Hydrolysis of Poplar for Cellulosic Ethanol Production

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Outline

- Overview/Project definition
- Feed
- Pretreatment
- Enzymatic hydrolysis
- Enzymes
- Separating sugars
- Furnace/Flue gas clean up
- Pricing/Economics
- OSHA and permitting

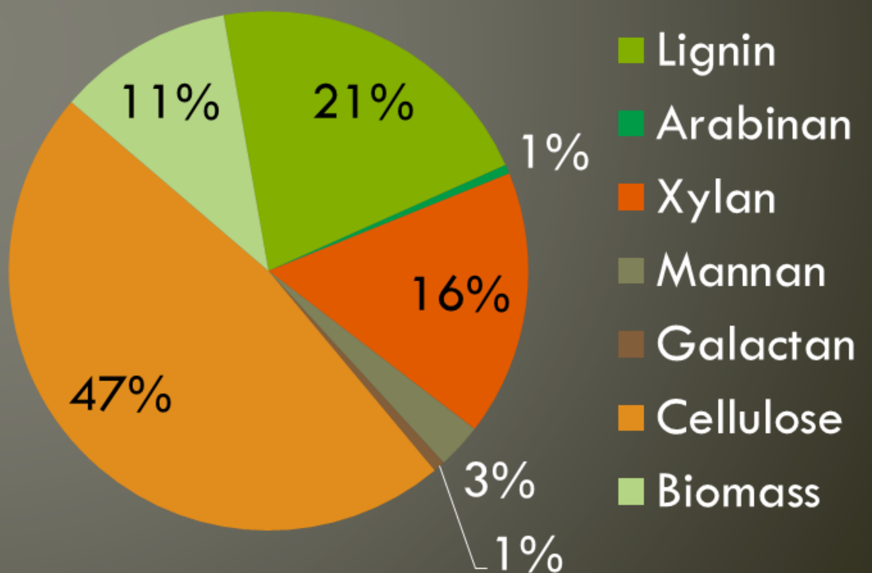
Project definition

- To convert cellulose in poplar tree biomass to sugars, in preparation for fermentation into ethanol
- Requirements
  - 80+% total sugar conversion
  - 90+% sugar purity in each sugar stream

Overview

- Location
  - Oregon (Grant or Harney county)
- Size
  - 120 tons per day
  - 5.2 times size of ZeaChem pilot plant
- Feed
  - Hybrid poplar 29
  - Debarked

Hybrid Poplar 29-Debarked Feedstock Composition



Feed

- Six year maturity period
- ~800 trees per acre
- 10 tons/acre/year
- 730 acres/year
- ~4400 planted acres

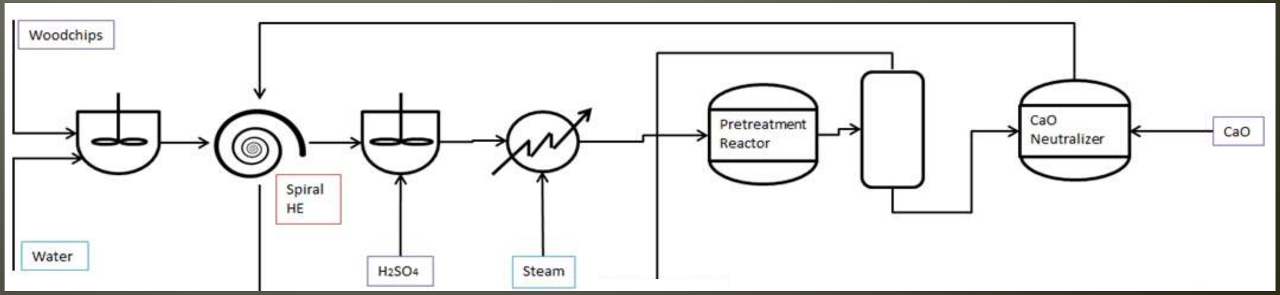
Feed

- ~45,000 acres grown in Oregon and Washington
- Over 50,000 acres in a few years
- 5.2 million gallons of ethanol per year (theoretical)

