#### **Lignin and Economics of Lignocellulosic Biomass Fractionation**





Ali Manesh, Ph.D., P.E. (American Science and Technology) Kevon Tabrizi and Teng Yang (University of Wisconsin, Platteville) **A Foundation for Future Energy BIOD REN** CHEMICAL



- American Science and Technology (AST), founded in 2003, provides common sense scientific, technological, and manufacturing solutions to its customers;
- ➢ AST is a full service scientific and engineering company specialized in research, development, deployment, and commercialization of advanced technologies and products;
- Our major strength is our working relationships with various domestic universities and research institutions;
- ➤ AST's headquarter is in Chicago IL; manufacturing facilities are located in Wausau WI, and R&D labs in Brookings SD;
- ➢ BioRen Chemical is formed to be the manufacturing arm of AST.





#### AST Main Office, Chicago, IL









# **Outline of this presentation:**

Crude oil based products that can be replaced by renewable resources;

- ➤What are our raw materials;
- ➤Our technologies and our capabilities;
- ➤Our core products;
- ➢ Review costs, incomes, and how the ends can meet;
- Collaborating with the UW Platteville, use lignin to mix with polymers, extrude sheets and injection mold samples;
- Review the results of some tests performed to evaluate MP;
  Conclusion.





Typically products from every barrel of Crude Oil are:

- ✓ 43% Gasoline
- ✓ 22% Diesel Fuel
- ✓ 9% Jest Fuel
- ≻ 4% LPG
- ➤ 4% heavy Oil
- > 18% Other Products including:
  - > Lubricants,
  - ✓ Feed-stocks for petrochemicals such as:
    - ✓ Plastics,
    - ✓ Surfactants,
    - ✓ Fibers, and
    - ✓ Elastomers



#### Our Feedstock comes from Non-Edible Renewable Resources



















Agricultural waste, forestry products/wastes, and other lignocellulosic wastes materials





Pretreatment of Biomass:

Physio-Chemical (mostly for Agricultural wastes)

- Steam Explosion
- ➤ Liquid Hot Water
- ➤ Co2 Explosion
- Ammonia Fiber Explosion

Chemical Methods (for Agricultural wastes and forestry products)

- Acid Hydrolysis
- Alkali Hydrolysis
- > Ozonolysis (Ozone cracking the organic compound)
- Organosolv Process
- Oxidative Delignification

Ref: Sun and Chang 2002

Most of the Hydrolysis processes produce a mixture of C5 / C6 sugar and furfural;

Furfural is a fermentation inhibitor and should be removed prior to fermentation;

- >Typical fermentation efficiency for C6 sugar is 95%, while for C5 is only 70%;
- Organosolv fractionation produces cellulose, pure lignin, and organic solvents;
- > Enzymatic hydrolysis of cellulose produces C6 sugar with no fermentation inhibitor;
- > C6 sugar is used to make chemicals that are produced by fermentation and Biofuel.





 $\geq$  A 50 Lb batch digestion system to break down the lignocellulosic materials into cellulose, chemicals, and lignin;

- > Various separation equipments to recover solvents, lignin, and fiber;
- > A 160 Gallon hydrolysis to convert cellulose to sugar;
- > A 50 Gallon fermenter to convert sugar to chemicals or bio-fuel;
- > A 2 Lb/hr fluidized bed fast pyrolysis to evaluate gasification of wastes;

➤ One 15 Lb/hr augur type fast pyrolysis to convert all process wastes to bio-oil.









Our Fractionation Process (Part of AST's Integrated Bio Refinery Pilot Plant)







# Chemicals From Pretreatment



- BI O REN CHEMICAL







### **Products / Economics**

One Ton of Dry Biomass	Min	Max	Typical
Lignin	10%	30%	20%
Cellulose	35%	50%	45%
Hemi (to organic solvents)	15%	35%	25%
Extractives	0%	10%	10%

Per One Ton of Dry Biomass	% Product	\$/Kg	Value
*Lignin	20%	\$0.50	\$100.00
√ Fiber	45%	\$0.15	\$67.50
✓ Extra Solvent	20%	\$0.70	\$140.00
Tot	al		\$307.50
Costs of Raw Materials		\$0.07	\$70.00
Processing Costs		\$0.21	\$210.00
	al 100%		\$280.00
Net Potential Profit			\$27.50

Price of organic solvents are the current Market price. To have sugar at \$0.30/Kg, we have to price our fiber at \$0.15/Kg, and key to that is to have a well developed market for our lignin.



### What is Lignin:

Lignin is a complex chemical compound, a cross-linked racemic macro-molecule with molecular masses in excess of 10,000 atomic mass units that fills the spaces in the fills the spaces in the fill wall between cellulose, hemi, and pectin components that confers mechanical strength to the cell wall.
 Lignin is relatively hydrophobic and aromatic in nature.

➤Lignin is one of the most slowly decomposing components of dead vegetation.







