule
- Beet molasses
- Sugar cane
- Wood
- Residues

Outputs (Conversion)

Building blocks (Separation)

- Starch
- Cellulose
- Lignin
- Other Carbohydrates
- Oils

Butadiene
- Pentanes, pentene
- BTX
- Phenolics
- Organic acids
- Furfural
- Resorcinol
- Levulinic acid
- Levoglucosan
- Peracetic acid
- Tetrahydrofuran
- Anthraquinone
- Sorbitol

The Biorefinery is Flexible
Advantages to Biomass Feedstocks

- Lowered demand for diminishing crude oil supplies
- Sustainability
- Recycling of CO$_2$
- Lessened dependence on politically unstable nations for feedstock supply
- New types of complexity in building blocks
- Flexibility through biotechnology/bioprocessing as a growth industry
## Projected Raw Material Costs

<table>
<thead>
<tr>
<th></th>
<th>Oil</th>
<th>Natural Gas</th>
<th>Coal</th>
<th>Corn</th>
<th>Lignocellulosics</th>
</tr>
</thead>
<tbody>
<tr>
<td>$/dry tonne</td>
<td>129</td>
<td>122</td>
<td>33</td>
<td>98 (kernels, $2.50/bushel)</td>
<td>44 (poplar, switchgrass)</td>
</tr>
<tr>
<td></td>
<td>($17.5/barrel)</td>
<td>($2.50/1000 scf)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>94 ($12.7/barrel)</td>
<td></td>
<td></td>
<td>19 (stover)</td>
<td></td>
</tr>
<tr>
<td>$/GJ</td>
<td>44 ($6/barrel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>2.3</td>
<td>1.0</td>
<td>5.0 (kernels, $2.50/bushel)</td>
<td>2.3 (poplar, switchgrass)</td>
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<tr>
<td></td>
<td>($17.5/barrel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.3 ($12.7/barrel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.2 ($6/barrel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Feedstock/Building Block Costs**

<table>
<thead>
<tr>
<th>Material</th>
<th>$/kg</th>
<th>$/lb</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>0.44 - 1.10</td>
<td>0.20 - 0.50</td>
<td>Industrial sources</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.07 - 0.13</td>
<td>0.03 - 0.06</td>
<td>Fuel value</td>
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<tr>
<td><strong>Carbohydrates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glucose</td>
<td>0.60 - 1.10</td>
<td>0.27 - 0.50</td>
<td>NCGA estimate</td>
</tr>
<tr>
<td></td>
<td>0.13 - 0.26</td>
<td>0.06 - 0.12</td>
<td>NCGA estimate</td>
</tr>
<tr>
<td>xylose/arabinose</td>
<td>0.07 - 0.13</td>
<td>0.03 - 0.06</td>
<td>NCGA estimate</td>
</tr>
<tr>
<td>sucrose</td>
<td>0.40</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>lactose</td>
<td>0.65</td>
<td>0.30</td>
<td>2</td>
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<tr>
<td>maltose</td>
<td>0.50 - 1.50</td>
<td>0.23 - 0.68</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2.69</td>
<td>1.23</td>
<td>2</td>
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<tr>
<td>fructose</td>
<td>0.90</td>
<td>0.41</td>
<td>1</td>
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<tr>
<td>sorbitol</td>
<td>1.60</td>
<td>0.73</td>
<td>1</td>
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<tr>
<td><strong>Other</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Levulinic acid</td>
<td>0.18 - 0.26</td>
<td>0.08 - 0.12</td>
<td>Industrial sources</td>
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<tr>
<td>α-pinene</td>
<td>5.50</td>
<td>2.50</td>
<td>Chemical Marketing Reporter</td>
</tr>
<tr>
<td>β-pinene</td>
<td>6.38</td>
<td>2.90</td>
<td>Chemical Marketing Reporter</td>
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</tbody>
</table>

Meeting the organic chemical needs of North America from petrochemical raw materials

