Ethanol from Biomass and Cellulose; Challenges and Solutions

Kevin Edgar
Wood Science and Forest Products Department

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Today We Will Discuss:

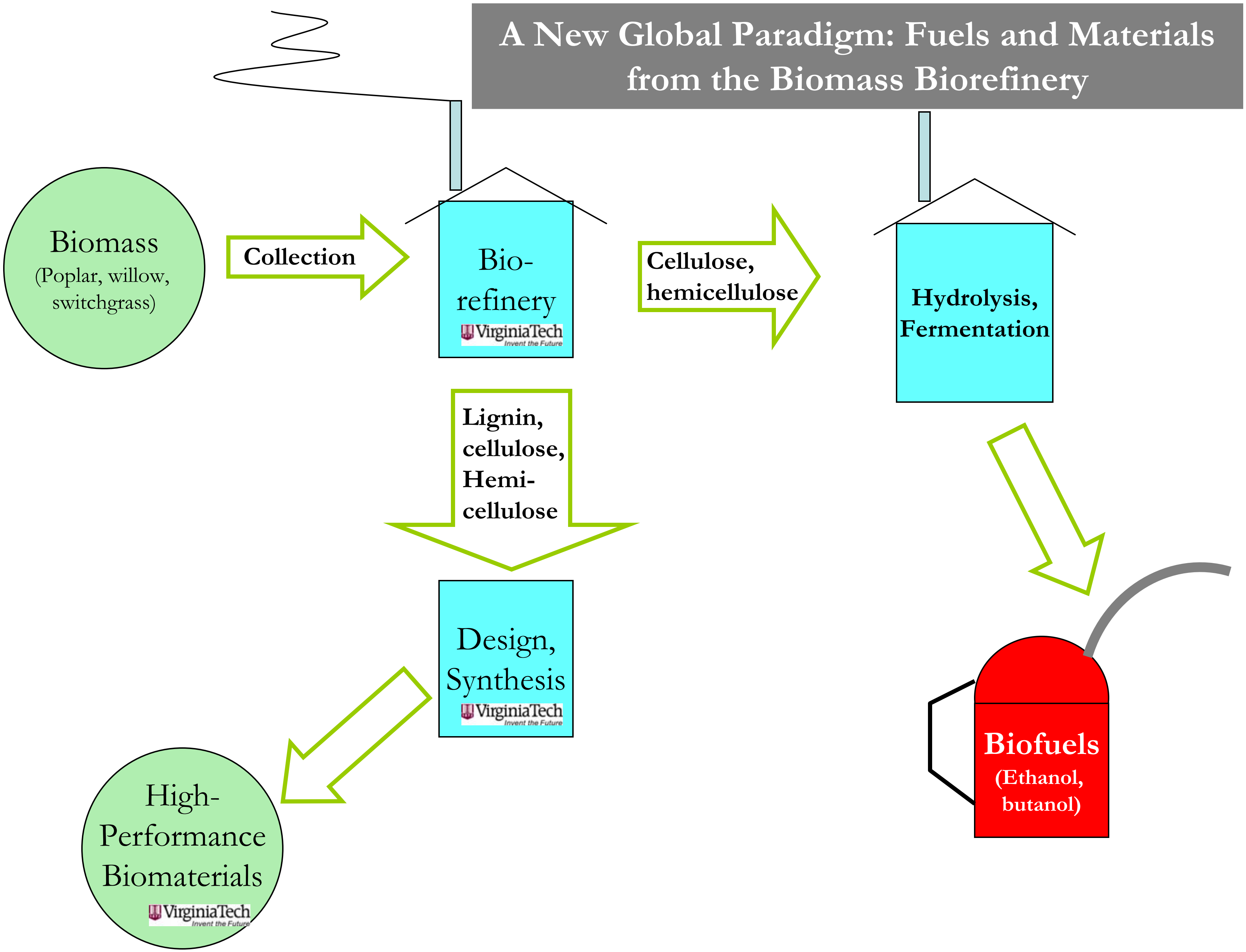
- Why biomass to biofuels?
- Key elements of conversion of biomass to biofuels and biomaterials.
- Key issues and impediments.
- Recent progress and remaining obstacles.
- The shape of a future biorefinery-based economy.
- The example of ethanol from sugarcane

Why Biomass to Biofuels?

- Energy independence - 60% of our fuel is now imported, with approximately 60% of that from unstable or threatened parts of the world

- Security of supply – demand for petroleum for fuel and chemicals accelerating vs. a limited global supply

- Reduce greenhouse gases – biomass growth removes CO_2 to balance that emitted when it is burned.


A New Global Paradigm: Fuels and Materials from the Biomass Biorefinery
Biomass
(Poplar, willow, switchgrass)
Collection
Bio-refinery
VirginiaTech
Invent the Future
Cellulose, hemicellulose
Hydrolysis, Fermentation
Lignin, cellulose, Hemi-cellulose
Design, Synthesis
VirginiaTech
Invent the Future
High-Performance Biomaterials
VirginiaTech
Invent the Future
Biofuels
(Ethanol, butanol)

Population and GDP Estimates

Region	2000		2025		2050	
	Pop,M	pcGDP,k$	Pop,M	pcGDP,k$	Pop,M	pcGDP,k$
North America	306	30.6	370	40	440	50
Latin America	517	6.7	700	20	820	35
Europe	727	14.7	710	30	660	40
Africa	799	2.0	1260	12	1800	25
Asia	3716	3.6	4760	20	5310	35
World	6065	6.3	7800	20	9030	33

J.J. Siirola, Eastman Chemical

Medium Term Economic Trends

- Much slower growth in the developed world
- Accelerating growth in the developing world
- World population stabilizing at 9-10 billion
- 6-7 X world GDP growth over next 50 or so years (in constant dollars)
- 5-6 X existing production capacity for most commodities (steel, chemicals, lumber, etc.)
- 3.5 X increase in energy demand
  - 7X increase in electricity demand

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Fossil Fuel Reserves

	Recoverable Reserves, GTC	Reserve Life @ Current Rate, Yrs	Reserve Life @ Projected GDP Growth, Yrs
Oil	120	35	25
Natural Gas	75	60	45
Coal	925	400	?

Fossil Fuel Reserves; the BP Perspective

	Reserve Life @ Current Rate, Yrs Siirola	Reserve Life @ Current Rate, Yrs British Petroleum
Oil	35	41
Natural Gas	60	64
Coal	400	155

British Petroleum, BP Statistical Review of World Energy, 2006

Consequences of Continuing Carbon Dioxide Emissions

- At 380 ppm, 2.2 GTC/yr more carbon dioxide dissolves in the ocean than did at the preindustrial revolution level of 280 ppm
- Currently, about 0.3 GTC/yr is being added to soil carbon and to terrestrial biomass due to changing agricultural and land management practices
- The balance results in ever increasing atmospheric CO_2 concentrations

J.J. Siirola, Eastman Chemical

Current World Energy Consumption

Per Year

	Quads	Percent	GTC
Oil	150	40	3.5
Natural Gas	85	22	1.2
Coal	88	23	2.3
Nuclear	25	7	
Hydro	27	7	
Solar	3	1	

Approximately 1/3 transportation, 1/3 electricity, 1/3 everything else (industrial, home heating, etc.)

