



Bioconversion of lignocellulosic biomass to ethanol: Challenges and opportunities

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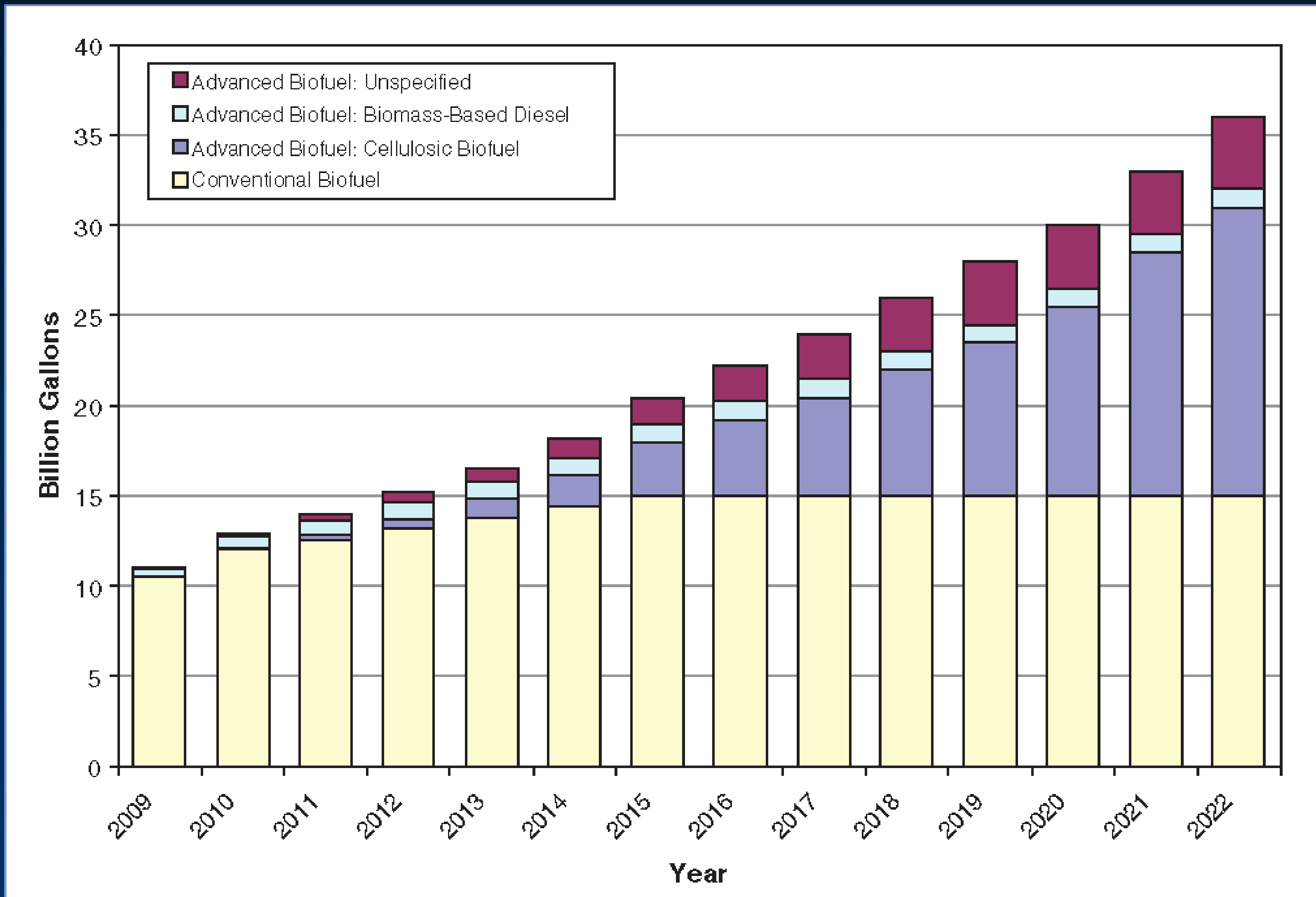
Outline

- Challenges and opportunities
  – How are we doing
  – Biomass
  – Processing (pretreatment)
  – Hydrolysis
  – Fermentation
  – Commercialization

Energy Independence and Security Act 2007- How are we doing?



