Biofuels and Bioenergy: Challenges and Opportunities
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ETHANOL FROM LIGNOCELLULOSIC BIOMASS – A TECHNO-ECONOMIC ASSESSMENT

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The SFA Quarterly Report

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SFA Pacific's Fuels and Power Program

FEATURE ARTICLE

Fuel Ethanol—Part 2: Is Lignocellulosics-to-Ethanol Real?

Abstract

Our analysis identified many issues with proposed lignocellulosic biomass to ethanol processes:

- high costs of biomass for commercial-scale plants (>200 million liters/year output for economics of scale),
- pretreatment processes must be optimized for each case
- high energy consumption of the overall process.
- low rates and yields of sugars from enzymatic hydrolysis,
- resulting low sugar and ethanol concentrations
- low yields and ethanol tolerances of genetically modified bacteria or yeast for hexose –pentose fermentations

Most problematic: any such fermentations are susceptible to contamination, requiring prohibitively expensive containment

Abstract (Contd.)

Even if ignoring these problems, our analysis estimated the cost of ethanol from corn stover at well over twice ethanol from corn.

Forest residues and wastes, biomass crops, and municipal wastes are even less promising.

After five decades of intensive R&D, only one pilot plant (Iogen, Canada), using wheat straw, is producing one million liters of ethanol per year, a quarter of initially announced capacity.

Conclusion: none of the existing processes are ready for commercial applications in any foreseeable time frame. Continuing fundamental and applied R&D is required.

Some near-term opportunities applications of such technologies to specific, modest-scale, agricultural wastes

USING MSW AND INDUSTRIAL RESIDUES AS ETHANOL FEEDSTOCKS

ETHANOL, a clean burning fuel, is being converted from waste biomass today. The technology is here; demand for ethanol is increasing dramatically; and the profit model for biomass conversion has vastly improved. The economic and environmental benefits are in place for ethanol production.

Many scientists, engineers and others feel that municipal solid waste (MSW) is an intriguing feedstock for ethanol production. Although we should recognize right away that MSW conversion is still in the pilot plant phase, the technology is ripe for commercialization. In fact, Masada Resources Group plans to break ground on the first MSW-to-ethanol facility in upstate New York in 2002.

Large-scale TVA facility in Muscle Shoals, Alabama processes biomass feedstocks such as sorted municipal solid waste and agricultural residues into fermentable sugars, which are converted into ethanol.

TVA ACID HYDROLYSIS PROGRAM

TVA project started in 1982 with the design/construction of a 4 TPD concentrated acid and 2 TPD dilute acid hydrolysis pilot plants, with solid iridium reactors.

By 1990 the two stage dilute acid hydrolysis of MSW became main focus, but concentrated acid also pursued

By 1996 (after $70 million) these processes were ready for commercial applications based on the work at TVA, according to the Project Manager and staff.

