Biggest Bang
Forestry and Biochemicals

Alan Rudie
USDA Forest Service
Forest Products Laboratory
Madison, WI

What is the real question?

Biggest bang in:

- Oil replacement?
- CO_2 reduction?
- Value (ROI)?

Three Laws of Thermodynamics

- Cannot convert matter from one form (chemical) to another without using energy.
- This means the highest energy value is achieved with direct combustion and would dictate that biomass be used to generate heat (oil) and electricity (coal).

Oil replacement

- Probably pellet stoves. Largely displaces heating oil and some coal.
- Energy committed to the process includes
  - transportation to the pellet manufacture
  - Grinding and drying
  - Pellet press
  - Shipping to store or customer.
- Net is about 70% conversion efficiency

Wahlund et al, Biomass Biorenergy, 23: 271(2002)

CO_2 reduction

- Replacing coal in electrical power generation.
- Hydrocarbons burn to produce CO_2 and H_2O. Fuels with high carbon content produce a disproportionate amount of CO_2 relative to energy released. Coal is higher carbon content than oil which is higher than gas.

What is the highest ROI?

	Yield	Value (m^3)
Lumber	80	$100
Paper	45	$100
Pellets	90+	$35
Ethanol	25	$50

2 X 4 X 8 at $310/1000 bf, paper at $650/ton, wood pellets at $120/ton and ethanol at $2.00 per gallon

Biggest bang, biomass chemicals

- The question asked is biggest bang for forestry and biochemicals.
  - Need to put the biggest bang for forestry into perspective relative to biochemicals.
  - Need to understand what biochemicals are and the technical status of biochemicals from forest materials.
  - Need to understand the realities of competitive markets with high value products.

Chemically, what is biomass?

- Biomass is a mixture of soluble substances and polymers
- Carbohydrates represent the bulk of all biomass, as much as 80%. They can be crudely classified as Cellulose, Starch and Hemicellulose. All carbohydrates are sugars or polymers of sugars.
- Lignin typically comprises 10-30%. Lignin is a cross-linked phenolic polymer. For practical purposes, it is not biologically processable.

Cellulose

- Cellulose is a polymer of the simple sugar glucose. It is a structural component in biomass and forms the fibers used in paper and textiles.
- Cellulose is a linear – straight chain polymer with a 1,4-ß-glucoside linkage.
  - I know that is a lot to swallow for a non-chemist. Suffice it to say that this linkage is chemically robust. This is one reason trees live a long time and we do not eat sawdust.

Starch

- Starch is also a polymer of the simple sugar glucose.
- The major linkage is a 1,4-**α**-glucoside.
  - Changing from the ß to the α orientation at C1 changes the polymer from a structural and biologically robust form to a food storage and universally digestible form.
- As a storage polymer, starch is primarily found in seeds and storage organs like tubers and bulbs.

Hemicellulose

- Hemicellulose is a group of polymers of mixed sugars.
  - Xylans (xylose and glucuronic acid)
  - Mannans (Mannose, glucose and galactose)
  - Arabinogalactan
- Hemicellulose is more easily hydrolyzed-saccharified-digested than cellulose, but is much harder than starch.