EISA targets:

- 100 million gallons advanced fuel by 2009
- 200 million gallons of advanced fuel by 2010 – We might hit 10 million

16 billion gallons/year cellulosic fuel

200 Biorefineries

~ 1 million tons/year biomass

80 million gallons/year
$0.25/lb product

$400 million capital

100 Kraft pulp mills

750, 000 tons/year biomass

350,000 tons/year
$0.40/lb product

$500 million capital

Lignocellulosic biomass appropriate for bioconversion







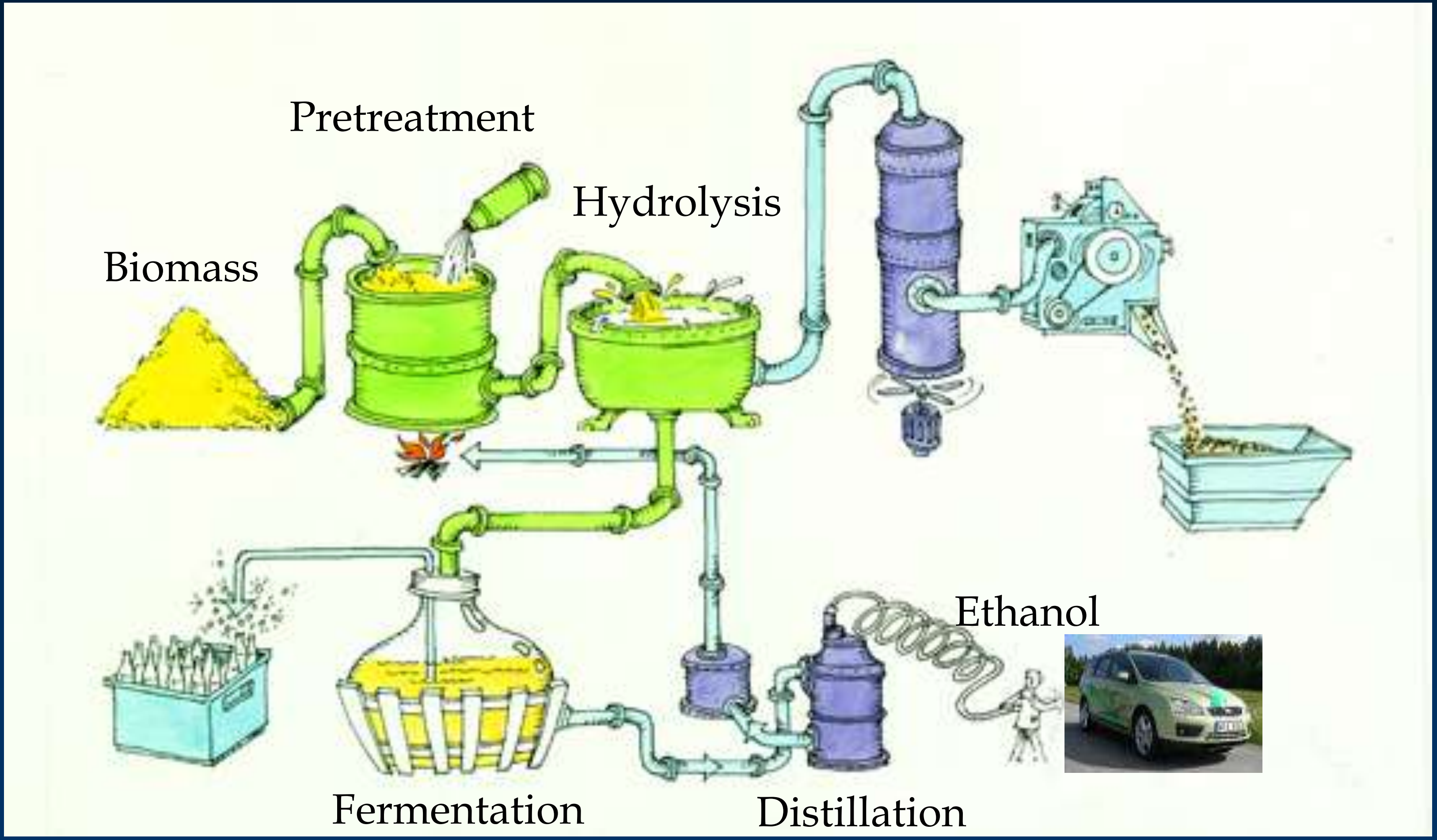
- Agricultural residues (corn stover, corn fibre, wheat straw, rice straw, switchgrass, sugar cane bagasse)
- Wood residues:
  - Hardwood (poplar, willow, pine)
  - Softwood (Douglas fir, pine)
- Paper waste
- Municipal solids waste