Flow diagram

Pretreatment

- Milling process
  - Arrives as chips
  - Shredder
  - Knife mill
  - Hammer mill
- Particles ~1.6 mm
- 15% solid solution



Pretreatment

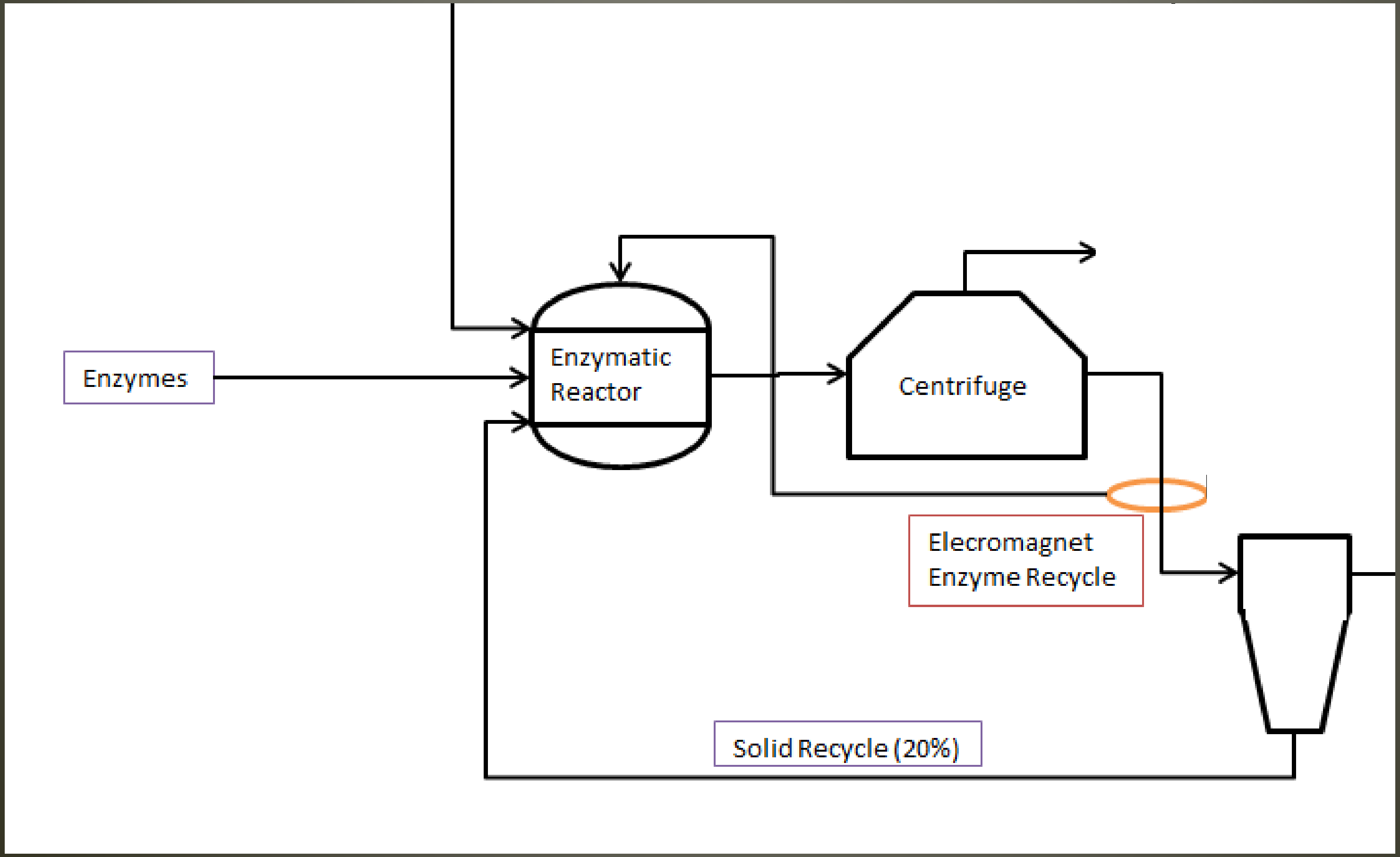
- Use 96% sulfuric acid
- 1.6% acid solution
- Reactor
  - 200°C
  - 15.3 atm
  - Side reactions
    - Lignin components
    - Furfural
    - Slight hydrolysis