June 1994 REVIEW PANEL FOR THE TVA ACID HYDROLYSIS PROGRAM

John R. Benemann, Chair, Consultant, Walnut Creek, CA

Ting Carlson, Cargill Co., Minneapolis, MN

Charles E. Dunlap, Quadrex Co., St. Louis, MO

Karl Grohmann, USDA, Citrus Lab., Winter Haven, FL

Mark Holtzapple, Texas A&M Univ., College Station, TX

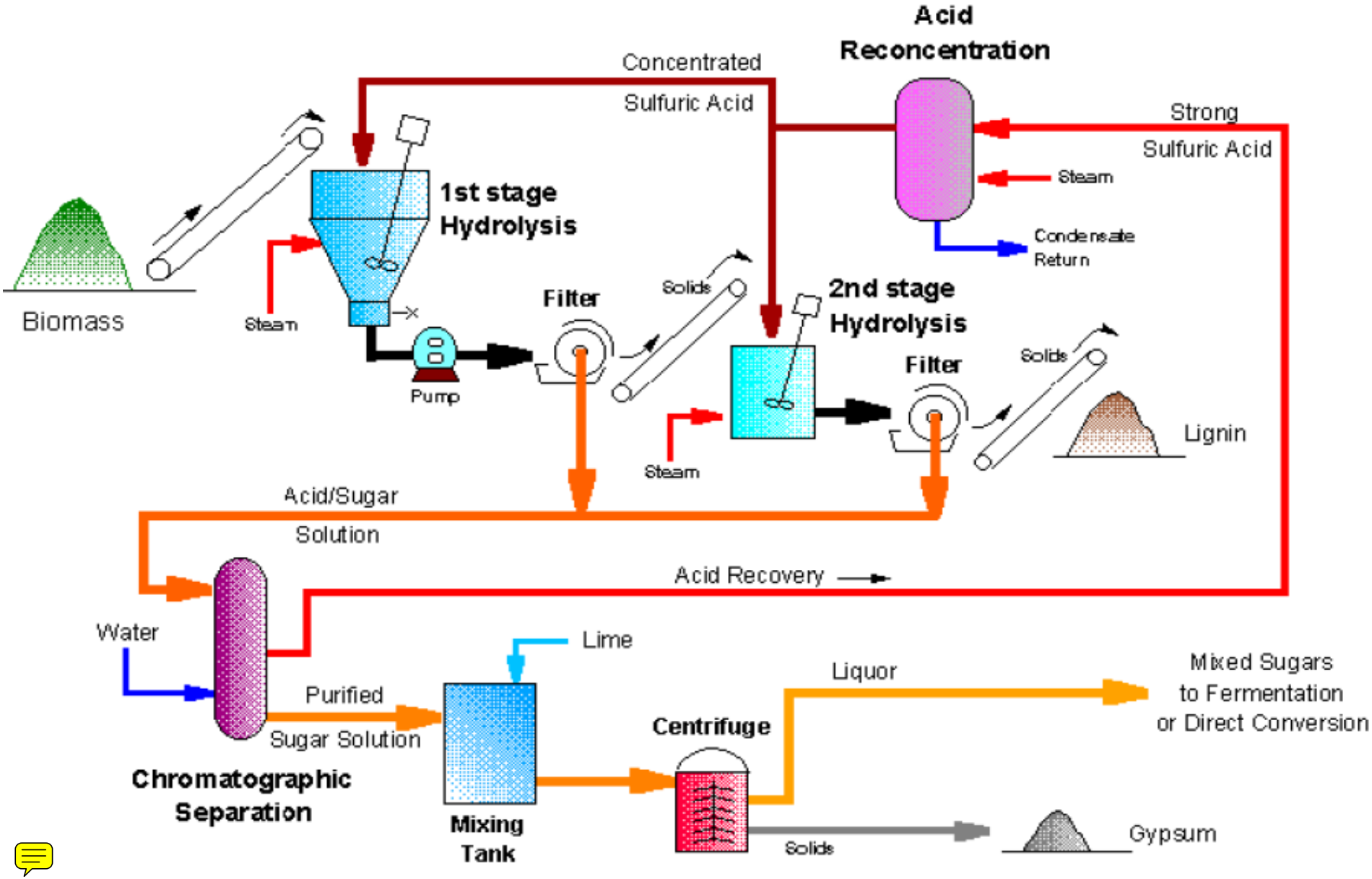
Tom Jeffries, USDA, Forest Products Lab., Madison, WI