Biomass-challenges

- Regional availability (state, county)?
- How expensive is the biomass?
  - Location, location, location
  - Competing industries
- Stable and consistent feedstock supply available all year around
- For producer it must be profitable and fit into existing farm operations
- Biomass handling
  - Easy to storage
  - Transportation
  - Pre-pretreatment

Bioconversion of biomass to ethanol



Bioconversion-pretreatment

Pretreatment

Hemicellulose

Cellulose
Lignin

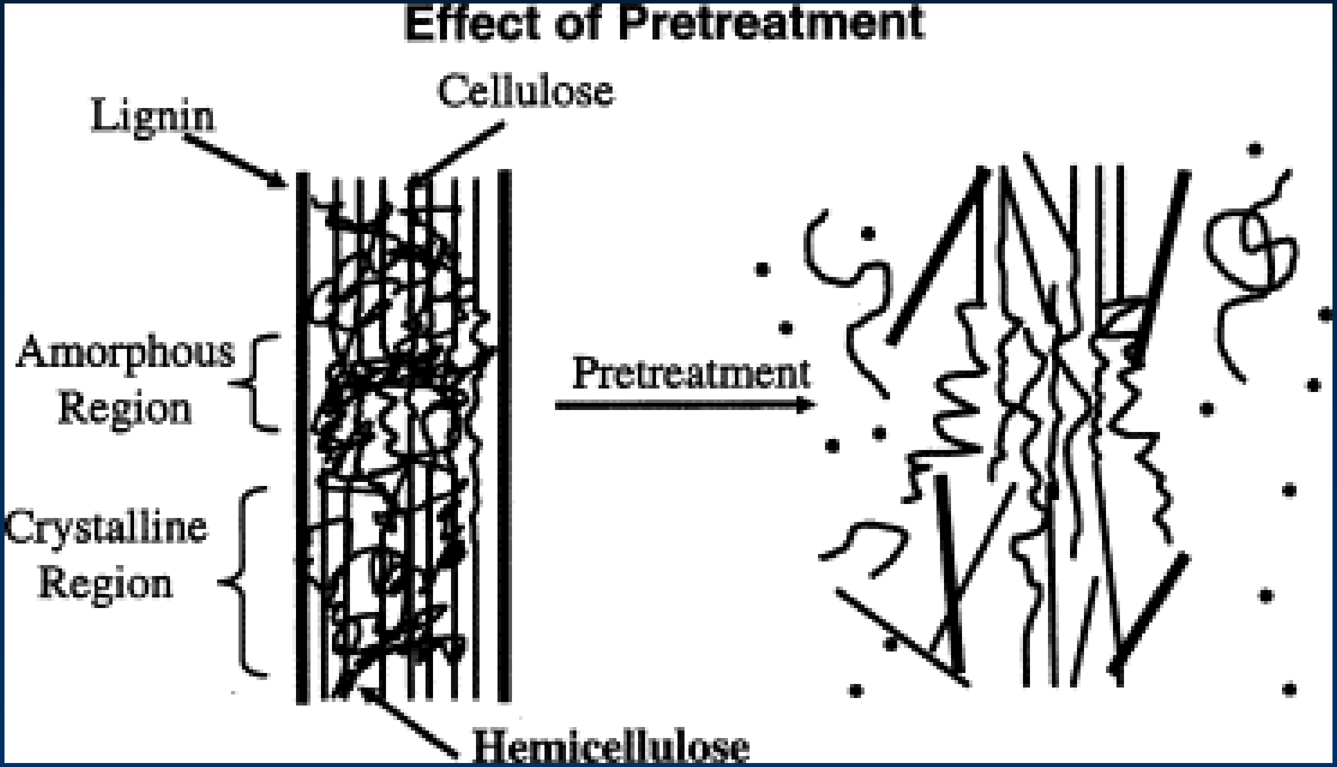
Hydrolysis

Sugars

Fermentation

Ethanol

Pretreatment



Schematic of goals of pretreatment on lignocellulosic material (adapted from Hsu et al., 1980).

Various pretreatment methods

	Increases accessible surface area	Decrystalizes cellulose	Removes hemicellulose	Removes lignin	Alters lignin structure
Uncatalyzed steam explosion	■		■		□
Liquid hot water	■	ND	■		□
pH controlled hot water	■	ND	■		ND
Flow-through liquid hot water	■	ND	■	□	□
Dilute acid	■		■	□	■
Flow-through acid	■		■		■
AFEX	■	■	□	■	■
ARP	■	■	□	■	■
Lime	■	ND	□	■	■

□ Minor effect ■ Major effect

Adapted from Mosier et al., 2005

Steam explosion

- Treatment of biomass with high-pressure steam for a short period of time followed by sudden decompression
- Physico-chemical pretreatment
- Acid (H_2SO_4, SO_2) impregnation of wood increases SE efficiency
- Typical conditions:
  - Pressure: 1.2-1.7 MPa (12-17atm)
  - Temperature: 170-250^{o}C, 338-482 F
  - Time: 10sec-10min
- One of the most cost effective and efficient pretreatment for agricultural, hardwood and softwood residues

Steam explosion equipment and process






Optimization of pretreatment

- Corn fibre: 190°C, 5min, 3% SO_2 (Bura *et al.,* 2004)
- Corn stover: 190°C, 5min, 0% SO_2 (Bura *et al.,* 2005)
- Mixture: corn fibre, corn stover, poplar (1:1:1) 190°C, 5min, 3% SO_2 (Bura *et al., 2005)*
- Rice straw: 200°C, 6min, 0% SO_2
- Poplar: 200°C, 5min, 3% SO_2
- Lodgepole pine: 205°C, 5min, 3% SO_2





Pretreatment-challenges (1)

- Not a clear winner
- Many different pretreatment options
  - Biomass
  - Products, co-products
- Pretreatment chemistry and kinetics
- Reactor design
- Large scale pretreatment operations





Pretreatment-challenges (2)

- Optimization of feedstock particle size and shape
  - Joint research with Forest Concepts
- Operate at high solids consistency to reduce energy and water usage
- Integrated to use surplus heat/steam from other processes at the facility
- Pretreatment methods for wood