J.J. Siirola, Eastman Chemical

Key Issues in Developing a Biorefinery Economy

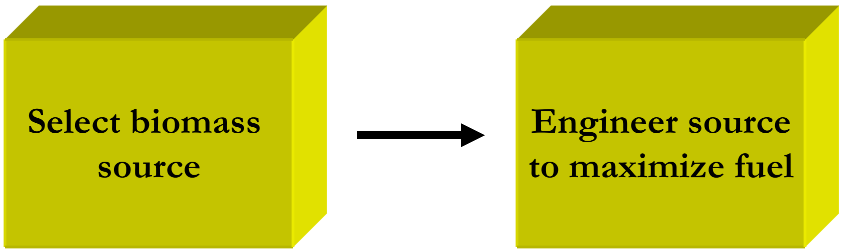
Select biomass source

Willow, poplar, eucalyptus, switchgrass, wood waste

Key issues:

Density
Year-round availability
Yield (kg biomass/hectare/yr)
Minimal energy input required
No competition with food markets

Key Issues in Developing a Biorefinery Economy



Select or engineer strains that maximize cellulose, make it easier to separate

Key issues:

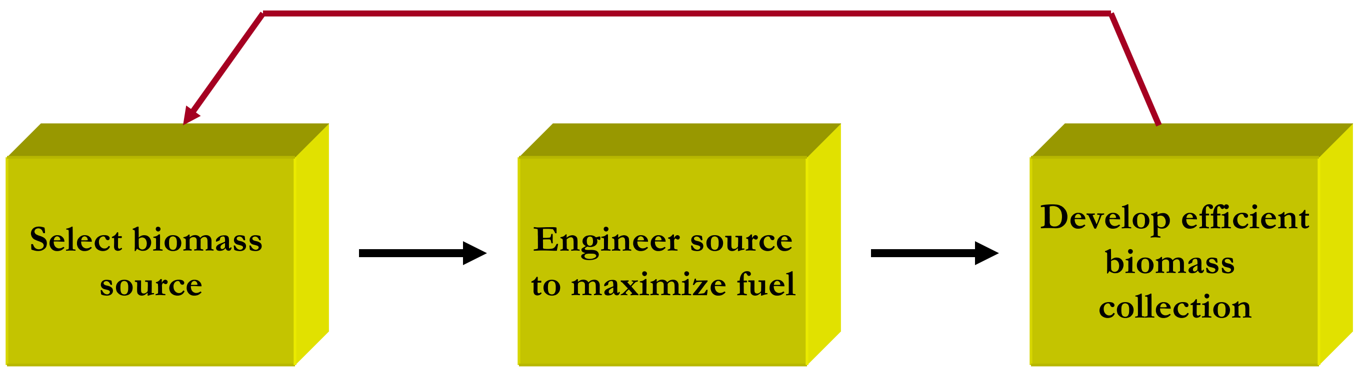
Cellulose/hemicellulose content

Accessibility (ease of hydrolysis)

Growth rate

Minimize components that will tend to inactivate enzymes(s)

Key Issues in Developing a Biorefinery Economy



Key issues:

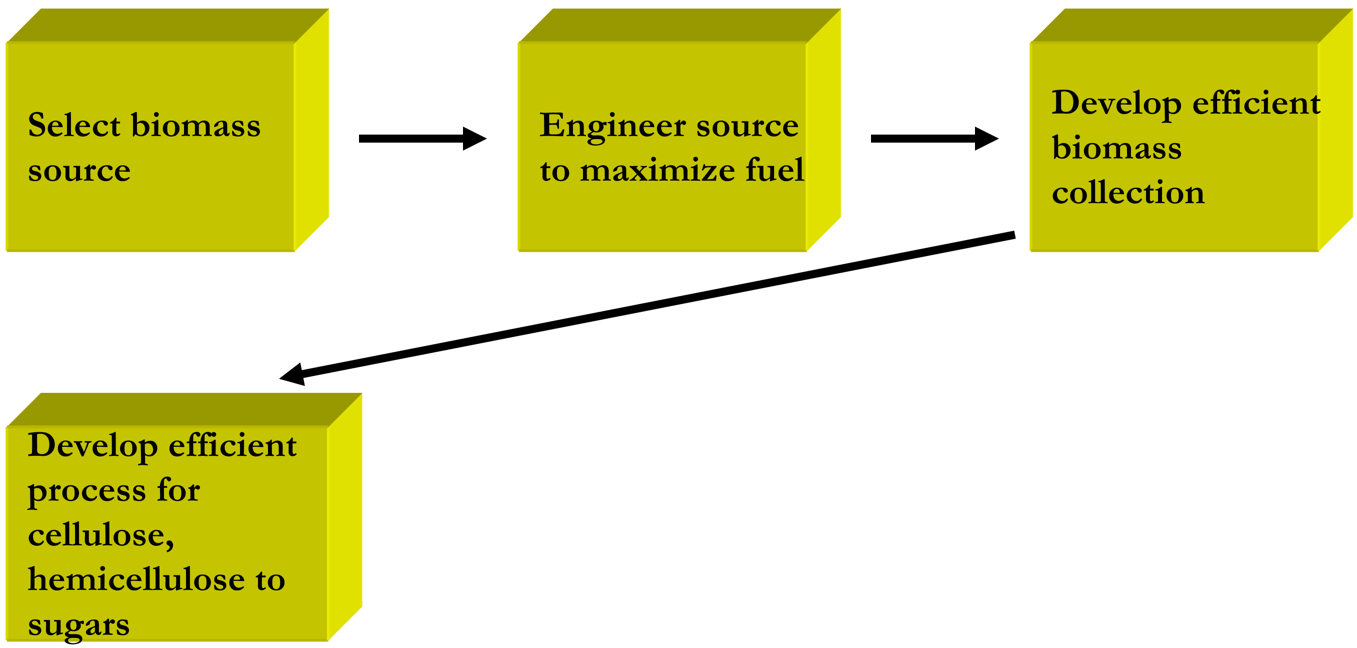
Annual grasses have low bulk density, limited growing season

Plant must run year round

No lengthy storage of perishable raw material

Plants will be numerous (100's), located close to raw mtl sources

Key Issues in Developing a Biorefinery Economy



Key issues:

