Adding Value to Almond Co-Products

William Orts – Research Leader, Bioprodunctions

USDA

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Our USDA Research Mission:

Add value to agricultural products to help the rural economy

Agricultural Research Service
Albany, California
~450 people
~50 in Biofuels/
& Bioproducts

Known for biotechnology, especially crop biotech.
McDonald’s sells 65 million lbs/yr of apples in the U.S. USDA continues to collect royalties
Almond Co-Products

Almond Biomass $\Leftrightarrow$ 2.4 million Tons/yr

- Hulls 53%
- Shells 22%
- Trees 18%

SOURCE: Guangwei Huang, CA Almond Board, 2015 data, dry mass basis
## Biomass from Shellers/Hullers

<table>
<thead>
<tr>
<th></th>
<th>Wet Mass (MT)</th>
<th>Dry Mass (MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hulls</td>
<td>1,416,413</td>
<td>1,235,112</td>
</tr>
<tr>
<td>Shells</td>
<td>538,174</td>
<td>520,414</td>
</tr>
<tr>
<td>Twigs</td>
<td>66,972</td>
<td>42,192</td>
</tr>
<tr>
<td>Totals</td>
<td>2,021,558</td>
<td>1,797,718</td>
</tr>
</tbody>
</table>

**SOURCE:** Guangwei Huang, CA Almond Board, 2015 data, dry mass basis
Locations of hulling plants providing samples from 2012/13 season
# Sugars in Almond Hulls

<table>
<thead>
<tr>
<th></th>
<th>Sucrose</th>
<th>Glucose</th>
<th>Fructose</th>
<th>% Fermentable sugars</th>
<th>Xylose</th>
<th>Inositol</th>
<th>Sorbitol</th>
<th>% Total sugars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Pareil</td>
<td>3.84</td>
<td>17.61</td>
<td>15.04</td>
<td>36.49</td>
<td>1.03</td>
<td>2.36</td>
<td>4.37</td>
<td>44.24</td>
</tr>
<tr>
<td>Butte/Padre</td>
<td>0.38</td>
<td>12.87</td>
<td>12.55</td>
<td>25.80</td>
<td>0.77</td>
<td>0.99</td>
<td>2.84</td>
<td>30.40</td>
</tr>
<tr>
<td>California</td>
<td>0.14</td>
<td>6.79</td>
<td>3.53</td>
<td>10.46</td>
<td>0.64</td>
<td>1.89</td>
<td>1.76</td>
<td>14.75</td>
</tr>
</tbody>
</table>
Almond Hull Sugars

% Fermentable Sugars

By variety and county - hulls only, dry basis, 5 samples per bar

Nonpareil, 2011/12 Season vs. 2012/13 Season
% Fermentable Sugars, Dry Basis (ave 5 samples each county)

<table>
<thead>
<tr>
<th>County</th>
<th>2011/12</th>
<th>2012/13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresno</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Madera</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merced</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stanislaus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colusa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glenn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butte</td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

% Fermentable Sugars, Hulls only, Dry basis

Graph showing the comparison of % fermentable sugars between the 2011/12 and 2012/13 seasons for different counties.
Extracting Sugar From Hulls

- Countercurrent extraction

At steady-state, fermentable sugar concentration will be enriched

gpL ferm. sugars

(1) 1st pass 71.3
(2) 2nd pass 103.2
(3) 3rd pass 121.6
Almond hulls → 1° washer → 2° washer → 3° washer → spent hull filter cake

88 % fermentable sugar recovery

concentrated filtrate (131 g/L fermentable sugar)

fermentor

7.4 % (v/v) ethanol

86 % fermentation efficiency

185 mL/g AH ethanol yield

distillation column

90 % SCOD conversion efficiency

attached growth anaerobic reactor

concentrated thin stillage

75 mL/g AH CH₄ yield

low SCOD effluent
### Ethanol Production from Hull Sugars?