Bioconversion-hydrolysis

Hemicellulose

Pretreatment

Cellulose
Lignin

Hydrolysis

Sugars

Fermentation

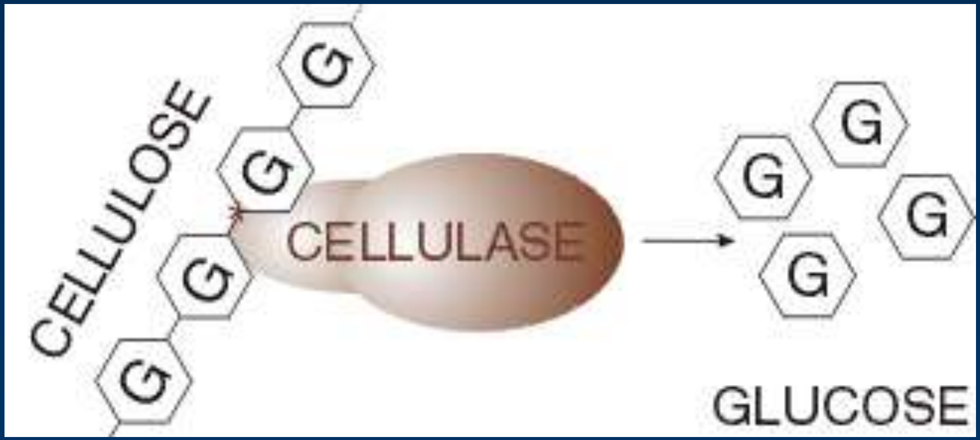
Ethanol

What are cellulases?





- Produced by many strains of bacteria and fungi
- Catalyzes the depolymerization of cellulose chains
  - Endoglucanases
  - Exoglucanases
  - β-glucosidases







Hydrolysis-challenges (1)

- Enzyme requirements
  - Low dosage (2PFU/g of cellulose)
  - High consistency solid hydrolysis (>10 %)
  - Short hydrolysis time (24-48 hours)
- Factors influencing enzymatic hydrolysis
  - Enzyme
  - Substrate (lignin, hemicelluloses, crystallinity, DP, accessible surface area)





Hydrolysis-challenges (2)

- Cost of cellulases
  - Enzyme recycling/cost
- Incomplete hydrolysis/economics
  - Accessory enzymes
  - Additives
    - Surfactants
    - Protein