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Annual production (10⁹ lb)</th>
<th>Location/source/year</th>
<th>Include in evaluation?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>61.4</td>
<td>NA/CEH/2001</td>
<td>x</td>
</tr>
<tr>
<td>Propylene</td>
<td>32.7</td>
<td>NA/CEH/1998</td>
<td>x</td>
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<tr>
<td>Ethylene dichloride</td>
<td>30.3</td>
<td>NA/CEH/2002</td>
<td>No Š from ethylene</td>
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<td>Benzene</td>
<td>20.4</td>
<td>NA/CEH/2002</td>
<td>Š first evaluation only</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>16.9</td>
<td>NA/CEH/2002</td>
<td>No Š from ethylene</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>15.9</td>
<td>NA/CEH/2002</td>
<td>No Š from benzene</td>
</tr>
<tr>
<td>Styrene</td>
<td>14.0</td>
<td>NA/CEH/2000</td>
<td>No Š from benzene</td>
</tr>
<tr>
<td>Methanol</td>
<td>9.77</td>
<td>NA/CEH/2001</td>
<td>x</td>
</tr>
<tr>
<td>Xylene</td>
<td>13.8</td>
<td>NA/CEH/1999</td>
<td>Š first evaluation only</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>11.4</td>
<td>NA/CEH/2003</td>
<td>x</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>11.1</td>
<td>NA/CEH/1999</td>
<td>No Š from xylene</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>10.5</td>
<td>NA/CEH/2002</td>
<td>x</td>
</tr>
<tr>
<td>Toluene</td>
<td>11.1</td>
<td>NA/CEH/2002</td>
<td>Š - first evaluation only</td>
</tr>
<tr>
<td>Cumene</td>
<td>7.37</td>
<td>NA/CEH/2001</td>
<td>No Š from benzene</td>
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<tr>
<td>Ethylene glycol</td>
<td>8.44</td>
<td>NA/CEH/2002</td>
<td>x</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>4.23</td>
<td>NA/CEH/2002</td>
<td>x</td>
</tr>
<tr>
<td>Phenol</td>
<td>5.09</td>
<td>NA/CEH/2001</td>
<td>Š - first evaluation only</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>4.08</td>
<td>NA/CEH/2001</td>
<td>x</td>
</tr>
<tr>
<td>Butadiene</td>
<td>4.37</td>
<td>NA/CEH/2002</td>
<td>x</td>
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<tr>
<td>Isobutylene</td>
<td>1.54</td>
<td>NA/CEH/2001</td>
<td>x</td>
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<td>Acrylonitrile</td>
<td>3.47</td>
<td>NA/CEH/2000</td>
<td>x</td>
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<tr>
<td>Vinyl acetate</td>
<td>3.38</td>
<td>NA/CEH/1999</td>
<td>No Š from acetic acid</td>
</tr>
<tr>
<td>Acetone</td>
<td>3.13</td>
<td>NA/CEH/2001</td>
<td>x</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>3.01</td>
<td>NA/CEH/2001</td>
<td>x</td>
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<tr>
<td>Cyclohexane</td>
<td>2.52</td>
<td>NA/CEH/2001</td>
<td>x</td>
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<tr>
<td>Adipic acid</td>
<td>1.88</td>
<td>NA/CEH/2001</td>
<td>x</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>2.38</td>
<td>US/CEH/2001</td>
<td>No Š from benzene</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>1.96</td>
<td>NA/CEH/1999</td>
<td>No Š from acetone</td>
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</tbody>
</table>
## Production of aromatics from lignin

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>Production (10⁹ lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>20.4</td>
</tr>
<tr>
<td>Xylene</td>
<td>13.8</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>11.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>11.1</td>
</tr>
<tr>
<td>Phenol</td>
<td>5.09</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>61.5</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>Lignin required (10⁹ lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTX</td>
<td>90.7</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>12.7</td>
</tr>
<tr>
<td>Phenol</td>
<td>9.75</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>113</strong></td>
</tr>
</tbody>
</table>
Impact of products on fuel production

- \((113 \times 10^9 \text{ lb}) (1/0.25) = 453 \times 10^9\) lb lignocellulosic feedstock required,
- \((453 \times 10^9 \text{ lb} \text{ lignocellulosic feedstock})(0.75) = 339 \times 10^9\) lb of sugar available
- \((339 \times 10^9 \text{ lb} \text{ of sugar as glucose})(92/180) = 174 \times 10^9\) lb of EtOH possible
- \((174 \times 10^9 \text{ lb} \text{ of EtOH})(454 \text{ g/lb})(1\text{ ml}/0.816 \text{ g})(1\text{ l}/1000\text{ ml})(0.264 \text{ gal/l}) = 25.5 \times 10^9\) gal EtOH possible

- U. S. gasoline consumption: 136 \times 10^9\) gal/yr (EIA)
- Making products in the biorefinery that meet the current aromatic organic chemical needs of the U. S. could enable EtOH production equivalent to almost 19% of our current supply.
- What is the impact on fuel supplies if the biorefinery makes products? Significant, and potentially very large
Key Issues in Chemical Production

- **Supply**: Where does the starting feedstock come from? How much is there? How long will it last? How is it obtained?