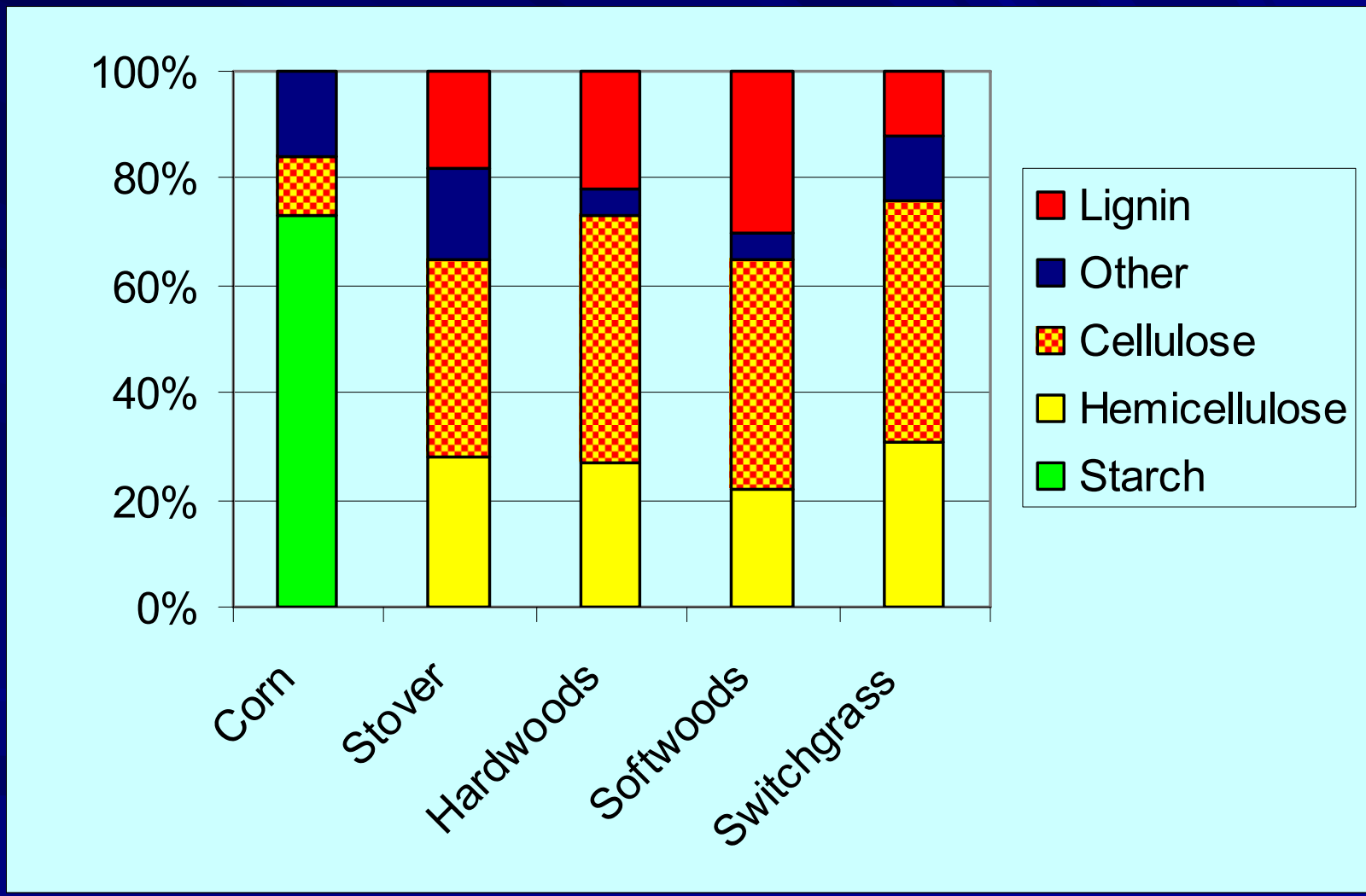
With apologies: More Chemistry

- Glucose, mannose and galactose are six carbon sugars and are all fermented by brewers yeast (*Saccharomyces cerevisiae*) and other organisms.
- Xylose and arabinose are five carbon sugars. They are not fermented by *S. cerevisiae* but can be fermented by other organisms

Are you really bored?

- The critical take home point is that *S. cerevisiae* is the only organism capable of functioning at high ethanol concentrations.
  - High ethanol concentration reduces the size of the processing equipment and energy cost in distillation to isolate the ethanol or another fermentation product.
- Science to the rescue?
  - There are about five very active efforts to increase alcohol tolerance of organisms that do ferment five carbon sugars.

Biomass Composition



Transportation

- It costs a lot of money to move water and air.
  - Wood is typically 30 to 50% water
  - Bulk density (OD basis)
    - 40-80 kg/m^3 for chopped corn stover
    - Without compaction, corn stover will require 40 semi-trailer loads per harvester per day.
    - Birrell estimates that at $35/ton, farmers will lose money hauling more than 15 miles.
    - 176 kg/m^3 for wood chips
    - 700 kg/m^3 for corn grain
    - 900 kg/m^3 for coal

Birrell: Iowa State University, Dept Ag and Biosystems Engineering

Are we asking the right questions

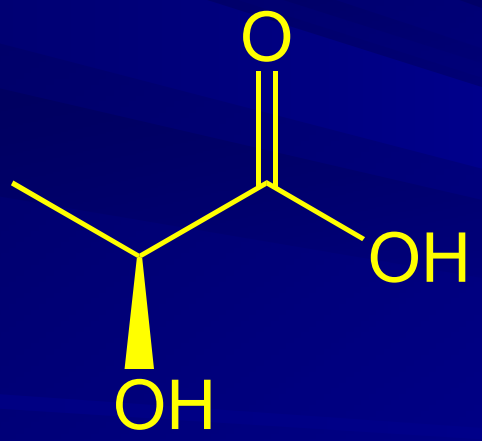
- Who will controls the markets?
- What can we get the product from trees and cannot get it at lower cost by other means?
- AF&PA VPP Partners picked ethanol for a reason:
  - it is the one market they can get into without depressing price.