REPORT OF THE REVIEW PANEL OF THE TVA ACID HYDROLYSIS PROGRAM

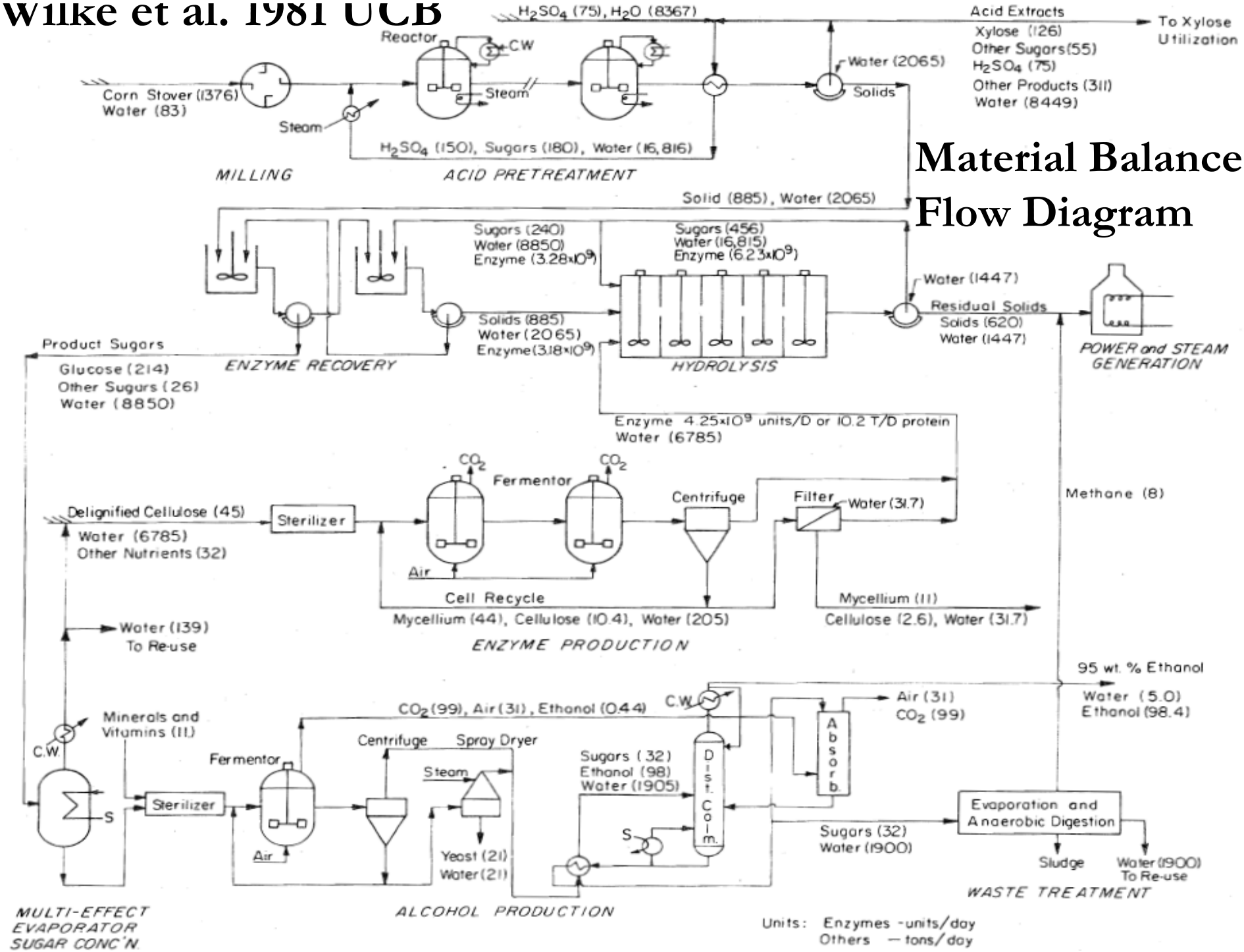
"The consensus of the panel was that the data collected by the TVA team at the laboratory and pilot-scale did not validate the process for MSW conversion to alcohol…."