Cellulose crystallinity; slow hydrolysis

Relatively fast hemi hydrolysis

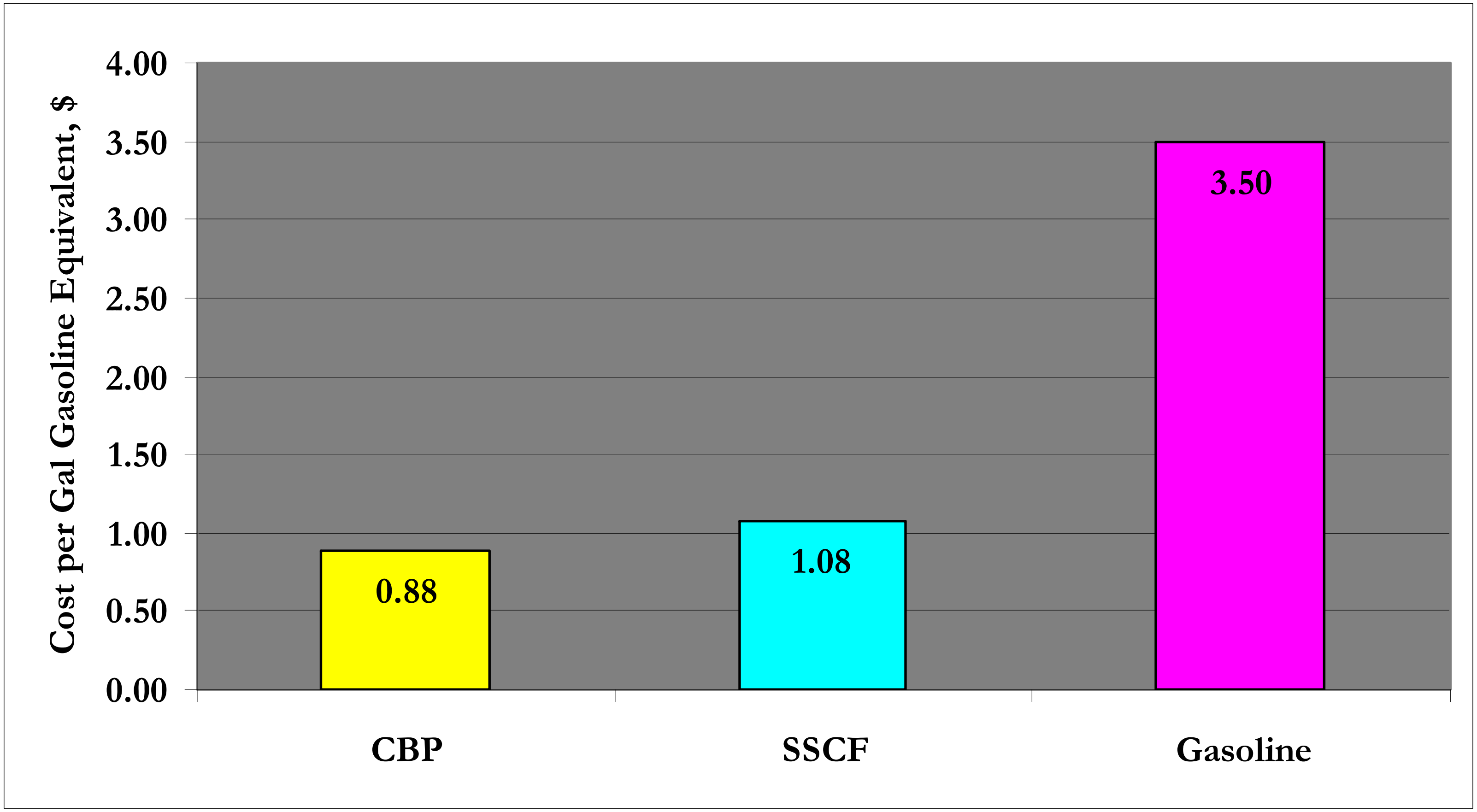
Cost of cellulase enzymes

High yield

Cellulose Hydrolysis is the Key

- Cellulose hydrolysis is rate determining step
- Dilute acid hydrolysis is fairly fast but results in much lost yield (difference in hydrolysis rates between substrates present; hemicelluloses; glucose, xylose, galactose, mannose, glucuronic acid monosaccharides; cellulose)
- SSCF (simultaneous saccharification and co-fermentation) process gives best yield; short chemical hydrolysis followed by enzyme catalyzed hydrolysis (combination of exocellulase, endocellulase, cellobiohydrolase, and hemicellulases), with simultaneous fermentation
- Drawback of SSCF is slow nature of process; reaction time is 7 days
- Issues; crystallinity of cellulose, product inhibition by glucose and other monosaccharides, inhibition by lignin fragments, high cost of cellulase enzymes
- Genencor and Novazyme responded to USDA/DOE challenge by reducing manufacturing cost of cellulase enzymes by about an order of magnitude, to 10-20 cents per gal gasoline equivalent. Feeling is that 4-5 cents is needed and achievable
- Most promising is the Consolidated Bioprocessing Process (CBP). This involves an organism that possesses both polysaccharide hydrolysis and fermentation capability. This will eliminate product inhibition of hydrolysis as well as cellulase costs. Evidence also that cellulase is more effective as part of organism than as isolated enzyme.
- Cellulase activity has been added with some success to fermentation bacteria like *E. coli*, *Klebsiella oxytoca* and the yeast *S. cerevisiae*. Conversely, fermentation capability has been added to native cellulolytic organisms like *Clostridium cellulolyticum* and *Thermoanaerobacterium thermosaccarolyticum*.

Integrating Polysaccharide Hydrolysis and Sugar Fermentation



CBP: Consolidated bioprocessing; expression of cellulase and fermentation capabilities by the same organism.

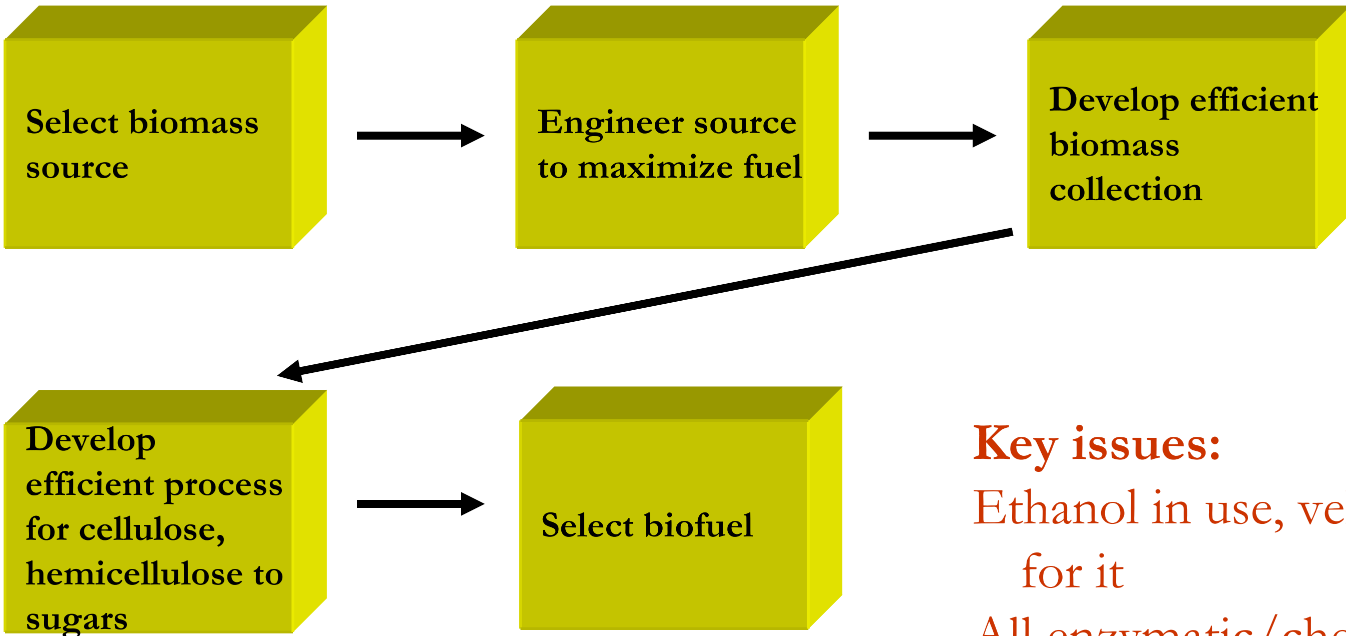
SSCF: Simultaneous saccharification and co-fermentation. Carrying out hydrolysis and fermentation simultaneously (but with separate cellulase production).