Pretreatment

- Flash drum
  - 130°C
  - 2.7 atm
- pH control
  - Lime (CaO)
  - pH 4.95

Flow diagram

- Enzymatic hydrolysis



Enzymatic reactor

- Stoichiometric reactor
  - Main reactions:

$$Xylan + H_2O \rightarrow Xylose$$
$$Galctan + H_2O \rightarrow Galactose$$
$$Mannan + H_2O \rightarrow Mannose$$
$$Arabinan + H_2O \rightarrow Arabinose$$
$$Cellulose + H_2O \rightarrow Glucose$$

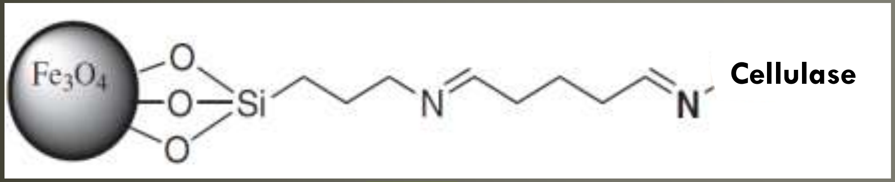
C6 sugar

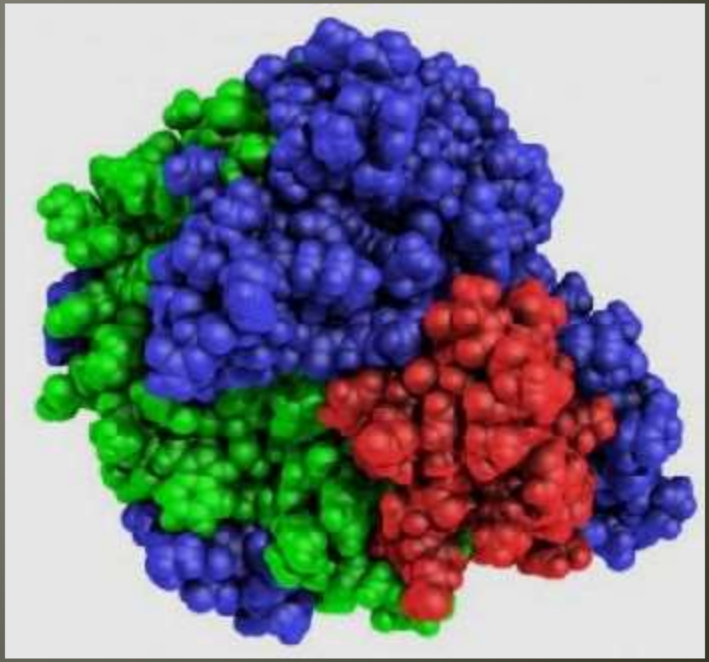
  - 70°C and 1 atm
  - pH at 4.95
  - Enzyme feed separate
  - Conversion set to 80%

NREL's reactors

Enzyme

- Cellulase enzyme “cocktail”
  - Provides essential sub-enzymes for the process
  - Lowers cost
  - Potential to be immobilized