Who controls the market?

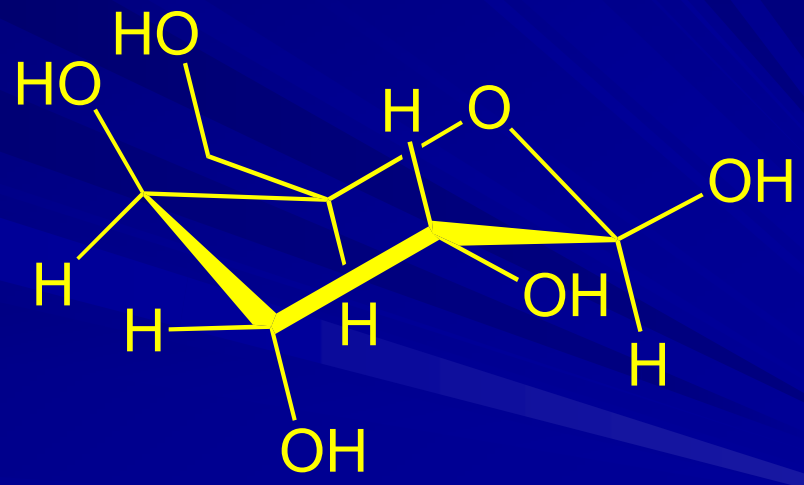
To get

1,3-Propanediol

You Start With



Lactic Acid



Glucose

To get glucose, start with

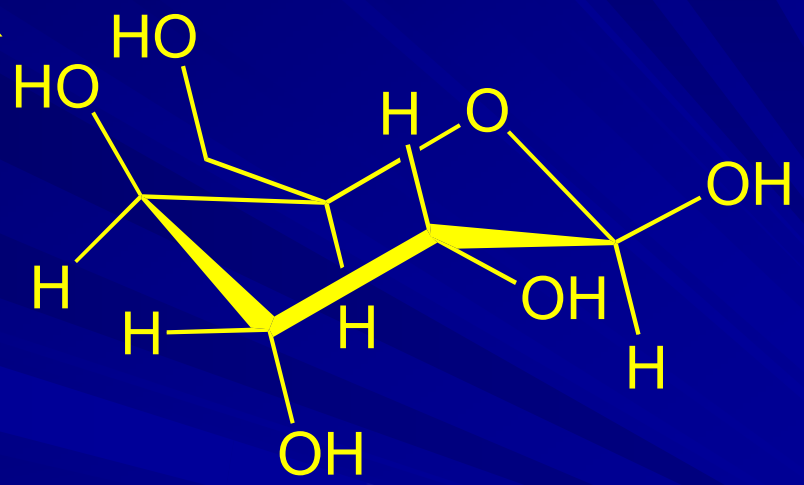
Sugar Cane

Corn Starch

70%

Wood & Residuals

35%



Estimated Ethanol Costs

Corn	1.22
Cellulose	1.76
Fischer-Tropsch (biomass)	1.80
Methanol	1.28

Wright and Brown, Biofuels, Bioproducts and Biorefining: 1: 49-56(2007)

