Biomass: Building a California Bioeconomy with Hulls and Shells

December 7, 2016

California Almonds®
Almond Board of California
Biomass: Building a California Bioeconomy with Hulls and Shells

Karen Lapsley, Almond Board of California (Moderator)

Bill Orts, USDA Albany

Dr. Glenda Humiston, UC Davis
Karen Lapsley,
Almond Board of California
Bill Orts, USDA Albany
Adding Value to Almond Co-Products

William Orts – Research Leader, Bioproducts

December 7, 2016
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 ↔ 2.4 million Tons/yr

- Hulls 53%
- Shells 22%
- Trees 18%
- Pruning & Twigs

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)
Integrating Ethanol Plant

Almond hulls $\rightarrow$ 1st washer $\rightarrow$ 2nd washer $\rightarrow$ 3rd washer $\rightarrow$ spent hull filter cake

- 88% fermentable sugar recovery
- Concentrated filtrate (131 g/L fermentable sugar)
- 7.4% (v/v) ethanol yield
- 185 mL/g AH ethanol yield
- 75 mL/g AH CH$_4$ yield

attached growth anaerobic reactor

Distillation column

- 90% SCOD conversion efficiency
- Concentrated thin stillage

low SCOD effluent

FW

First washer

1st washer

2nd washer

3rd washer

Fermentor

86% fermentation efficiency

88% fermentable sugar recovery

Integrated Almond Hulls

1st washer

2nd washer

3rd washer

Spent Hull Filter Cake

Distillation Column

Attached Growth Anaerobic Reactor

Low SCOD Effluent

USDA

16
# 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)

USDA
• 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: ????
Comparison of Extraction Approaches
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
Spent Hulls ↔ Uses?

Key issue: Not practical to ferment hulls directly

• Hulls absorb 4-8 times weight of water
  – Highest stirrable slurry is ~15% hulls in water.

Water: 90%  80%  70%  60%  50%
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

- Hulls 53%
- Shells 22%
- Trees 18%
- Pruning & Twigs

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>

TORREFIED FILLERS FOR PLASTICS

TO STUDY THE EFFECTS OF TORREFIED FILLERS ON THERMAL AND MECHANICAL PROPERTIES OF PP
Torrefaction ⇔ “Burning” in Limited Oxygen

- Torrefaction: 200°C to 300°C under inert atmosphere
- Removes moisture and volatiles → stable to microbial attack
- Densify torrefied biomass → cheaper to transport
- Energy value ~ low rank coal
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

Time:
- 60 min
- 85 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

- Alternative to wood-polymer composites
Heat Distortion Temperature

a.k.a. ⇔ the softening point

Temperature at which material deforms under specific load
Heat Distortion Temperature

a.k.a. ⇔ the softening point
Temperature at which material deforms under specific load

![Bar chart showing the effect of fillers on HDT of polypropylene.

- PP Pine
- Talc
- CaCO3
- Fiber
- Almond

HDT (°C)
130 135 140 145 150 155 160 165

EFFECT OF FILLERS ON HDT OF POLYPROPYLENE]
EFFECT OF TORREFIEd FILLERS ON HEAT DEFLECTION PROPERTIES OF PP

- SIGNIFICANT DIFFERENCE IN HDT BETWEEN VIRGIN AND RECYCLED PP
- ADDITION OF TORREFIEd FILLERS IMPROVED THE PROPERTY OF RECYCLED PP

PP grades provided by Kevin Stevenson, FDS MFG
THERMALLY TREATED BIOMASS FOR OTHER APPLICATIONS

TIRE INDUSTRY, FILTERS, SOIL ADDITIVES, BIOENERGY
### Elemental Analysis of Carbon Black & Torrefied Biomasses

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>% C</th>
<th>% H</th>
<th>% O</th>
<th>% N</th>
<th>% Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARBON BLACK</td>
<td>88.48</td>
<td>0.91</td>
<td>4.74</td>
<td>0.19</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>TORREFIED WALNUT SHELLS</td>
<td>62.51</td>
<td>5.68</td>
<td>28.84</td>
<td>0.49</td>
<td>1.06</td>
</tr>
<tr>
<td>TORREFIED RICE HULL</td>
<td>40.70</td>
<td>4.22</td>
<td>26.14</td>
<td>0.45</td>
<td>10.77</td>
</tr>
</tbody>
</table>