"The panel found that the yields and concentrations of fermentable sugars achieved were too low for economical ethanol production, and that many other aspects of this process still present major technical problems, not likely to be solved in the near-term. "

Concentrated Acid Process (Arkenol)



Wilke et al. 1981 UCB



Material Balance Flow Diagram

From a participant in this program (Aug 15, 2006)

US DOE had a large, national program supporting research at

UC Berkeley (25 PhDs, 3-5 staff members, 10 years)
MIT, [Penn State, single organism, makes cellulase & ferments]
Dartmouth (acid pretreatment),
Rutgers (the T. reesei strain development),
Iotech (now Iogen - steam explosion) and others.

"…. We developed a fairly complete process based on cellulase conversion of pretreated wood, corn stover, rice straw, newsprint, … yeast ethanol fermentation, ethanol recovery, xylose fermentation".

"Curiously, much of this is being rediscovered, especially by DOE who seem unaware of its own previous efforts."

Lignocellulose to Ethanol Processes – 1981

Madison (Scholler, Proteus, etc.) Dilute Acid Hydrolysis
Issues: Toxic side products, low yields, corrosion

Natick First enzyme process using *Trichoderma viride*
Issues: pretreatment, enzymes, sterile fermentations

Gulf Oil/U. Arkansas Combines enzyme saccharification with fermentation. Issues: Same as Natick

MIT/Penn/GE Enzymes produced and sugars fermented by single microbe. Issues: Pretreatment, needs sterility

Costs of Sterile vs. Open Processes (1981$)

Source: Don Augenstein & John Benemann, 1981, unpublished

Based on 200 million liters/year Cellulose-to-Ethanol Plant

Non-sterile (open) process (assumes proposed process)

Capital Costs $130 million; fermenters are 15%

Operating Costs $0.4/liter, capital related 60%

Sterilizable fermentation system (based on low-cost batch)

Capital Costs $305 million; fermenters are 65%

Operating Costs $0.7/liter capital related 80%

(This assumed only difference was fermenter capital cost)

Current Pretreatment Process Options

- **Mechanical** - milling, grinding, other size reduction (very small!)
- **Thermal** - hot chemical solutions or high pressure steam.
- **Rapid decompression** - steam and ammonia explosion
- **Chemicals** - strong acids or alkalis (e.g. paper making)
- **Organosolv** - using organic solvents (ethanol, acetone, etc.).
- **Combined processes** - two or more of the above: <u>typical process</u>

PRETREATMENT DETERMINES WHAT FOLLOWS (and prior)

Cellulases

Novozymes and Genencor reported 30-fold cost reductions gratifying but was already anticipated

Enzymes have not changed; cost reduction is not a breakthrough

Enzyme kinetics still hampered by attachment sites, surface limitations, outside-in reaction

Enzyme attachment and loss /reuse issue not been resolved

Enzyme feedback inhibition by released glucose is still issue

Specificities of the different enzymes and their spectrum issue

However, overall, cellulase enzymes not main limiting factor

Cellulose, Hemicellulose, and Lignin Contents of Biomass, wt%

	Hardwoods	Softwoods	Corn Stover	Wheat Straw
Cellulose	43-47	40-44	28-40	25-35
Hemicellulose	18-35	14-29	20-35	24-30
Lignin	16-24	25-31	11-21	8-14
Extractives	2-8	1-5	N.A.	10-20

Genetically Engineered Microbes for Hexose-Pentose Fermentations

Saccharomyces Cerevisiae Yeast – the "Purdue Yeast."

Advantages: high EtOH tolerance, fast growth, selective conditions (low pH), and byproduct credit (animal feed).

Disadvantage: limited yield of ethanol from pentoses.

Pichia Stipitis Yeast – USDA/Madison.

Advantages: similar to S. cerevisiae, better yield from pentoses.

Disadvantages: requires O2 for growth, animal feed value uncertain

Escherichia Coli Bacteria – University of Florida.

Advantages: fast growth and good yields.

Disadvantages: lower EtOH tolerance than yeast, regulatory issues

Zymomonas Mobilis Bacteria – NREL.