Point I

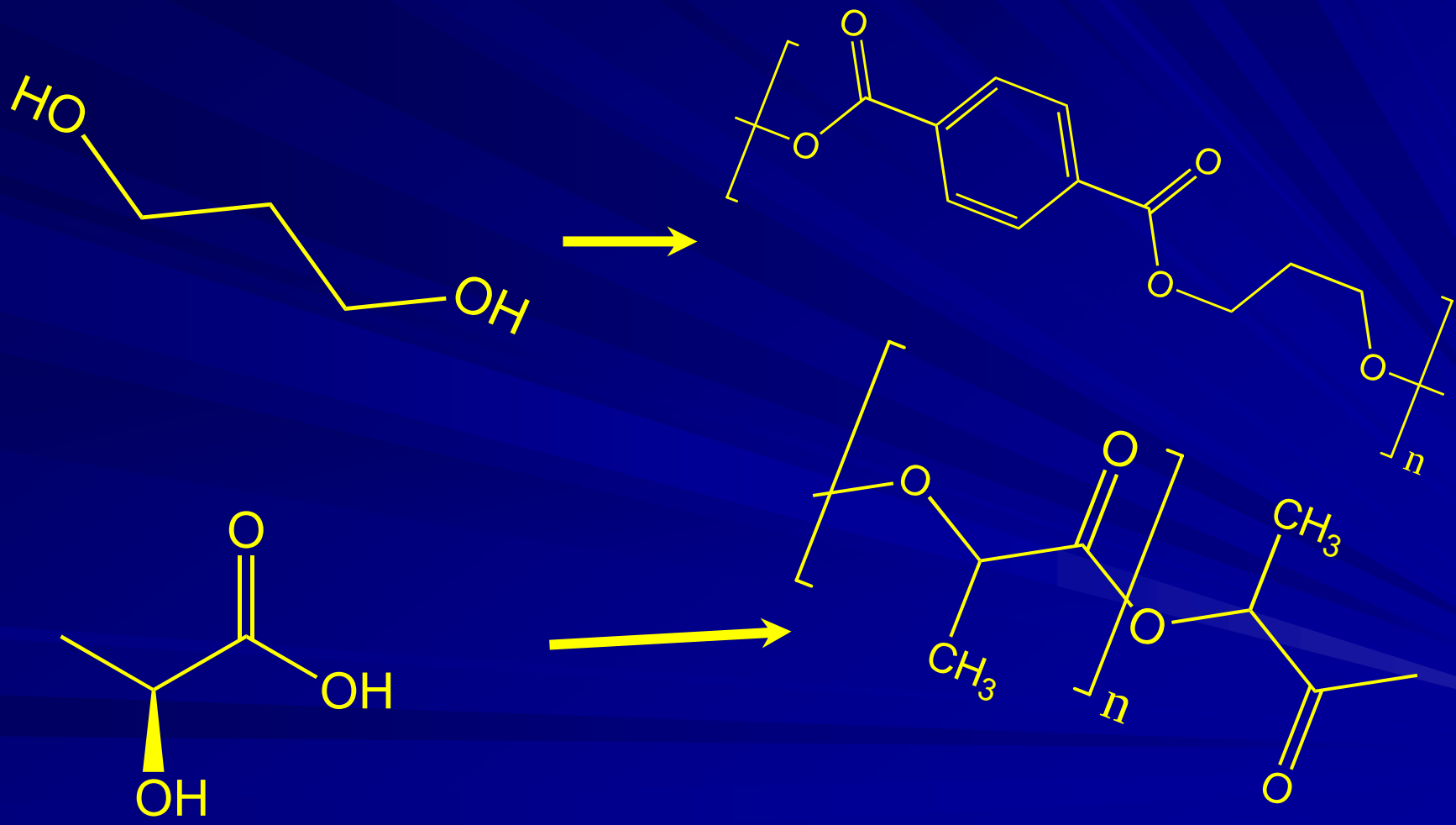
- The costs of distillation etc are similar for all sources of alcohols. Therefore – the cost difference represents the differences in capital and production costs for the rest of the process.
- Under most reasonable assumptions, corn is a lower cost route to glucose (and ethanol) than is cellulose saccharification.
- Corn will dominate glucose fermentation based markets.

High Value Chemicals

The champions of value added

- Polylactic acid
  - **A polymer of lactic acid**
  - **Introduced by Cargill and Dow as a substitute for clamshell food packaging and other applications.**
- 1,3-Propanediol
  - Used in polyester, cosmetics and antifreeze
  - DuPont with Tate and Lyle started production by fermentation of corn starch this summer.

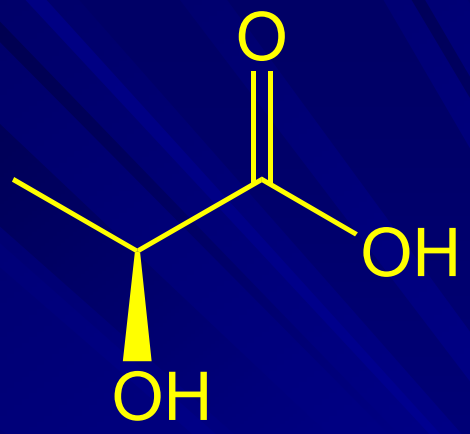
PLA and Polytrimethylene terephthalate



What makes them champions

- In commercial production
- Capable of competing with petroleum based products.
- If successful, they will provide expanding markets for these two biomass derived chemicals.
- Markets are controlled by intellectual property
  - Polymerization catalyst: Cargill/Dow
  - Fermentation organism: DuPont/Tate and Lyle

Lactic Acid



- Fermentation of sugars
- Estimated cost $0.50/lb (2003: DOE)
- Food and beverages (72 million lbs/yr)
- Polylactic acid polymer (300 million lbs/yr)
- Chemicals
  - Acrylic acid (adhesives and polymers 2 billion lbs/yr)
  - Ethylacrylate (solvent, 10 billion lbs/yr)

1,3-propanediol

- 250 MM lbs/yr
- Fermentation of sugars (100 million lb/yr)
- Polytrimethylene terephthalate is an improved polyester that has been limited by availability and cost of the diol.