Bioconversion-fermentation

Pretreatment

Hemicellulose

Cellulose
Lignin

Hydrolysis

Sugars

Fermentation

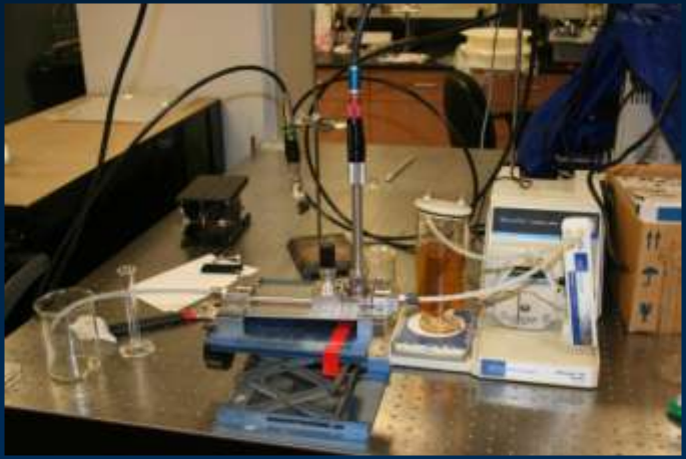
Ethanol

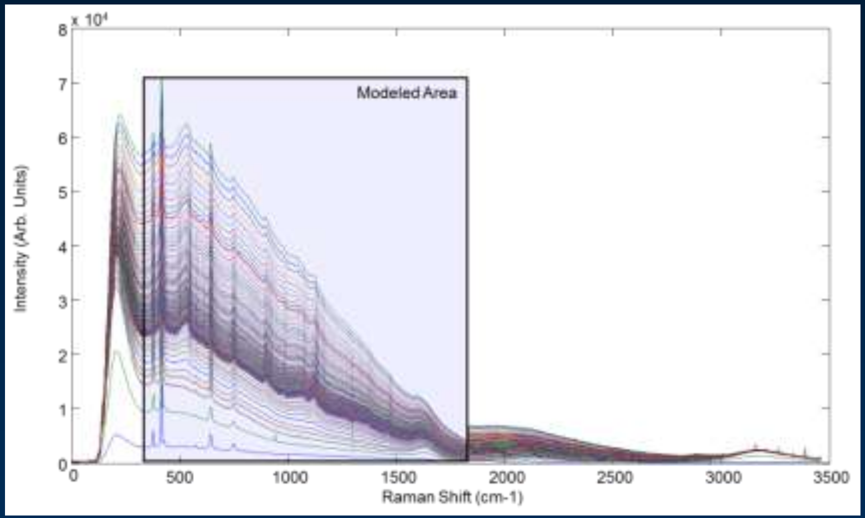
Fermentation-challenges

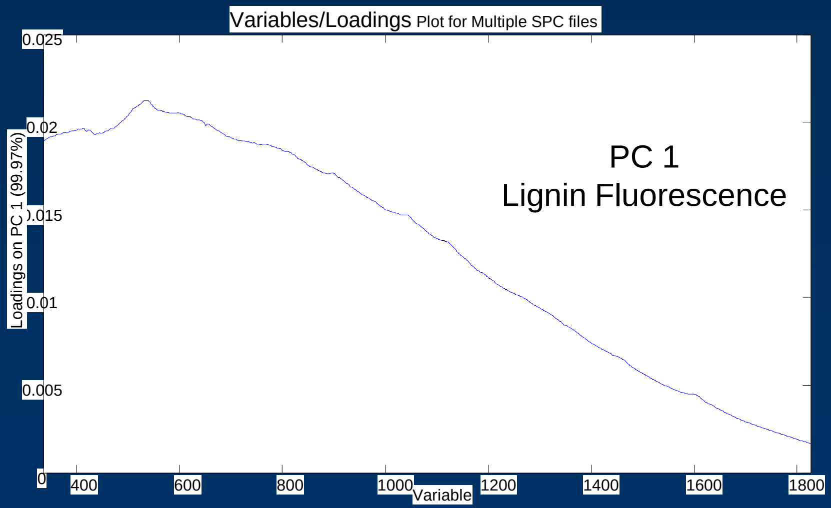
- Pentose sugars to ethanol fermentation microorganism
  - (*E.coli* KO11, *Z. mobilis*, *P. stipitis* and various strains of genetically modified *S. cerevisiae*)
- Microorganisms have to be proven in the large scale facilities with the real substrate on the continuous basis
- Fermentation requirements (nutrients, O_2)/economics