Torrefied biomasses are **oxygen-rich**

Torrefied rice hull contains ~ 11% silica
## ELEMENTAL ANALYSIS OF BIOMASS

<table>
<thead>
<tr>
<th>TORREFIED BIOMASS</th>
<th>% C</th>
<th>% H</th>
<th>% O</th>
<th>% N</th>
<th>% Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SORGHUM</td>
<td>54</td>
<td>3</td>
<td>20</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>ALMOND</td>
<td>54</td>
<td>6</td>
<td>36</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>WALNUT</td>
<td>63</td>
<td>6</td>
<td>29</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>PISTACHIO</td>
<td>65</td>
<td>5</td>
<td>32</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>RICE HULL</td>
<td>41</td>
<td>4</td>
<td>26</td>
<td>0.5</td>
<td>11</td>
</tr>
</tbody>
</table>

- TORREFIED BIOMASS RETAIN FUNCTIONALITY AFTER PRETREATMENT
- SORGHUM AND RICE HULL CONTAINED SILICA
PARTICLE SIZES

<table>
<thead>
<tr>
<th>TORREFIED BIOMASS</th>
<th>AVERAGE PARTICLE SIZE (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SORGHUM</td>
<td>3</td>
</tr>
<tr>
<td>ALMOND</td>
<td>150</td>
</tr>
<tr>
<td>WALNUT</td>
<td>150</td>
</tr>
<tr>
<td>PISTACHIO</td>
<td>150</td>
</tr>
<tr>
<td>RICE HULL</td>
<td>250</td>
</tr>
</tbody>
</table>

- SAMPLES WERE GROUND USING THE CRYO-GRINDER
- SORGHUM WAS TORREFIED AT ANOTHER LOCATION. IT MAY HAVE BEEN TORREFIED AT A HIGHER TEMPERATURE, THUS INCREASING IT’S GRINDABILITY
TEM OF CARBON BLACK & TORREFIED SORGHUM

CARBON BLACK

TORREFIED BIOMASS

CONFIDENTIAL
# Calorific Values

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Before Torrefaction (J/g)</th>
<th>After Torrefaction (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorghum</td>
<td>No value from Joe James</td>
<td>18,928</td>
</tr>
<tr>
<td>Almond</td>
<td>17,319</td>
<td>21,205</td>
</tr>
<tr>
<td>Walnut</td>
<td>18,574</td>
<td>23,810</td>
</tr>
</tbody>
</table>

• House coal has a calorific value **30,000 J/g**
• Energy density of increases after torrefaction

**CONFIDENTIAL**
USDA researchers are partnering with tire companies to provide a domestic source of rubber to make US-produced rubber tires.
Grow Plastics Technology in Packaging

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

**Greener**
- 100% Bio Based
- Up to 80% CO$_2$ Reductions from Materials

**Lower Cost**
- Beat Solid Plastics on Price by up to 40%
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
William Orts
510-559-5730
bill.orts@ars.usda.gov

Oils and Rubber
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Ken Lin
Tom McKeon

Biofuels
Kevin Holtman
Charles Lee
Kurt Wagschal
Dominic Wong

Bioproducts
Greg Glenn
Bor-Sen Chiou
De Wood
A player to be named
"a date which will live in infamy"

December 7th 1941
Pearl Harbor
Partnerships
Growing the Bio-Economy

Energy ~ Products

Dr. Glenda Humiston, Vice President
Agriculture and Natural Resources
University of California
California has many sources and very high volumes of biomass – this is both a challenge and an opportunity!

Distribution of annual biomass resources in California. SOURCE: Tittman et al. 2008.
Combustion for electricity is not the future...

Solar in, biomass energy is out—and farmers are struggling to dispose of woody waste

California’s Homeless Biomass Problem

Biomass power generation in California is threatened by expiring contracts, low energy prices and an uneven playing field, leaving millions of tons of biomass fuel without a use.

By Ron Kotrba | August 25, 2015

California’s immense stores of waste biomass once had a plush abode in the equitably priced, long-term power purchase agreements (PPA) that stemmed from the state’s aggressive interpretation of federal legislation—the Public Utilities Regulatory Policy Act of 1978—born out of the energy crisis of the early 1970s. At its peak in the early 1990s, the California biomass energy industry produced almost 4.5 billion kilowatt-hours (kWh) per year of electricity, according to the National Renewable Energy Laboratory, and each year provided a good home to more than 10 million tons of the state’s solid wastes. PURPA required electric utility companies to buy privately produced power at their avoided cost of generation, in essence spawning the development of the independent power industry in the U.S. High avoided cost rates, particularly in California, and favorable federal tax policy for renewable energy projects provided the impetus under PURPA for explosive growth for the state’s biomass power industry.

 awaits action: Greenleaf Power idled this 17 MW biomass power plant in Tracy, California, last fall when it could not compete on an uneven playing field with solar and wind, and low natural gas prices, the basis for pricing under new PPAs.