Projections are that cost could be as low as $ 0.63/gal by roughly 2015 if targets are met.

Note: gasoline figure is rough estimate of retail cost as of 5-1-08

L.R. Lynd, Curr. Opin. Biotech. *16*, 577-583 (2005)

Key Issues in Developing a Biorefinery Economy



Key issues:

Ethanol in use, vehicles designed for it

All enzymatic/chemical processes optimized for ethanol

n-Butanol has more energy/volume, is less volatile, will contain less water so is less corrosive

Is n-Butanol a Better Product?

- Ethanol is fully miscible with water; water has low solubility in n-butanol. Lower water content will reduce corrosion in storage, transfer and operation
- n-Butanol has lower oxygen content per gram and higher energy content than ethanol
- n-Butanol is less volatile than ethanol (bp 117 vs. 78ºC), so losses in transfer will be less
- n-Butanol is much easier to separate from water; separation costs would be minimized

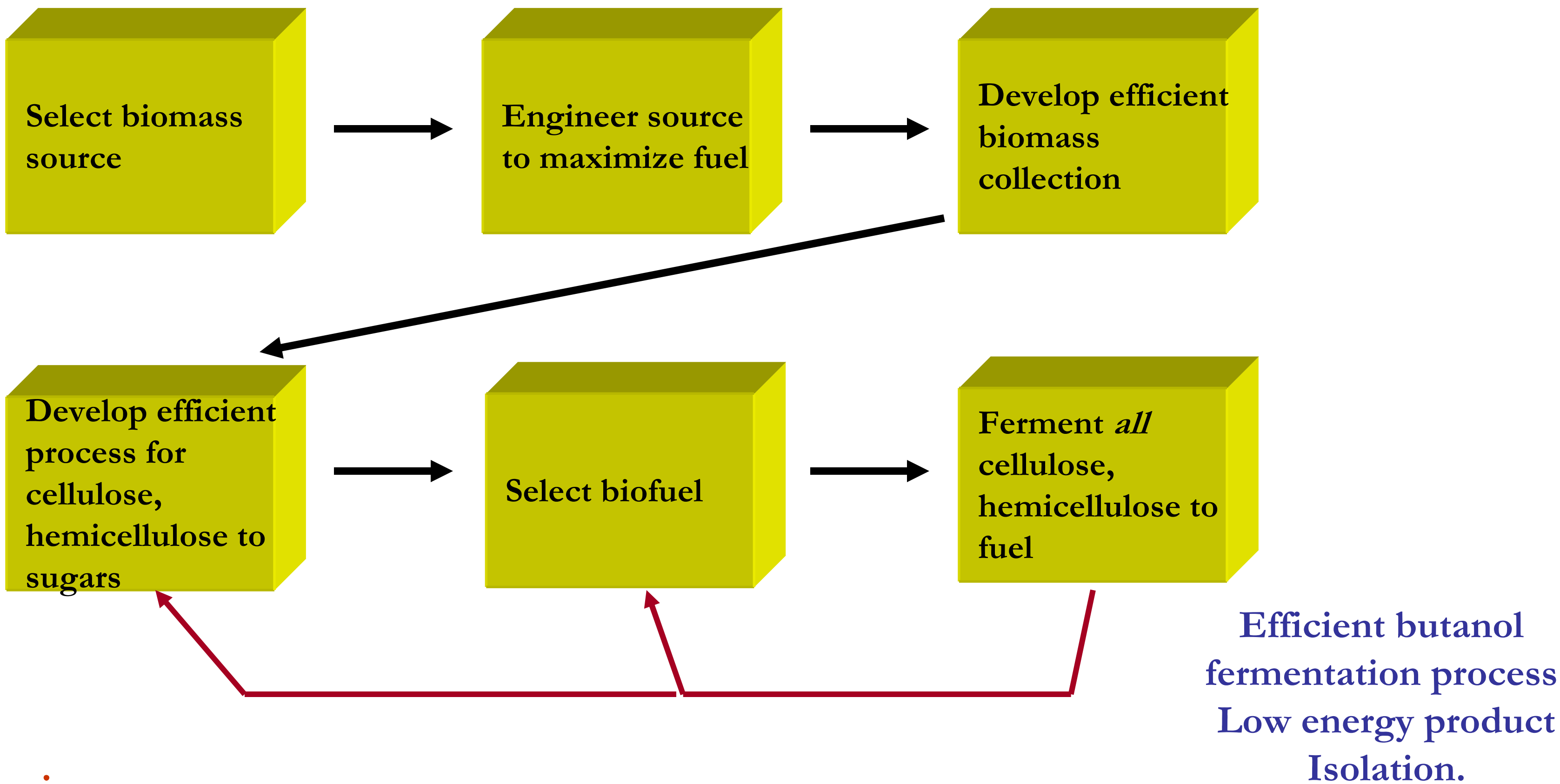
Bottom line; n-butanol would unquestionably be the superior motor fuel to ethanol.

So why not n-butanol?

- Vast majority of process data so far is on ethanol fermentation; we will need to learn how to integrate n-butanol fermentation with polysaccharide hydrolysis and the rest of the process
- Fermentation as a method of making n-butanol has been known since at least the 1920s. It can be done.
- Fermentation process far less well developed than that for ethanol. Need to deal with issues of yield, product inhibition, low product concentration.
- The impact of n-butanol upon materials in the car, the filling station, the tanker or pipeline, and so on will be quite different from that of ethanol. All of these material interactions need to be characterized, considering also the time dimension, and as necessary, new materials must be introduced that are compatible with n-butanol.
- This will be a very important area of research in the near future

Bottom line; it should be possible to build a biomass to biofuels industry based on ethanol, then convert over later to n-butanol as that technology matures. Much of the infrastructure will be the same.

Key Issues in Developing a Biorefinery Economy



Key issues:

Integration of fermentation with hydrolysis; cellulase genes in yeast, or fermentation genes in cellulase, to accelerate process, prevent product inhibition of hydrolysis (RDS), eliminate cellulase cost

Fermentation is more straightforward

- Thermophilic fermenting organisms have been identified
- Strains with the ability to ferment pentoses as well as hexoses have been identified
- Minimizing sensitivity to product inhibition, as well as inhibition by lignin fragments, acetic acid, and other by-products is crucial.
- The higher the achievable ethanol concentration, the easier it is to isolate and purify the product ethanol
- These issues will be solved by a combination of optimization of the organism, and process optimization such that ethanol and other products can be removed as they are formed

Ideal Bioethanol Producing Organism Will:

- Ferment all biomass sugars
- Be tolerant of lignin monomers
- Be tolerant of acetate and other potentially inhibitory co-products
- Produce a synergistic combination of cellulases needed for full cellulose hydrolysis

Key Issues in Developing a Biorefinery Economy

Select biomass source → Engineer source to maximize fuel → Develop efficient biomass collection → Develop efficient process for cellulose, hemicellulose to sugars → Select biofuel → Ferment *all* cellulose, hemicellulose to fuel → What to do with by-products?

