Furanics: versatile molecules applicable for biopolymers applications

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Outline of the presentation

• Why novel Biopolymers & Biofuels
• Avantium’s approach
• Furanics as starting material for polyesters
• Key elements & learning points
• Conclusions
The ideal Biopolymer & Process

- Big market
- Comparable characteristics with commodity plastics
  - $T_g$
  - Molecular Mass
  - Transparency
  - Color
- Low raw material and production costs
- Proven technologies
  - Monomer production
  - Polymer processing
- High efficiency route
- Integration with current refineries
Avantium’s approach

- Cheap & abundant renewable feedstocks: carbohydrates
  - Both C5 and C6 sugars
- Use of platform chemicals: furanics
- Discovery, screening and optimization by application of High Throughput Methodologies
- Catalytic, fixed bed process
- Partnering up- and downstream
HTT Methodology

HTT is about the Methodology – Not just technology:

*IT IS THE COMPLETE WORK FLOW*

Not just conventional experimentation faster
Working in new ways
Expanding the parameter space
Renewable Raw Materials

- Carbohydrates are excellent starting materials for the production bulk and specialty-chemicals
- Intelligent usage of the intrinsic functionality already present in carbohydrates
- Furanics (HMF) identified as high potential starting material

Source: Gruber, Biorefineries, Wiley 2006
Avantium’s Approach to Catalytic Biomass Conversion

Unlocking the potential of a new class of biofuels: Furanics

Crops → Carbohydrates → Plant → Products

- Cellulose
- Starch
- Glucose

Avantium catalysts and process

Avantium Furanics

- Biofuels
- Biobased bulk chemicals
- Biobased Specialty & Fine chemicals
Biopolymers from Furan-based Monomers
Potential Monomers

Sugars (Fructose, Glucose)

Dehydration

5-HydroxyMethylFurfural

Reduction

2,5-Hydroxymethyl Tetrahydrofuran

Oxidation

2,5-FuranDiCarboxylic Acid
Target Polymers from FDCA

- Polyesters
- Polyamides
- Copolymers
Dimethyl 2,5-Furandicarboxylate

DM-FDCA

As Monomer in Polyester Synthesis
Polyester Synthesis

**Transesterification**

\[
\text{MeOOOC-} - \text{COOMe} + 2\text{HOROH} \xrightarrow{\text{heat/catalyst}} \text{HOROOOC-} - \text{COORH} + 2\text{CH}_3\text{OH}
\]

**Polycondensation**

\[
\text{HOROOOC-} - \text{COORH}_n \xrightarrow{\text{vacuum, heat, catalyst}} \text{HOR} \left[ \text{OOC-} - \text{COOR} \right]_n \text{OH} + (n-1)\text{HOROH}
\]
Production of Polyesters in Film Reactor

Establish appropriate conditions in reactor

High molecular weight, Low coloration

Parameters to change

- Catalyst – catalyst mixtures
- Catalyst concentration
- Temperature
- Reaction time

Production in larger scale
## Thermal Properties of FDCA based polyesters

<table>
<thead>
<tr>
<th>Diol</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;</th>
<th>PD</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;(°C)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;(°C)</th>
<th>T&lt;sub&gt;cryst&lt;/sub&gt;(°C)</th>
<th>TG</th>
<th>T&lt;sub&gt;start&lt;/sub&gt;(°C)</th>
<th>T&lt;sub&gt;inf&lt;/sub&gt;(°C)</th>
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</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>52000</td>
<td>2.81</td>
<td>86.2</td>
<td>211.4</td>
<td>160.3</td>
<td></td>
<td>312</td>
<td>394</td>
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<tr>
<td>1,3-propanediol</td>
<td>59300</td>
<td>2.57</td>
<td>56.9</td>
<td>171.9</td>
<td>140.0</td>
<td></td>
<td>312</td>
<td>392</td>
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<tr>
<td>2,2-dimethyl-1,3-propanediol</td>
<td>36000</td>
<td>2.28</td>
<td>67.5</td>
<td>199.6</td>
<td>143.3</td>
<td></td>
<td>294</td>
<td>408</td>
</tr>
<tr>
<td>1,4-butanediol</td>
<td>59100</td>
<td>2.52</td>
<td>44.5</td>
<td>171.5</td>
<td>115.3</td>
<td></td>
<td>286</td>
<td>388</td>
</tr>
<tr>
<td>Cis-2-butene-1,4-diol</td>
<td>11800</td>
<td>2.95</td>
<td>47.8</td>
<td>164.3</td>
<td>113.0</td>
<td></td>
<td>264</td>
<td>330, 341</td>
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<td>1,6-hexanediol</td>
<td>53500</td>
<td>2.35</td>
<td>13.2</td>
<td>144.5</td>
<td>116.3</td>
<td></td>
<td>292</td>
<td>390</td>
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<tr>
<td>3-hexene-1,6-diol</td>
<td>37500</td>
<td>2.67</td>
<td>23.3</td>
<td>126.7</td>
<td>78.4</td>
<td></td>
<td>278</td>
<td>354</td>
</tr>
<tr>
<td>1,4-bis(hydroxymethyl) cyclohexane</td>
<td>33600</td>
<td>2.33</td>
<td>102</td>
<td>271</td>
<td>229</td>
<td></td>
<td>319</td>
<td>396</td>
</tr>
</tbody>
</table>

T<sub>start</sub> = starting point of decomposition  
T<sub>inf</sub> = inflection point of TG curve  
T<sub>cryst</sub> = crystallization temperature
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- Why novel Biopolymers & Biofuels
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- Conclusions & Future Steps
Conclusions:

Key elements & learning points

- High throughput methodologies necessary to accelerate process and product development
- Multidisciplinary and knowledgeable team essential
- Involvement of raw material suppliers in early stage
- Availability of large quantities necessary for testing
- Parallel process and application studies
- Involvement of application developers and end users for process and application know-how & future developments
- Early assessment of necessary product characteristics
- Early assessment of economics and consequent essential elements of process
Our Amazon Program in a Nut Shell
2009 - 2010 Time Frame

Feedstock

- Crops
- \(C_5 / C_6\) sugars

Process

- Conversion
- Lab-pilot
- Pilot

Testing

- Properties
- Material properties
- Engine test

Application Development

- Plastics
- Fuels