- 1) Traditionally Lignin has been used as a low density fuel to generate heat
- 2) Paper industries use Lignin to make high strength papers and cardboard
- 3) Lignin is a natural antioxidant and is used in cosmetics, http://lib.bioinfo.pl/paper:15288274
- 4) Lignin improves the compressive strength of concrete http://biomassmagazine.com/articles/8756/scientists-build-stronger-greener-concrete-with-lignin
- 5) Lignin is also used as crack filling materials for asphalt http://www.intrans.iastate.edu/publications/\_documents/t2summaries/lignin-asphalt.pdf
- 6) Lignin is a good board binder (mixed it with saw dust to make liquid wood) http://www.matternetwork.com/2009/1/from-lignin-comes-liquid-wood.cfm
- 7) Lignin is an ideal materials for carbon fiber manufacturing http://ncsu.edu/bioresources/BioRes\_06/BioRes\_06\_4\_4566\_Luo\_GCF\_Lignin\_Based\_Carbon\_Fiber\_1219.pdf
- 8) Lignin application for plastics/polymers





Current market price for polymers is over \$1000/Ton. Successful insertion of lignin to replace some of the polymer has increased the price for pure lignin to at least over \$500/T.

AST, in collaboration with the University of Wisconsin Platteville has developed the required processes to mix lignin with polymers such as:

- 1) Poly Lactic Acid;
- 2) Polypropylene;
- 3) High Density Polypropylene.

Process includes: Grinding, Drying, Mixing, followed by extrusion into sheet or injection into a mold to make parts.





University Wisconsin Platteville – Plastic Process Center

One of the most advanced educational Plastics Processing labs in the nation that started in 1992.







# **UWPLAT Student Team**

# Teng Yang & Kevon Tabrizi

- Major: Industrial Technology Management
- Minor: Plastic and Drafting
- Hometown: Oshkosh ,WI
- Feeling s on working with Lignin?
- Teng- "Great research to look into its mechanical properties"



- Major: Biology
- Minor: Plastic
- Hometown: Platteville, WI
- Feelings on working with lignin?
- Kevon- "Always heard about it from different science classes, but never knew much about it until researching its properties now"



#### **AST / UWP Collaboration**



#### Grinding



Mixing



T



Extruder



#### **Extruded Samples**





#### **Injected test Samples at UWP**





# Effects of Lignin on Mechanical Properties of PLA

The following shows the tensile properties of pure PLA and PLA plus about 1% lignin

![](_page_20_Figure_4.jpeg)

Ultimate Stress Vs Elongation at break (%)

About 5% increase in elongation and about %10 increase in UTS (Recycled PLA used) (performed by METLAB at South Dakota State University)

![](_page_20_Picture_7.jpeg)

![](_page_21_Picture_1.jpeg)

## Effects of Lignin on Mechanical Properties of Polypropylene The following shows the tensile property of pure Polypropylene (PP) plus 10% lignin as additive

Ultimate Stress Vs Elongation at Break (%)

![](_page_21_Figure_4.jpeg)

At 10% lignin, about 9% reduction in Elongation and 1.3% increase in UTS.

![](_page_21_Picture_6.jpeg)

**AST / SDSU Collaboration** 

### Effects of Lignin on Mechanical Properties of HDPE The following is the tensile property of High Density Poly Ethylene (HDPE), and HDPE + 10% lignin as additive

![](_page_22_Figure_2.jpeg)

At 10% lignin, about 40% reduction in Elongation and 8% reduction in UTS.

![](_page_22_Picture_4.jpeg)

# 830-I Impact testing

![](_page_23_Picture_1.jpeg)

PP+1%Lignin

![](_page_23_Picture_3.jpeg)

1

PP+10%Lignin

![](_page_23_Picture_6.jpeg)

#### 1 Kg drops from 750 mm

![](_page_23_Picture_8.jpeg)

CHEMICAL

PP+2%Lignin

![](_page_23_Picture_10.jpeg)

PP+20%Lignin

![](_page_23_Picture_11.jpeg)

![](_page_23_Picture_12.jpeg)

Pure Polyethylene

![](_page_23_Picture_14.jpeg)

![](_page_24_Picture_1.jpeg)

> AST's flexible process can produce cellulose (sugar), organic solvents, and pure lignin;

To decrease costs of sugar produced from lignocellulosic materials, we have to increase the value of our pure lignin;

AST/UWP have developed processes to mix lignin with polymers, extrude and inject test samples, and the results so far are:

- Elongation and ultimate strength reduced for HDPE and increased for PLA;
- Drop test suggests adding more than 10% lignin can improve impact

resistance of the polypropylene;

► AST lignin can be used to replace some percentage of polymers

> The test results did not present any significant deteriorations in polymers' mechanical properties.

![](_page_24_Picture_10.jpeg)

![](_page_25_Picture_1.jpeg)

# How do we make the ends meet?

- ➤Our main products are <u>Chemicals</u>, Lignin, and Fiber;
- Our <u>flexible process</u> can make different percentage of Chemicals or Fiber (per market demand);
- Our process <u>regenerates</u> its solvent and some extra;
- ➤ We <u>recycle</u> our used water;
- > We have developed process to use lignin as polymer
- Production of high value lignin and solvent allows us to price our fiber low enough to have sugar at \$0.30/Kg (\$0.15/Lb);
- > Our sugar price can go further down, when we get more Levulinic Acid/Ester from unreacted fibers after hydrolysis (instead of Pyoil);
- > We are able to <u>use all biomass</u> with little to no waste.
- >At \$0.50/Kg, there are many customers lined up for our pure lignin.

![](_page_25_Picture_12.jpeg)

![](_page_26_Picture_0.jpeg)

### The Mission for BioRen Chemical

# Use Renewable Resources to manufacture Cost Competitive Chemicals that results in the Reduction of Crude Oil Consumption

![](_page_26_Picture_3.jpeg)