Key issues:

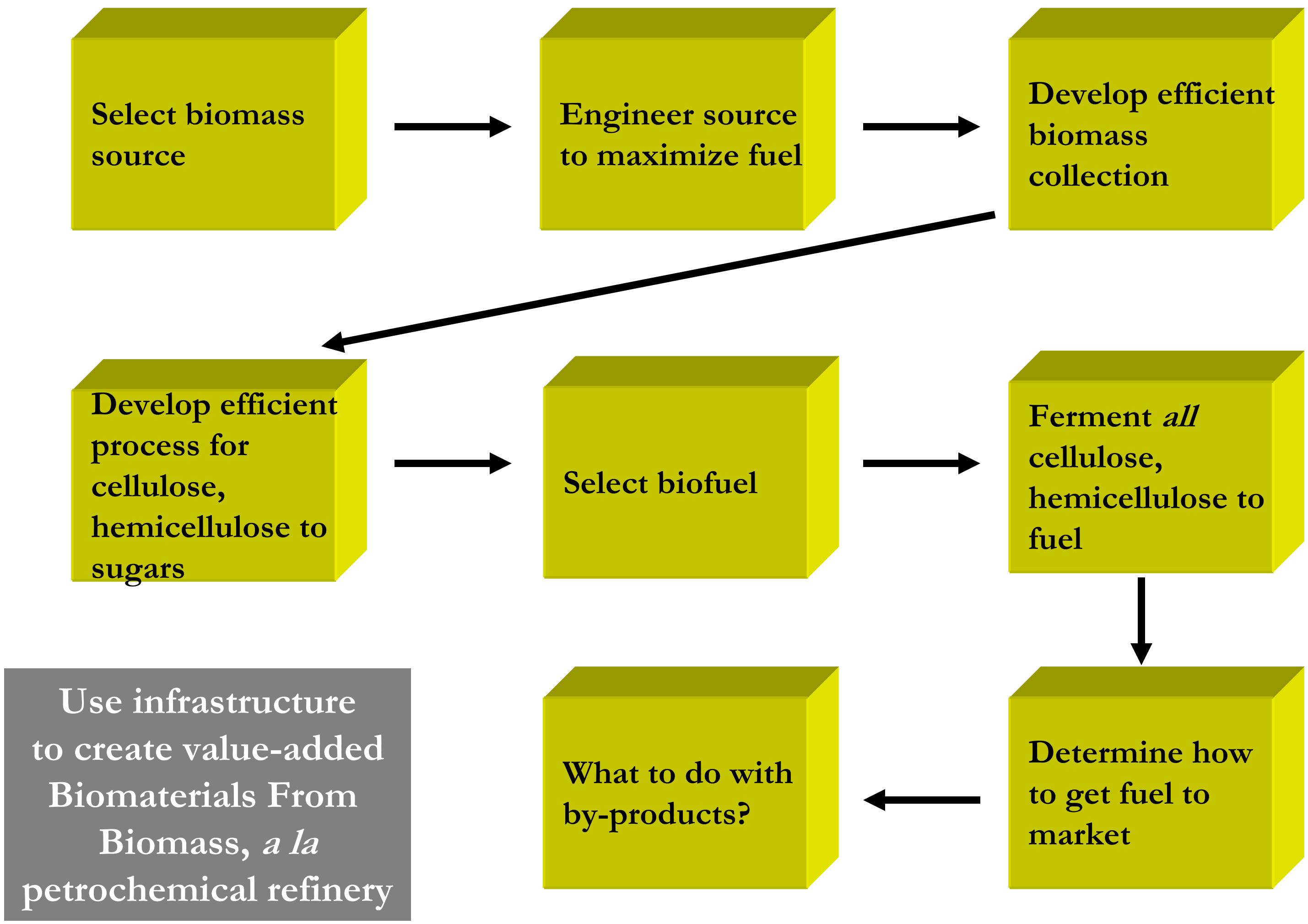
Use of lignin to power plant is a good fallback option

Lignin excellent gasification substrate; convert to CO/H_2 and thence to transportation fuels, chemicals

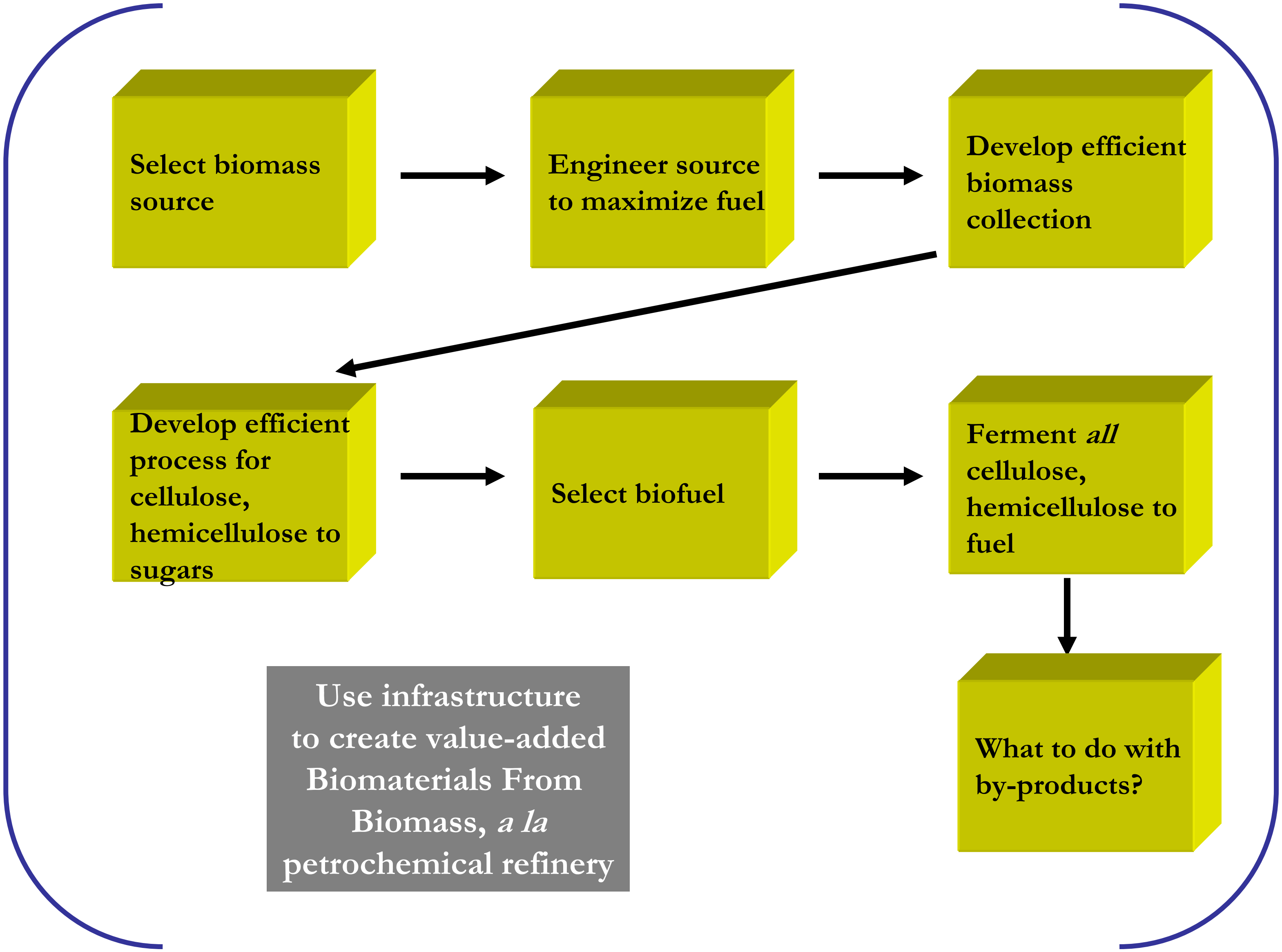
What do we do with the lignin?