- SHF/SSF or Consolidated Bioprocessing?

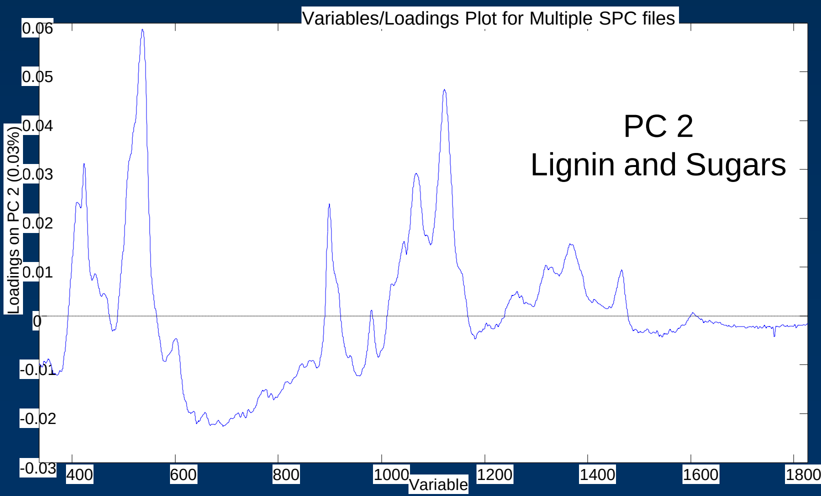
Hydrolysis & Fermentation Process Instrumentation













Commercialization-challenges

- Operating cost
  - Raw material is key: $50/bdt?
    - Transportation ($24/bdt for 100miles)
    - Storage (wheat straw requires covered storage-10-25% lost)
  - Enzymes are still expensive: 10-50 ¢/gal product
- Develop co-products
- Techno/economical modeling
- Life Cycle Assessment – no unintended consequences
- Integration of processes
- Scale-up issues





Why we do not have lignocellulosics to ethanol commercial process?