- **Separation**: What are the primary components of the feedstock? How is one component obtained apart from the others?

- **Conversion**: How are the components transformed into products? Which processes are most useful? What products are most useful?
How Will Biomass be Incorporated?

- Duplication of products and structures: biomass is used to prepare known petrochemical derivatives...relatively easy, but economically bad

- Duplication of properties: biomass is used to duplicate desirable marketplace properties...relatively difficult, but much greater economic opportunity
The NREL Clean Fractionation Process

lignocellulosic feedstock

insolubles

fiberize
wash

cellulose pulp

solubles

phase separation

aqueous

hemicellulose

organic

lignin
Typical Clean Fractionation Result

- U. S. patent 5,730,837
- >95% recovery of each fraction with <5% cross contamination
- Separate, isolable cellulose, lignin, and hemicellulose fractions
- Successful with a wide range of biomass raw materials
- Useful as a “front end” for a forest biorefinery
- Economically viable
Mechanism of Levulinic Acid Formation

any C6 containing feedstock: paper, paper sludge, ag fibers, wood, etc.

Cost: $4.00 - 6.00/lb
Difficult separation

Is Levulinic Acid a Viable Primary Chemical Building Block?

- Primary building blocks: $C_2H_4$, $C_3H_6$, BTX, etc.
- Their preparation from raw materials (petrochemicals) is simple, one step, and high yielding
- They are inexpensive
- Unit operations using these materials lead to a large family of chemical products

- Primary building block: levulinic acid
- Its preparation from raw materials (carbohydrates) is simple, one step and high yielding
- It is inexpensive
- There are no unit operations based on levulinic acid that lead to a large family of chemical products

Thus, developing a family of chemicals from cheap levulinic acid would lead to a new carbohydrate based unit op for the chemical industry!
Reaction Matrix

Renewable feedstocks (carbohydrate and lignin sources)

lignin

1, β-keto adipic acid

2-ketoglutaric acid

2-hydroxyglutaric acid

glucose from cellulose or starch

β-keto adipic acid

2-ketoglutaric acid

glutaric acid

2-hydroxyglutaric acid

1,2,5-pentanetriol

new polyesters, nyons

nylon-4 polymers

enzymatic conversion

chemical conversion

nylons

polymers

1,2,5-pentanetriol
Renewables Based Polyesters – 2

2-ketoglutaric acid + 1,4-BDO $\rightarrow$ Formation of an insoluble polymer within 5 hours

Possible initially formed units?

- HOOC\[-\text{COOH} - \text{COOH}\] + HO-\text{OH} $\rightarrow$ HO-\text{OH} - \text{H}_2\text{O}
Glycal Based Bolaform Research

Schematic

Glycal Based Bolaform Research

new carbohydrate based bolaforms
chain length variation
chain structure variation: stereochemistry, branching, heteroatoms

organometallic transformations

Ferrier chemistry

glycals

new methods of functionalization
new structural/electronic units in sugars

organometallic transformations

glycal based bolaforms

bolaform based monolayer membranes

OR
OR

OR
OR

OR
OR

OR
OR

OR
OR

self assembly

predictive models?

structure

shape

membrane supported bioactive molecules
biomimetic lipid/enzyme systems
infection control - hospitals
biosensors, detectors
bioactive filters
air quality
highly defined catalyst systems
cellular recognition, carbohydrate oligomers

covalently stabilized monolayer membranes
long lived catalyst supports
structurally defined catalysts
electronic devices
new nanostructures
predictable macromolecular arrays
macroporous Si catalyst templates

covalent linkages

phase 1 - establish baselines

phase 2 - bolaform properties and self assembly

phase 3 - stabilization of membranes, bioactive systems

approximate time

phases of work

current progress
Hypothetical assembly process

Single molecule \rightarrow Multimolecular array \rightarrow Large scale folding to tubes