- Lignin will not ferment, and in fact lignin fragments are inhibitors of cellulolytic and fermentation enzymes.
- Happily, lignin is an excellent substrate for gasification.
- Biomass can be gasified by heating to 800-900ºC in the presence of oxygen to give a mixture of synthesis gas (CO/H_2), CO_2 and water. This is a somewhat lower temperature than that required to gasify coal; the gasification of coal is of course a successful commercial process.
- Once synthesis gas is in hand, conversion to useful chemicals is relatively simple. Processes for methanol, acetic acid, and acetic anhydride are for example well known.
- The base case for lignin is burning to generate power for the biofuel plant. This is a perfectly acceptable and workable base case.
- The key is to cleanly separate out the lignin. Lignin has markedly different solubility properties than the polysaccharides and can, for example, be very cleanly separated by prehydrolysis followed by solvent extraction.
- Work remains to be done on lignin, especially on the separation process, but the lignin issues are not critical ones in the overall picture.

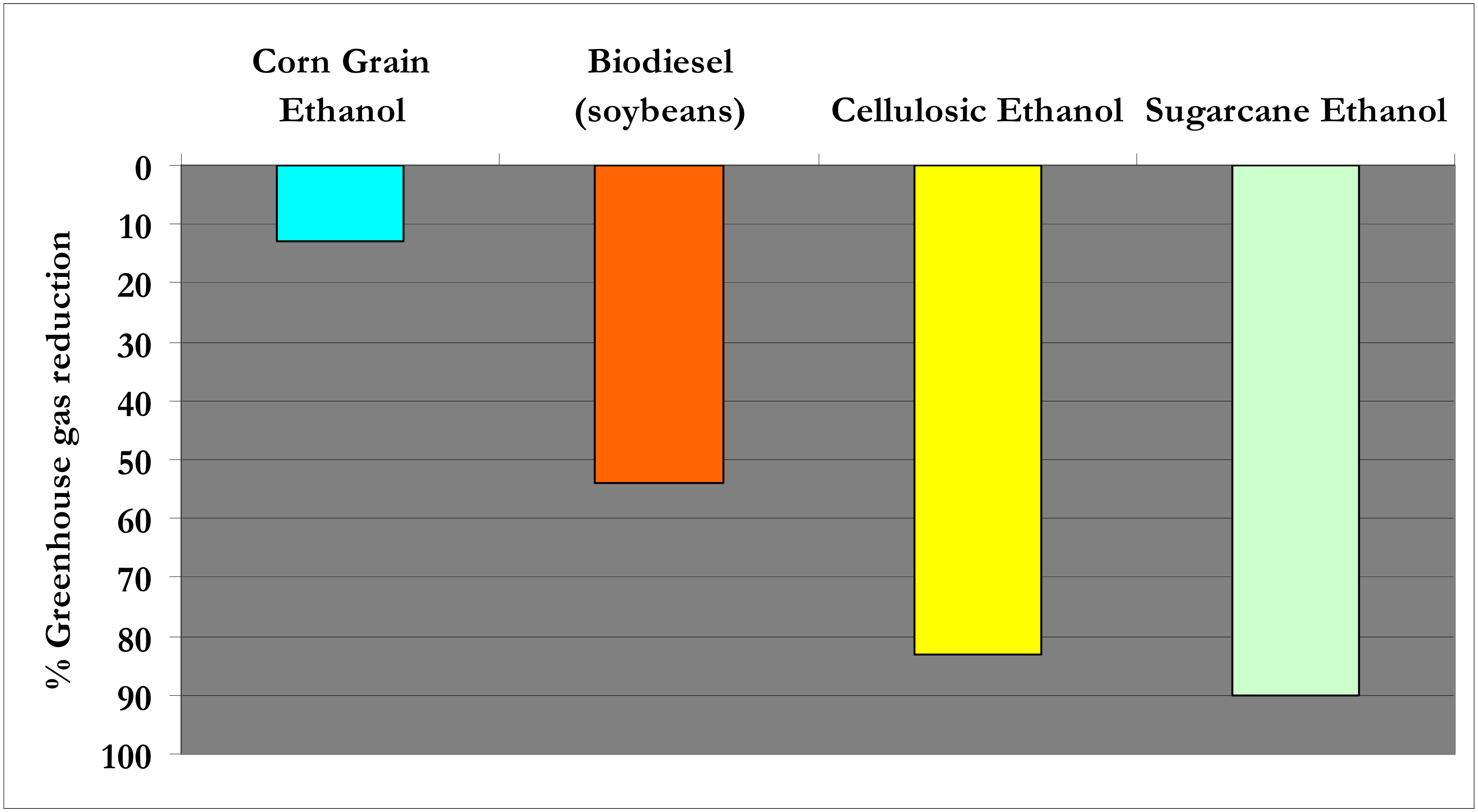
Key Issues in Developing a Biorefinery Economy



PROJECT MANAGEMENT



What is the impact of biofuel vs. petroleum on greenhouse gas emissions?



Most important issue is the fertilizer needed for a crop like corn, and the fact that fertilizer is not applied to trees or, apparently, sugarcane.
All the controversy in the literature (and popular press) has been over the number for corn grain ethanol, vs. petroleum.