<table>
<thead>
<tr>
<th>Raw Feed</th>
<th>$/ton</th>
<th>% sugar</th>
<th>Sugar (lbs)</th>
<th>Ethanol (gal)</th>
<th>$/gal Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn kernels</td>
<td>132</td>
<td></td>
<td>1286</td>
<td>95</td>
<td>1.38</td>
</tr>
<tr>
<td>Sugar beets</td>
<td>39</td>
<td>18.5</td>
<td>370</td>
<td>27</td>
<td>1.42</td>
</tr>
<tr>
<td>Molasses (feed)</td>
<td>180</td>
<td>79.5</td>
<td>1590</td>
<td>118</td>
<td>1.52</td>
</tr>
<tr>
<td>Sugar cane</td>
<td>39</td>
<td>14</td>
<td>280</td>
<td>21</td>
<td>1.88</td>
</tr>
<tr>
<td>Almond hulls</td>
<td>150</td>
<td>31</td>
<td>624</td>
<td>40</td>
<td>3.83</td>
</tr>
</tbody>
</table>
Almond Hulls vs. Sugar Beet Cossettes

Almond Hulls
30% fermentable sugar

Beet Cossette
15% fermentable sugar
Sugar Beet Extraction ↔ Hull Extraction?

cossette mixer

diffusion tower

From US Patent # 3,477,873
Comparison of Extraction Approaches

- pectinase steep
- control steep
- no steep, no enzyme

Sugar recovery, %

# extraction (wash stages)
• ONE IDEA: Make a concentrated sugar syrup
  • Countercurrent extraction with hot water
  • Concentrate syrup with multiple effect evaporators

• ETHANOL?
  • Ship to existing ethanol plant to co-feed with corn

• FOOD OR FEED SYRUP: ????
Nonpareil Lab Storage Tests
Normalized to starting concentrations
Each point average of 3 samples (North State, Cortina, Central hulls)

- Green mold observed
- No aflatoxin
- Little bugs (psocids) hatched from eggs on hulls, eating mold
Key issue: Not practical to ferment hulls directly

- Hulls absorb 4-8 times weight of water
  - Highest stirrable slurry is ~15% hulls in water.
Possible Outlets for Spent Hulls

Characteristics
- High in cellulose, lignin, hemicellulose; no sugars
- Milled to < 8 mesh, and full of water (~93% moisture!)

Cattle feed
- Feed value of dry spent hulls low (UC Davis analysis)
- As wet spent hulls, no monetary value
- Cost to dry the wet spent hulls too high: ~$150/ton

Anaerobic digestion to biogas
- Compressed natural gas (CNG) for local use
- BMP ~150 mL CH₄/T spent hulls
- ~50% methane, balance carbon dioxide. Upgrading needed

Boiler fuel or gasification for heat/power
- Same drying issue

Hydrothermal carbonization????
- Process suited specifically for high moisture wastes
- Produces biochar material
Almond Co-Products

Almond Biomass ⇄ 2.4 million Tons/yr

 SOURCE: Guangwei Huang, CA Almond Board, 2015 data, dry mass basis
## Almond Shell Characterization

### Previous work at USDA

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Average (g/kg)</th>
<th>Std dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>34</td>
<td>0.07</td>
</tr>
<tr>
<td>Hot water extractives (100°C)</td>
<td>105</td>
<td>0.35</td>
</tr>
<tr>
<td>Klason lignin</td>
<td>237</td>
<td>0.53</td>
</tr>
<tr>
<td>Glucan</td>
<td>228</td>
<td>0.48</td>
</tr>
<tr>
<td>Xylan</td>
<td>329</td>
<td>0.45</td>
</tr>
<tr>
<td>Galactan</td>
<td>45</td>
<td>0.04</td>
</tr>
<tr>
<td>Others</td>
<td>24</td>
<td>0.05</td>
</tr>
<tr>
<td>Mass balance</td>
<td>1002</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Torrefaction \(\Leftrightarrow\) “Burning” in Limited Oxygen