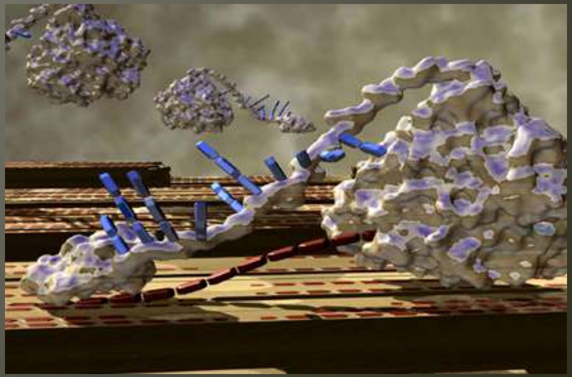




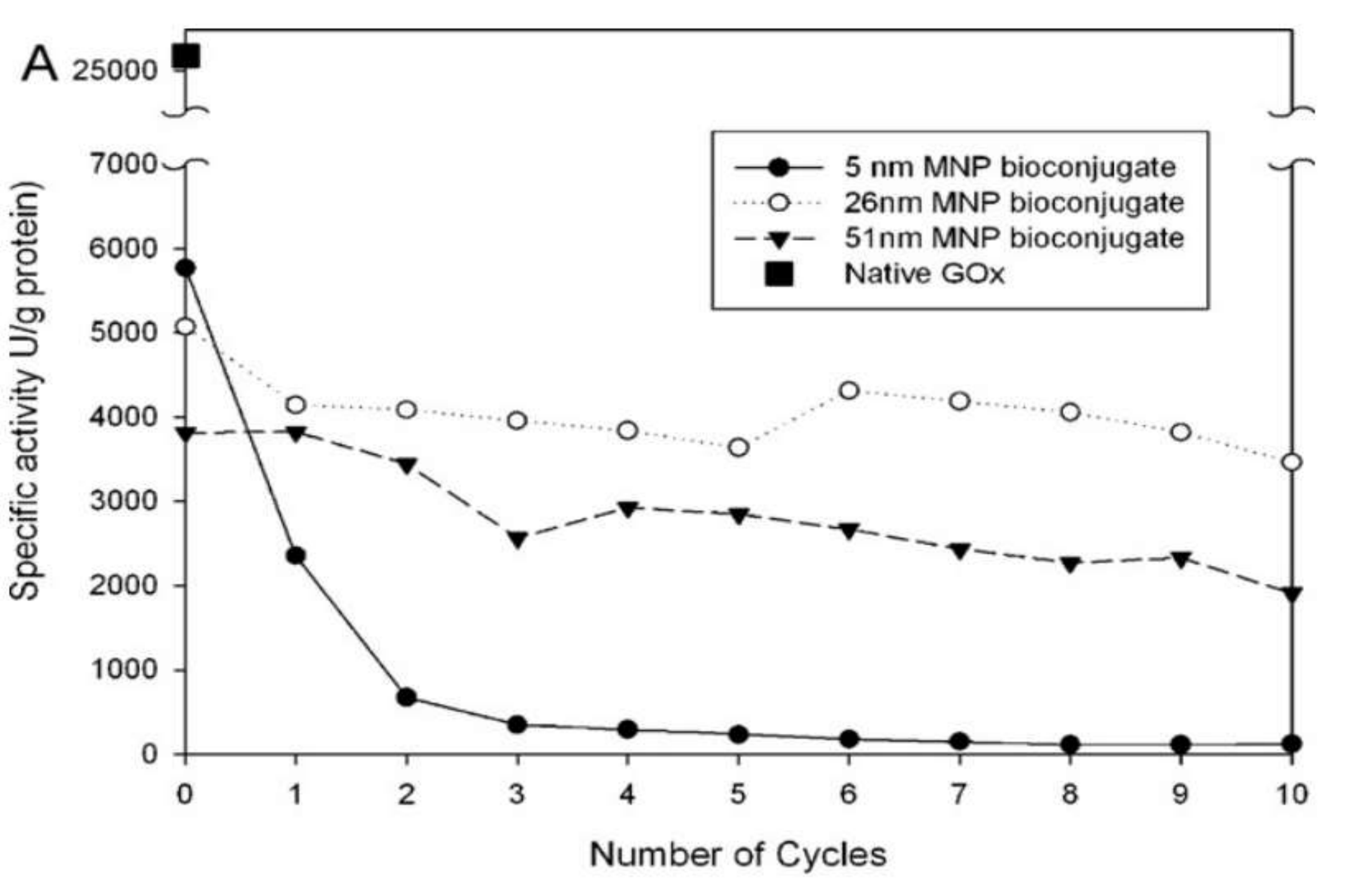
Cellulase enzyme

Immobilizing enzyme

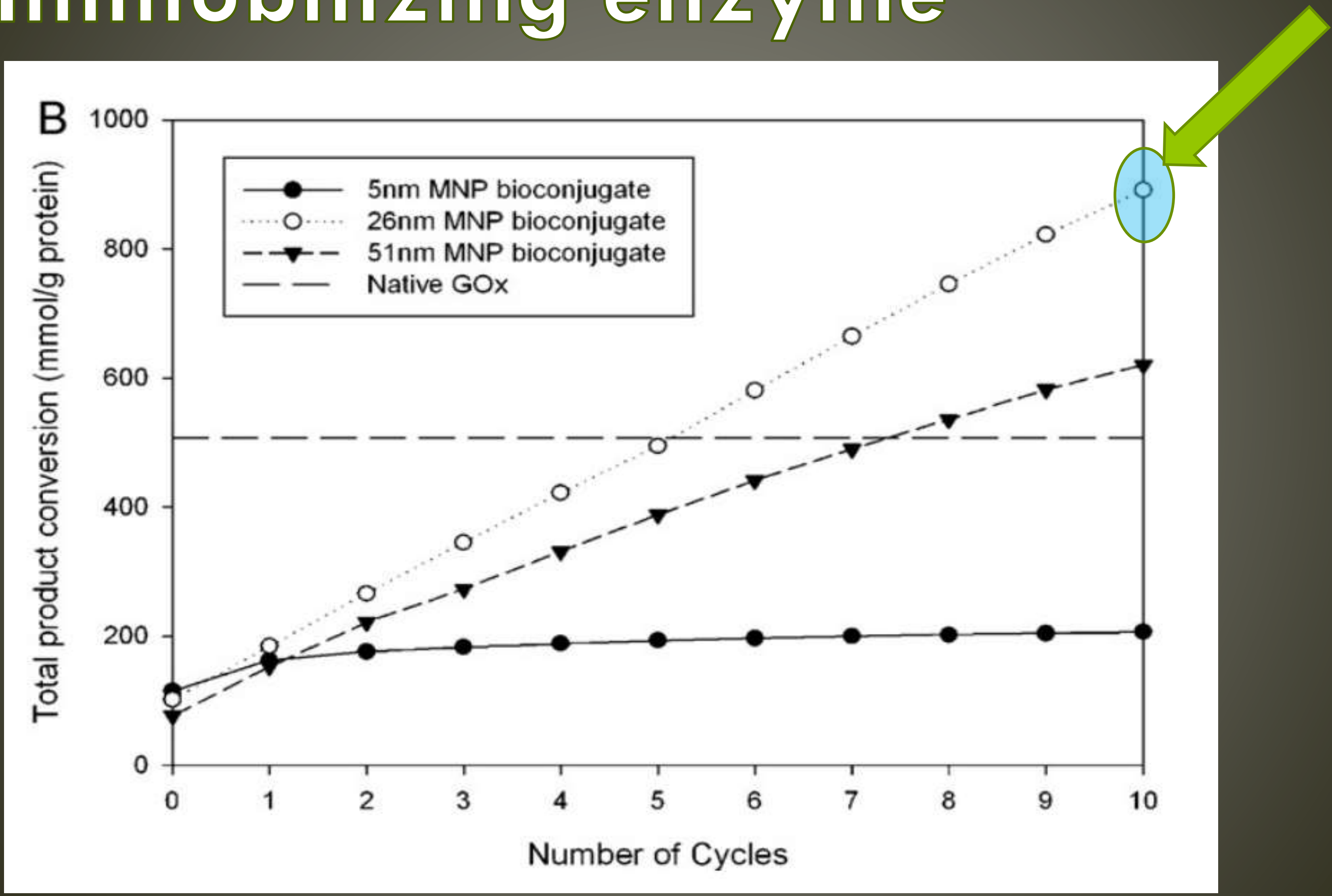
- Mentor: Hee Joon Park
- Magnetic nano particle immobilization
  - 13 nm to 36 nm
- Ten cycle maximum
  - Increase of conversion to 80% after 7 cycles
  - Decrease in activity after 5 cycles