Advantages: ethanol tolerance similar to that of yeast.

Disadvantages: yields on pentoses limited.

Thermotolerant Bacillus Strains -- Imperial College.

Advantages: fast fermentations at high temperatures, can't "escape"

Disadvantages: higher temperatures, unstable fermentations

General Issues with Genetically Engineered Microbes for Hexose-Pentose Fermentations

Yield from glucose lower and major problems/issues with pentose fermentations. Problems with regulation of metabolic pathways

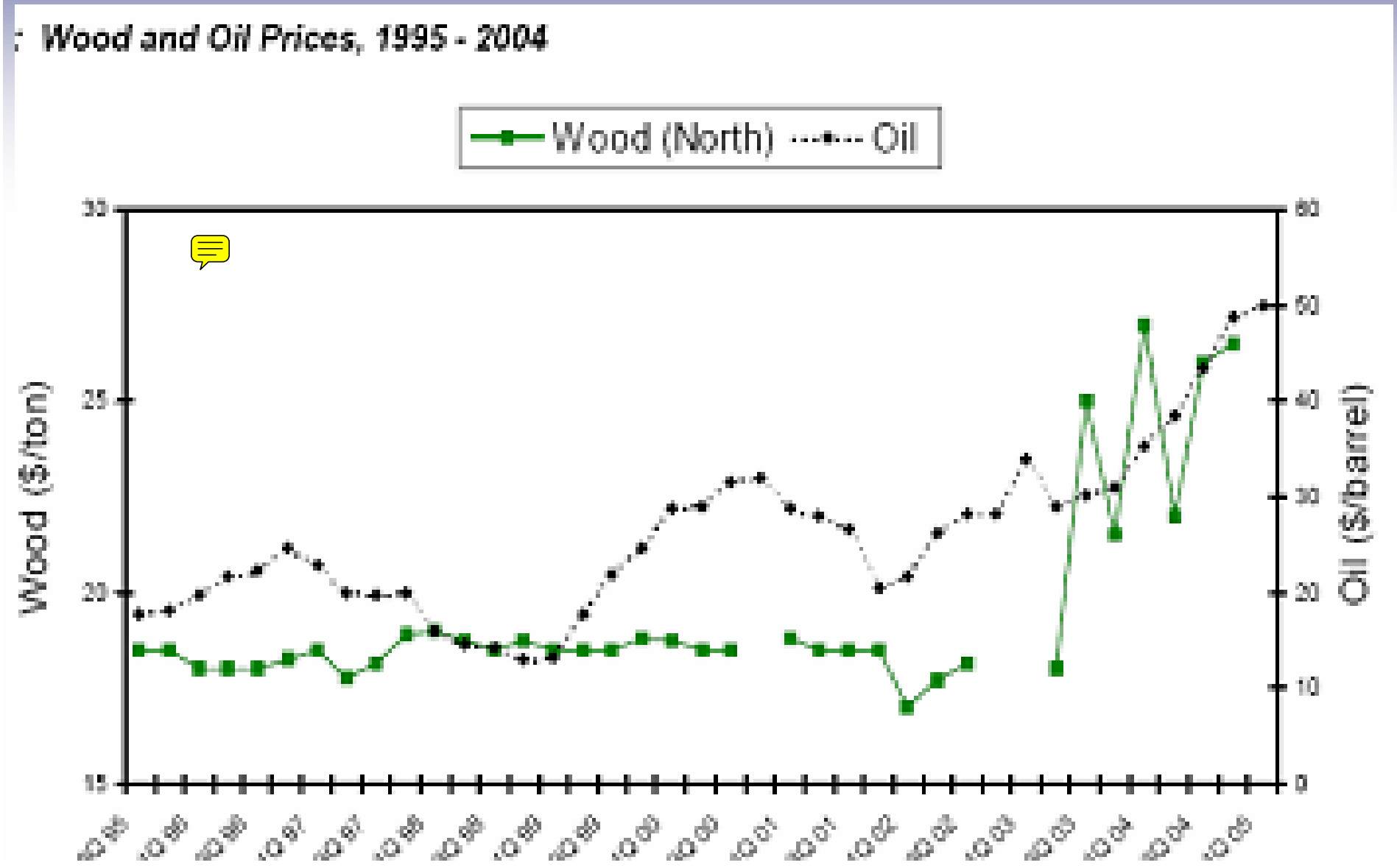
Genetically modified microbes less ‘robust”: slower growth, less resistant to ethanol,