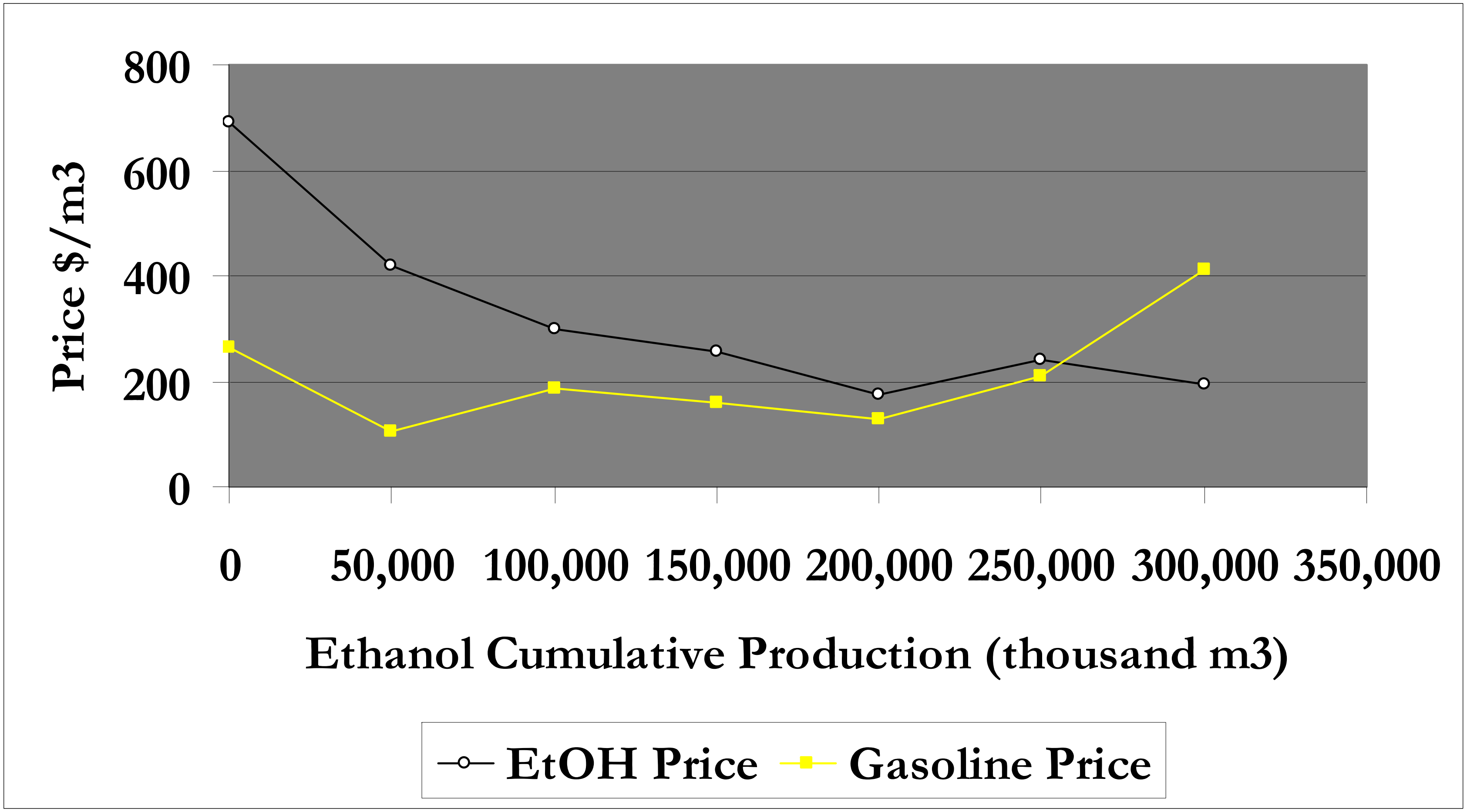
C. Schubert, Nature Biotech. *24*, 777-784 (2006)

Experience with Sugarcane Ethanol in Brazil

- Use of sugarcane ethanol in gasoline mandated by Brazilian government in late 70's to address global fuel crisis, hard currency depletion due to oil imports.
- Production grew from 0.9 billion gallons of ethanol in 1980, to 3.0 billion gallons in 1990, to 4.2 billion gallons in 2006.
- Overall subsidies from Brazilian government totaled $30 billion over 20 years
- 3 million hectares in Brazil grow sugarcane to produce 4.2 billion gallons ethanol; 10% cultivated land and 1% of agricultural land in Brazil.

J. Goldemberg, Science *315*, 808-810 (2007)

Experience with Sugarcane Ethanol in Brazil



- Since 2004, Brazilian ethanol fully competitive on international market without government subsidy.

J. Goldemberg, Science *315*, 808-810 (2007)

By 2007, Cost of Sugarcane Ethanol Competitive in US

Fuel	Cost /Gal
Corn ethanol	$1.03
Gasoline (retail)	$1.90
Sugarcane ethanol*	$1.35*

- Increase sugarcane acreage by 10X would supply enough ethanol to meet 10% of current ethanol demand.

* Includes 54 cent import duty

J. Goldemberg, Science *315*, 808-810 (2007)

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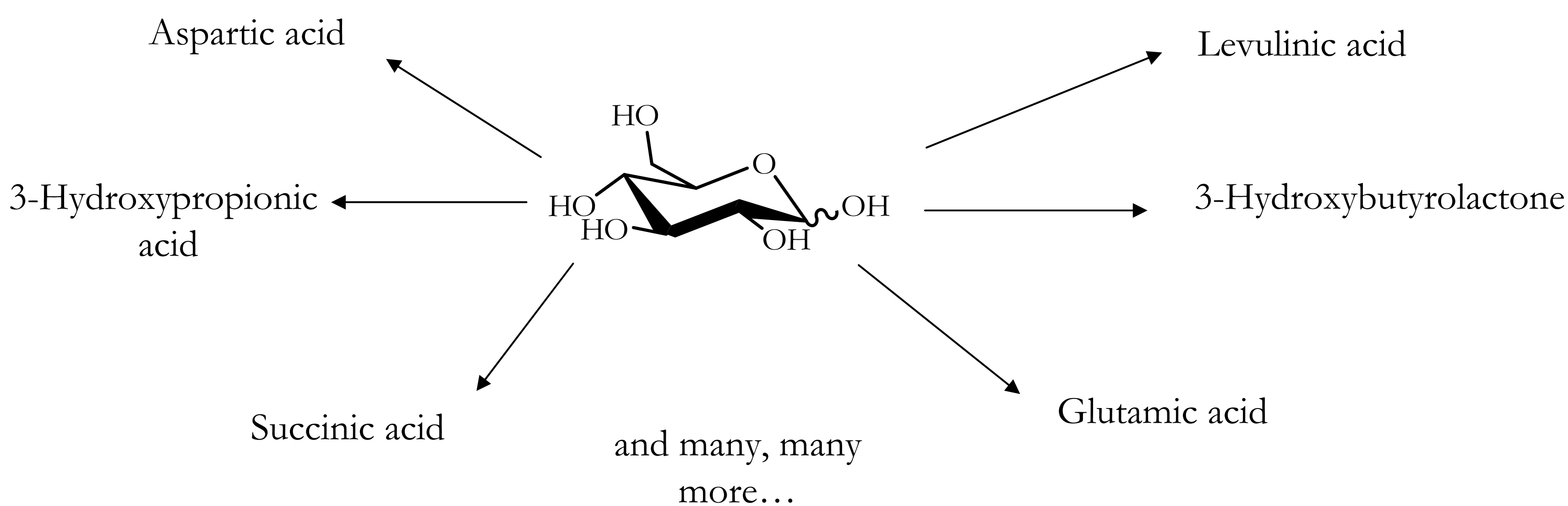
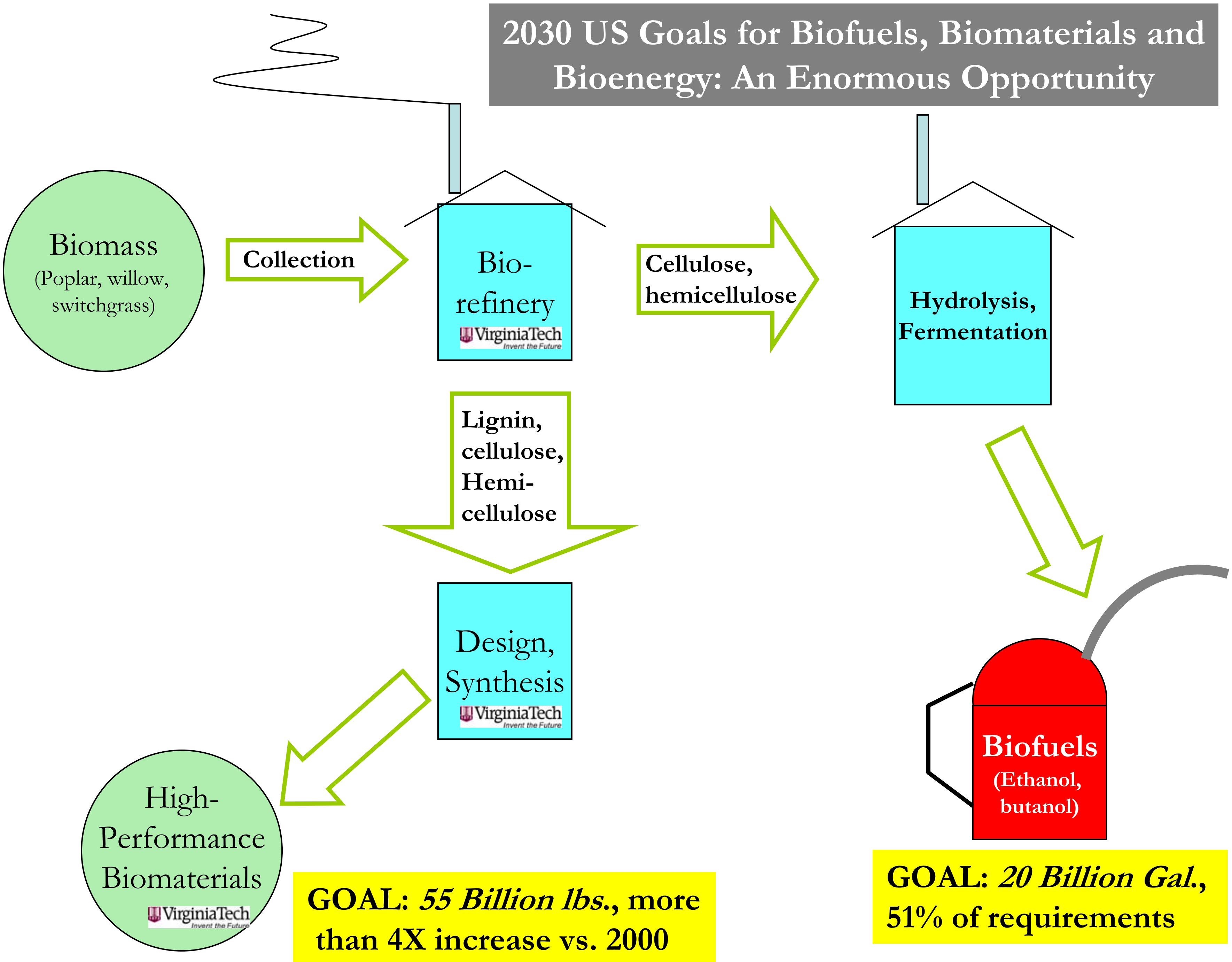
- Overall subsidies from Brazilian government totaled $30 billion over 20 years.