PHOTO: GREENLEAF POWER
Expanding BioProducts Requires Innovation & New Technology
Biodegradable Plastics from Biomass

Commercial bioplastic is already made from cellulose – replacing petroleum-based plastics. Scientists developed means to ferment a broader range of cellulosic materials – enabling large scale commercial production.

An estimated $375 billion market for chemical, plastic, and rubber products represents a huge bioeconomy opportunity.

www.milkeninstitute.org/publications/view/461
Opportunity: Cellulosic Nanomaterials (CNC)

✓ Stronger
✓ Lighter
✓ Cheaper
✓ Renewable

Forest products, biomass

Wood cells
Cell wall layers
Cellulose microfibrils

CNC’s consist of organized stacks of $I_\alpha$, $I_\beta$ cellulose chains

AFM image of a cellulose Nanocrystal (CNC)

Chemical treatment releases crystalline phase

SOURCE: USFS Forest Products Laboratory 2013
Opportunity: Cellulosic Nanomaterials (CNC)

- Wood pellets
  $155 (100% conversion)
- Fuel Ethanol
  $255 (@100 gallons/ton)
- High Brightness Paper
  $500 ($1,000/ton - 45% yield)
- Cellulose Nanocrystals
  $1,350 ($6,000/ton - 23% yield)

SOURCE: USFS Forest Products Laboratory 2013
Adding nanocellulose material to cement makes concrete about 22% stronger, lighter and more elastic. And, carbon is sequestered!

Siskiyou County is partnering with US Forest Service and several private sector partners on three possible applications for nanocellulose materials:

- as a cement additive to improve the structural characteristics of concrete.
- as a coating for fruit pallets to extend the usable life of wood pallets.
- as additives for bridge coverings and tennis courts (concrete and/or asphalt).
It is projected that cellulosic nanomaterial could have a market penetration as high as 3-4% across target markets building to over 24 million tons of demand.

This could create ~224,000 jobs and GDP value of over $100 billion in the US – as projected by the National Nanotechnology Initiative and National Science Foundation study.
Research on High-Value Biobased Products Supports Forest Health & Economic Development Opportunities.

Feedstocks for Chemical and Polymer Industries

Pellets

Bio-Diesel

Heat for Greenhouses

Compost

Bioproducts & Packaging

…and more!
UC Cooperative Extension
- 200+ Advisors who live/work in local communities
- 130+ Campus-based UCCE Specialists

Agricultural Experiment Station
- 650+ researchers across the entire UC system

Statewide Programs & Institutes
- Ag Issues Center
- Integrated Pest Management Center
- Informatics & GIS
- Nutrition Policy Institute
- Sustainable Ag Research & Education
- Water Research Institute
- Youth Development and 4-H

Research & Extension Centers
- 9 locations statewide
- Over 12,000 acres
Over 300 California Firms Produce a Wide Array of Bio-Based Products

February 2012: Presidential Executive Order requires federal agencies & contractors to utilize biobased products.
Healthy watersheds could produce 9–16% more water for California.

“Effect of forest management on water yields and other ecosystem services in Sierra Nevada forests”.

UCM Faculty: Roger Bales
UCB AES Faculty: Kevin O’Hara
UCCE Advisor: Susan Kocher
UCCE Specialist: Bill Stewart

http://aginnovations.org/images/uploads/CRWFS_Storage_FINAL.pdf
“Layers” of Funding & Economic Activity Will be Needed

Value of Biobased Products will help finance forest health activities – probably not enough.

Augment with Cap & Trade Credits

Need to monetize value of “reclaimed” water from forest health activities!
1.2 Million Jobs in California
$318 Billion Direct Sales & Exports
272,000+ New Jobs in Five Years
Strategy for a Sustainable California

= SYNERGY

Synergia (Greek): creation of a whole greater than the sum of its parts.

Synergos (Greek): "working together".

Synergos (Greek): "working together".
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Questions?