Other High Value Biochemicals

- George Hajny, USDA, Forest Service, Forest Products Laboratory, Forest Service Research Paper: FPL 385 (1981).
- Werpy and Petersen, “Top value added chemicals from biomass”, DOE: NREL and PNWL, 2004.
- “Biobased Products”, Wisconsin Biorefining development initiative, Energy Center of Wisconsin. (www.wisbiorefine.org)

1,4-diacids
succinic, malic and fumaric

- Fermentation followed by ion exchange
- Applications:
  - Polyester and epoxies (as the diacid)
  - 1,4-Butanediol (polyesters, polyurethane). 680 million lbs, $0.65/lb (2003)
  - Tetrahydrofuran (industrial solvent). 255 million lbs ($1.50/lb, 2003)

1,4-diacids

- Technical concerns
  - Petrochemical routes will dictate pricing
  - Fermentation organisms are limiting – pH, rate, concentration

Glycerol

- Available from neutral and alkaline fermentation
- Large existing market: 500 thousand tons
- 75% comes from bio-sources (fats and oils)
  - As a byproduct of biodiesel, market may get depressed.
- Although an attractive basic chemical, market expansion will be dictated by price.

2,5-furandicarboxylic acid

- Chemical route
  - Oxidative dehydroxylation from glucose.
  - Glucose → hydroxymethylfurfural →FDCA
- Potential replacement for hydrocarbon derived terephthalic acid used in polyester
- Technical concerns include yield of intermediate and lack of an existing PET market.

Other fermentation products

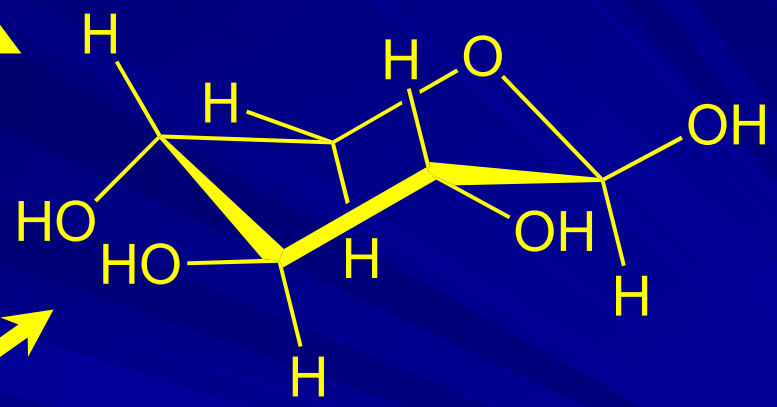
- Acetic acid (expect the market to get flooded)
- Butanol (2 billion lbs) (coproduct acetone). Butanol has been recommended as a fuel alcohol by DuPont. This will dictate value. Acetone is already a high volume industrial solvent.

To get xylose, start with

Hardwoods 17%

Corn Stover 20%

Wheat Straw 17%



Xylose

- Xylose is a five carbon sugar common in hardwoods and corn stover.
- Unlike glucose – there are no high concentration sources.
- Hardwoods can have an advantage in Xylose based products using the prehydrolysis-pulping concept.

The hitch: there is always a hitch

- Fewer product choices
- Fewer fermentation organisms and metabolic routes to products.

Xylose products: Furfural

- Produced by acid hydrolysis and decomposition of biomass with simultaneous distillation of product.
- An existing biobased market. Has already gone through one reduced cost market transition.
- Potential for market expansion but only if lower cost sources become available.

Xylose Products: Xylitol

- Xylitol is a sugar-alcohol. Sugar alcohols in general (sorbitol) contribute fewer calories than the base sugar but can be almost as sweet.
- Produced by catalytic reduction (hydrogenation) of xylose.
- Currently generated from beets and maize.

A perspective

- A product is usually high value because production capability is limited.
- Intellectual property, limited sources and small markets all contribute to high value.
- Starting with wood and using glucose, limited sources is not an option.
- The successful high value biorefinery is either going to develop a nitch product, develop it's own intellectual property, or align with someone who has.