- On the other hand, petroleum imports reduced by $50 billion over the same period!

The biorefinery economy

- Biofuel will drive the development of biomass conversion processes, as it should.
- Once we have biomass to biofuel plants in place, we will have the opportunity to develop biorefineries and biomaterial products analogous to the petrochemical refineries and petrochemical products that followed on the heels of the petroleum fuel industry.
- A rich palette of options exists for glucose fermentation products (and of course a rich palette of chemistries for these products).




2030 US Goals for Biofuels, Biomaterials and Bioenergy: An Enormous Opportunity
Biomass
(Poplar, willow, switchgrass)
Collection
Bio-refinery
VirginiaTech
Invent the Future
Cellulose, hemicellulose
Hydrolysis, Fermentation
Lignin, cellulose, Hemi-cellulose
Design, Synthesis
VirginiaTech
Invent the Future
High-Performance Biomaterials
VirginiaTech
Invent the Future
GOAL: *55 Billion lbs.*, more than 4X increase vs. 2000
Biofuels
(Ethanol, butanol)
GOAL: *20 Billion Gal.*, 51% of requirements

National Biomass Utilization Goals

Output	Units	2000 Data	2004 Data	2010 Goal	2015 Goal	2020 Goal	2030 Goal
Biofuels	Market Share (%)	0.7	1.2	4.0	6.0	10.0	20.0
	Consumption[1]	1.1	2.1	8.0	12.9	22.7	51.0
Biopower	Market Share (%)	3.0	3.0	4.0	5.5	7.0	7.0
	Consumption[2]	2.0	2.1	3.1	3.2	3.4	3.8
Bioproducts	Production[3]	12.8	17.6	23.7	26.4	35.6	55.3

[1]Billion gasoline-equivalent gallons
[2]Quadrillion BTU
[3]Billion pounds

Summary

- Conversion of biomass to biofuel involves polysaccharide hydrolysis to sugars, and fermentation of those sugars to a liquid fuel such as ethanol.
- Hydrolysis of crystalline cellulose is the key and rate limiting step. Acid prehydrolysis followed by cellulase-catalyzed hydrolysis is the lead technology.
- Fermentation is more straightforward but much optimization remains to achieve the reaction rates, product concentration, and tolerance to potential inhibitors that will characterize a robust, efficient process.
- The integration of hydrolysis and fermentation is of critical importance, to minimize product inhibition of hydrolysis as well as cellulase costs. Promising results have been achieved towards this end.
- Because of the need for year-round operation of the many biofuel plants, and the need for dense biomass to minimize transportation costs, trees such as eucalyptus, willow and poplar are highly favored biomass sources.
- Gasification of lignin is an attractive alternative for this portion of the tree, affording still more biofuel upon conversion of the resulting synthesis gas.
- Economics look promising, with costs per gasoline gallon equivalent of less than $1 from cellulosic biomass looking quite achievable.
- Potential exists to greatly reduce the greenhouse gas footprint of transportation fuels by using cellulosic biofuel instead of gasoline.
- n-Butanol promises to be the biofuel of the future due to higher energy content, lower water content, and lower volatility than ethanol.

References for Further Reading

Ethanol can contribute to energy and environmental goals. A.E. Farrell *et al.*, Science *311,* 506-508 (2006)

Consolidated bioprocessing of cellulosic biomass: an update. L.R. Lynd *et al.*, Curr. Opin. Biotechnol. *16,* 577-583 (2005)

Ethanol production from biomass: technology and commercialization status. J.R. Mielenz, Curr. Opin. Microbiol. *4*, 324-329 (2001)

Can biofuels finally take center stage? C. Schubert, Nature Biotech. *24*, 777-784 (2006)

Bioproduction of butanol from biomass: from genes to bioreactors. H.P. Blaschek *et al.*, Curr. Opin. Biotechnol. *18,* 220-227-6084 (2007)

The path forward for biofuels and biomaterials. A. Ragauskas *et al.*, Science *311*, 484-489 (2006)

Progress and recent trends in biofuels. C. Schubert, Prog. Energy & Combust. Sci. *33*, 1-18 (2007)