- Torrefaction: 200°C to 300°C under inert atmosphere
- Removes moisture and volatiles \(\rightarrow\) stable to microbial attack
- Densify torrefied biomass \(\rightarrow\) cheaper to transport
- Energy value \(\sim\) low rank coal
Torrefaction: Conversion of Biomass to “Biocoal”

Built a portable 8 tons/day unit to produce BioCoal on location.
The 28’ unit is mounted on an 18-wheel trailer

Almond hullers processing plant, Los Banos, CA
http://renewablefueltech.wordpress.com/
Torrefied Almond Shells

230°C

260°C

290°C

60 min  80 min  100 min
Making plastic parts with almond shell additives

Torrefied biomass:
   Almond shells at 280°C
   Wood at 280°C
   Almond shells at 300°C

Polymer: Polypropylene
Torrefied Biomass-Polymer Composites

Torrefied Almond Shell

Torrefied Almond Shell in Polypropylene
Torrefied Almond Shell in PET

– Alternative to wood-polymer composites
Heat Distortion Temperature

a.k.a. ↔ the softening point

Temperature at which material deforms under specific load

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Distortion Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>135</td>
</tr>
<tr>
<td>15% Almond Shells</td>
<td>155</td>
</tr>
<tr>
<td>15% Pine</td>
<td>160</td>
</tr>
</tbody>
</table>
Heat Distortion Temperature

**a.k.a. ⇔ the softening point**

Temperature at which material deforms under specific load

---

### EFFECT OF FILLERS ON HDT OF POLYPROPYLENE

<table>
<thead>
<tr>
<th>Fillers</th>
<th>HDT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>135</td>
</tr>
<tr>
<td>Talc</td>
<td>140</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>145</td>
</tr>
<tr>
<td>Fiber</td>
<td>150</td>
</tr>
<tr>
<td>Almond Shell</td>
<td>155</td>
</tr>
<tr>
<td>Pine</td>
<td>160</td>
</tr>
</tbody>
</table>
Torrefied Biomass in Plastics

F-D-S Manufacturing Co. Since 1950

Images:
1. Stacked plastic containers with a label.
2. A hand planting seeds in a tray of soil.
USDA researchers are partnering with tire companies to provide a domestic source of rubber to make US-produced rubber tires.
Partnerships: Industrial Cooperators

California Almonds

UC Davis
University of California

Method
Gel Hand Wash Refill

World Centric
Zero Waste Solutions

Agri-Tech Producers, LLC
"Meeting Tomorrow's Needs Today"
Glucaric acid production

Method Products uses “green” solvents

- glucaric acid
- gluconic acid,
- celllobionic acid, etc..

Why not make them from almond hull sugar?
Next Steps....

- Work to isolate sugars from hulls for ????
  - Feed? Ethanol? Food?
  - Explore synergies with sugar beet

- Find new uses for spent hulls.

- Explore new uses for torrefied shells,
  - Plastics
  - Rubber tires!

- Take advantage of the fact that the hulls and shells are aggregated, in California.....
Acknowledgements

- California Department of Food and Agriculture (Grant # SCB11021)

- RPAC Almonds for donating almond shells
Oils and Rubber
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Tom McKeon

Biofuels
Kevin Holtman
Charles Lee
Kurt Wagschal
Dominic Wong

Bioproducts
Greg Glenn
Bor-Sen Chiou
De Wood
A player to be named later

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Partnerships
Biogas Capacity: An ongoing story
USDA AD system schematic for lignocellulosic waste streams
Conveyor loading MSW to autoclave
MSW in the autoclave prior to treatment
MSW after steam treatment
Post-Autoclave MSW Sorting

Trommel Screen Side View

3/8"  1/2"  1"

Trommel Screen Front View
MSW fiber < 3/8”
Cellulose Recovery from Autoclaved MSW

Processed paper from recovered fiber
Grow Plastics Technology in Packaging

**Better**
- Equivalent/Superior Strength
- Thermally Stable

**Greener**
- 100% Bio Based
- Up to 80% CO₂ Reductions from Materials

**Lower Cost**
- Beat Solid Plastics on Price by up to 40%