More susceptible to contamination by invading organisms. <u>This could be “show-stopper”.</u>

PROCESS SCALE-UP ISSUES AND CHALLENGES

- Pre-treatment to separate cellulose and hemicellulose from the lignin.
- Enzymatic hydrolysis slow, incomplete, enzyme recovery poor, inhibited…
- Fermentation processes studied in controlled laboratory reactors
- Fermentations of hexose-pentose mixtures still a major problem.
- Difficult to scale-up such multi-phase processes (e.g. solid-liquid mixing)
- With acid processes iron from steel containers catalyzes glucose breakdown
- Relatively consistent feedstock quality (type, moisture, size, etc.) essential.
- Mixed urban wood waste is unsuitable – because of its softwood content
- Plant energy balance. Lignin by-product may not provide the energy needed
- Wastewater and solid wastes present significant issues
- Major issue: cost of the raw material (>1000 BDT/day for single facility).

Wood Prices and Oil Prices, 1995-2004



Theoretical and Achievable Practical Yields

Maximum Yield **gallons/Dry Ton**	Corn	Corn Stover	Wheat Straw	Switch Grass	Poplar (Hardwood)
1. Theoretical	128	108	113	109	116
2. Possible	113	95	100	96	102
3. Achievable	107	57	60	53	56

Theoretical is conversion of all sugars stoichiometrically,
Possible is after accounting for yeast growth,
Achievable is based on current/near-term technology available, +/- 5%
Based on dry milling for corn and dilute acid pre-treatment and enzyme hydrolysis

Ethanol from Enzymatic Conversion of Corn Stover

60 MMgal ethanol/yr plant, capital costs estimated @ 4.0 x corn-plant

Parameter	Units:	Value
Yield	gal/BDT	75
Yield %Theoretical	%	80
Capacity Factor	%	90
Feedstock Required	BDT/d	2500
Feedstock Costs	$/BDT	50
Capital Costs	$/gal	5.7
Feedstock Costs	$/gal	0.64
Enzyme Costs	$/gal	0.30
Other costs	$/gal	0.09
Denaturant	$/gal	0.08
Water and Waste	$/gal	0.05
Fixed O&M Costs	$/gal	0.55
Capital Charge	$/gal	0.82
Electricity Sales Credit	$/gal	-0.11
Total Production Costs:	$/gal	2.51
Costs gasoline equivalent	**$/gal**	4.44