- New process
  - – Biomass
  - – Pretreatment
    - Washington State-wood to ethanol comparative study
  - – Enzymatic hydrolysis
  - – Fermentation
  - – Process economics

Energy Independence and Security Act 2007

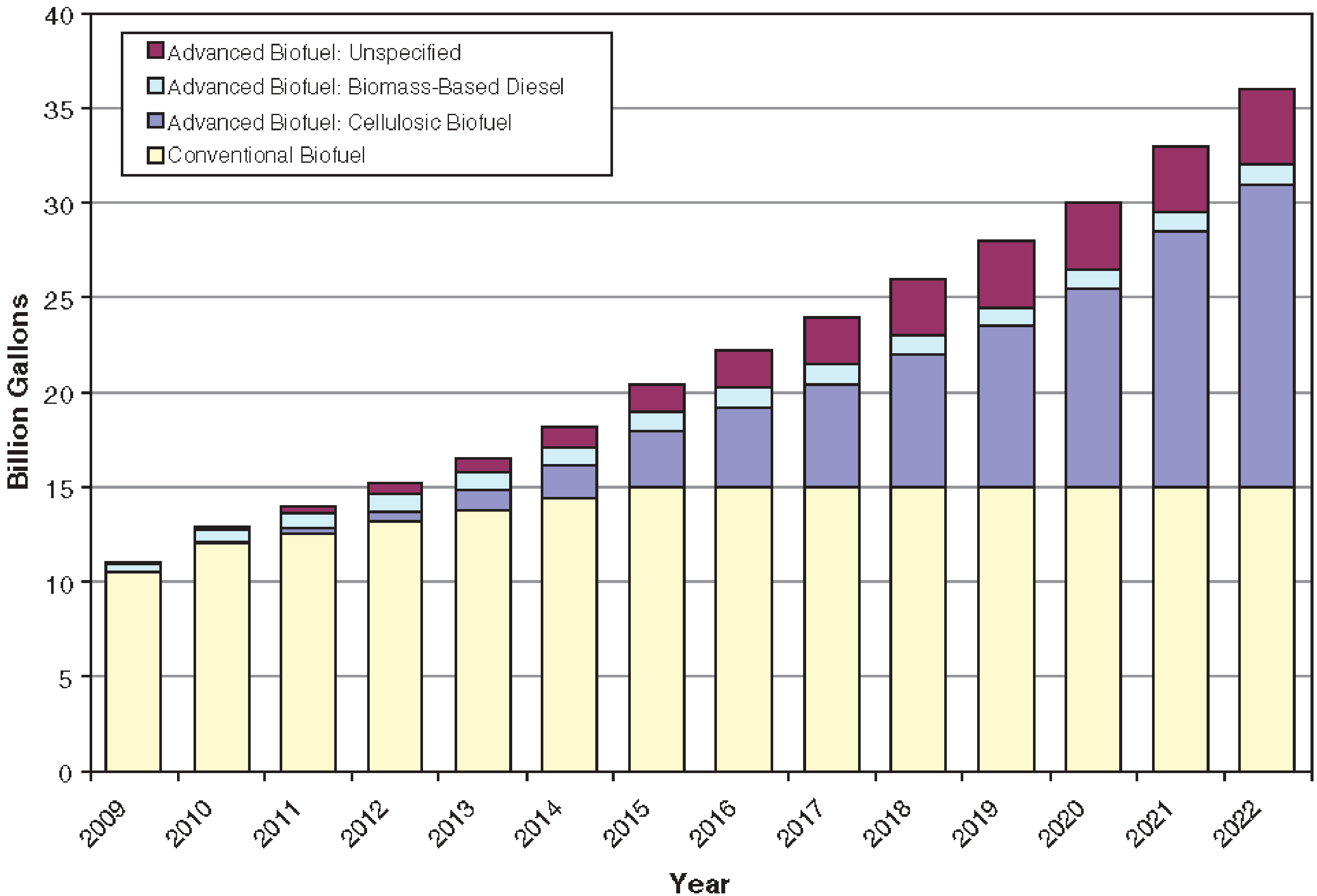


FIGURE 1 Volume changes over time.
Source: U.S. Environmental Protection Agency, Office of Transportation and Air Quality, Workshop Presentation by Bruce Rodan, June 23, 2009.




Biomass-challenges (2)

- New crops
  - Genetically modified species low lignin and high sugar content
  - Growing on marginal land
- Biomass growing cycle (high yield)
  - Use of fertilizers
  - Use of water
- Biomass residues
  - How much can we harvest without affecting the soil nutrition?

Chemical composition

Feedstock	**Glucan (cellulose) (%)**	**Xylan (hemicellulose) (%)**	**Lignin (%)**
Corn stover	37.5	22.4	17.6
Corn fiber	14.3	16.8	8.4
Pine wood	46.4	8.8	29.4
Poplar	49.9	17.4	18.1
Wheat straw	38.2	21.2	23.4
Switchgrass	31.0	20.4	17.6
Office paper	68.6	12.4	11.3

Chemical composition of biomass (adapted from Mosier et al., 2005).

Ideal pretreatment

- Cheap
- Fast
- Robust
- Simple
- Catalyst recycling
- Minimal environmental impact
- Very good overall sugar recovery in hydrolysable and fermentable form
  - Generates minimum amount of degradation products

Steam explosion (2)

- One of the most cost effective and efficient pretreatment for agricultural, hardwood and softwood residues
- 3 variables: time, temperature and pH
- Use of SO_2 as catalyst:

↓ reaction time and temperature

↑ enzyme accessibility to cellulose

↑ recovery of hemicellulose






Optimization of pretreatment

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We appear to have enough biomass