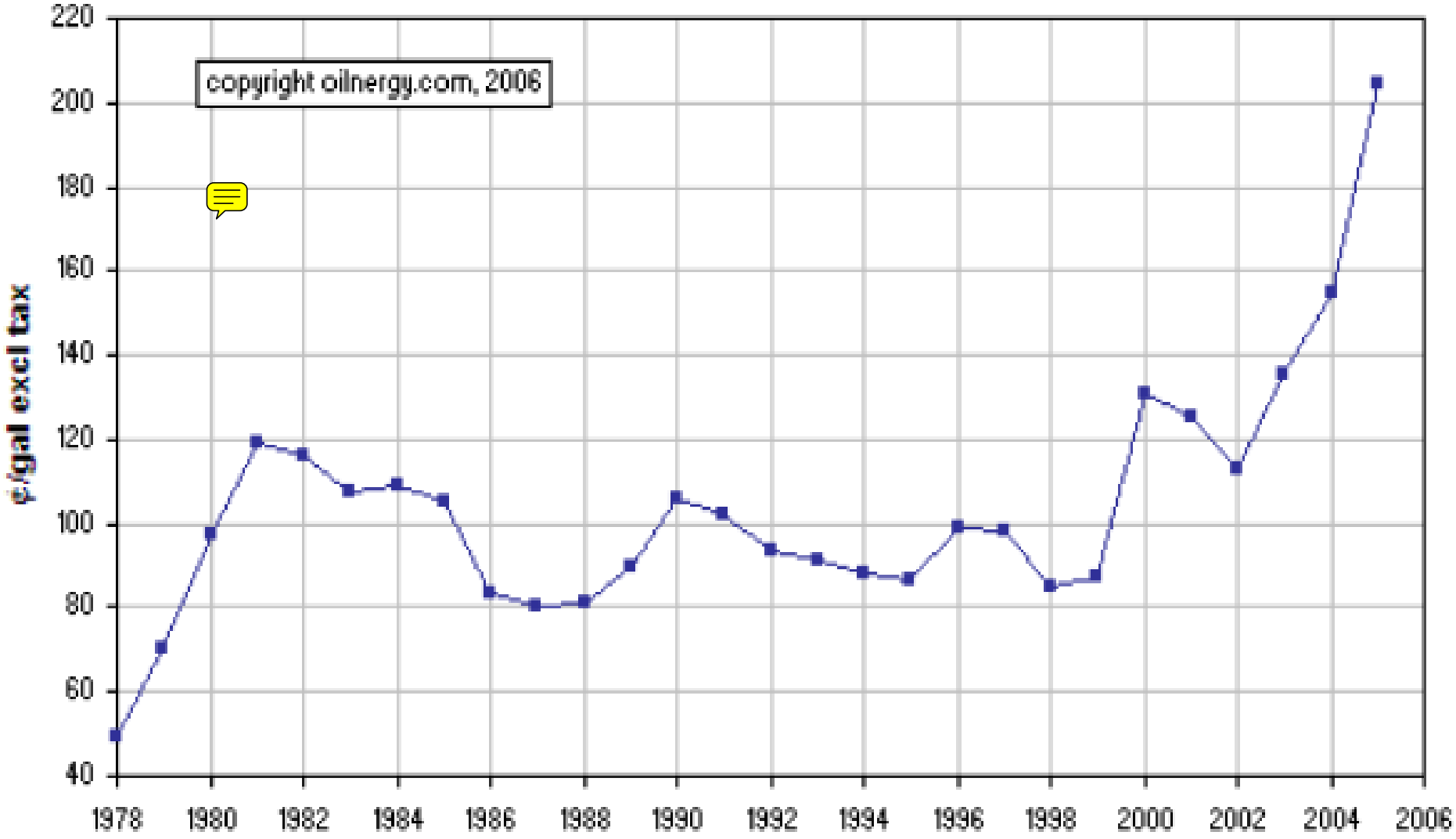
Economics of Lignocellulosics to Ethanol

Most cost estimations are based on lab-scale and, to some extent, pilot-scale data for individual process steps and should be treated with caution and not used to obtain an absolute production cost. The cost estimations are useful, though, for identification of bottlenecks and to compare the relative costs of different process strategies

Conclusions

- Current processes are not ready for commercialization
- Major R&D issues remain with most details of processes
- Fermentations are a particular area of concern/problems
- Long-term pilot plant work will be required for validation
- Push for commercialization will come at expense of R&D
- Even if successful, other uses for biomass will compete with ethanol fuels (e.g. pellet fuels, gasification, etc.)

U.S. Residential Heating Oil Prices 1978 - 2005



Indiana Prisons to start burning corn (June 6, 2006)

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Abengoa S.A. (Salamanca, Spain) Ethanol Plant

future pilot plant lignocellulose-to-ethanol