TABLE 1 Estimated Cellulosic Feedstock Production for Biofuels

	Millions of Dry Tons	
Feedstock Type	Current	2020
Corn stover	76	112
Wheat and grass straw	15	18
Hay	15	18
Dedicated fuel crops	104	164
Woody residues[a]	110	124
Animal manure	6	12
Municipal solid waste	90	100
Total	416	548

[a]Woody residues currently used for electricity generation are not included in this estimate.

Source: NRC America's Energy Futures Report: "Liquid Transportation Fuels from Coal and Biomass: Technological Status, Costs, and Environmental Impacts," Workshop Presentation by John Miranowski, June 23, 2009.

Pretreatment-role

- Pretreatment-the most important subprocess in biomass to ethanol fermentation
- Helps in separation of main biomass components (cellulose, hemicellulose and lignin)
- Increase available surface area
- Reduce particle size
- Ideally pretreatment:
  - Solubilizes hemicellulose
  - Increases enzymatic hydrolysibility of cellulose

Economics-challenges (2)

- Lack of performance guarantee
- Less than 1,000 hours of pilot operation
- New combination of processes
- Greater than 10:1 scale-up

Biomass to ethanol facilities

Company/ Location	Feedstock	Pretreatment	Conversion process
ZeaChem/Oregon	Poplar	Chemical	Bioconversion/ Thermoconversion
POET/ Iowa	Corn stover, corn fiber	Base (NH_3)	Enzymes, fermentation
Mascoma/ Michigan	Hardwood chips	Steam explosion	Enzymes, fermentation
Iogen/ Canada	Wheat straw	Steam explosion	Enzymes, fermentation
Bluefire Eth./ S. California	Green waste, wood waste	Acid	Fermentation
Alico/ Florida	Yard/Wood wastes	Thermal/ syngas	Fermentation
Range Fuels/ Georgia	Wood waste, wood crops	Thermal/ syngas	Chemical catalysis