Immobilizing enzyme



Immobilizing enzyme

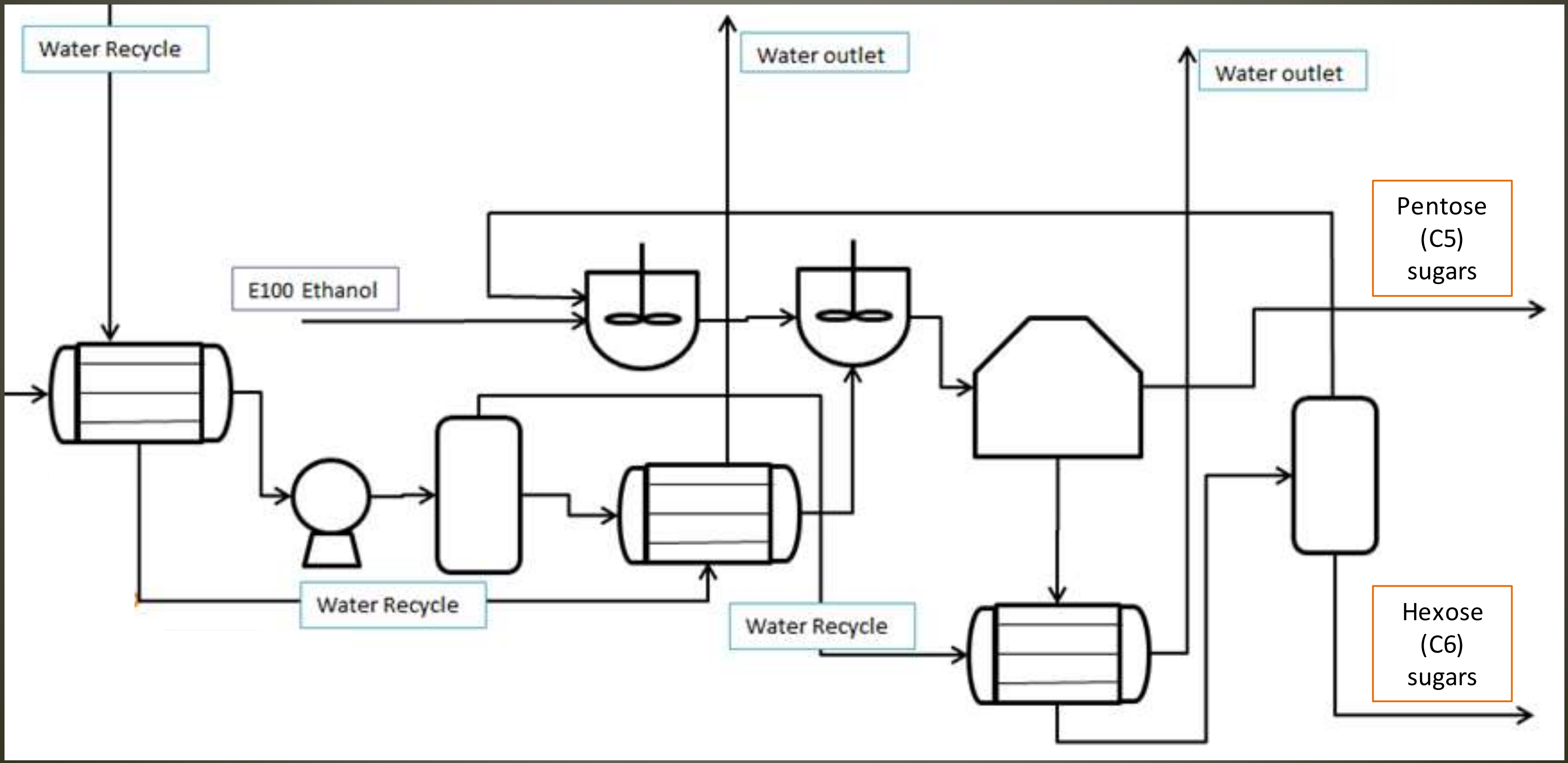


Immobilizing enzyme

- Add four times amount to get to 80% initially
  - Add small amounts after start-up
    - Compensate for loss of enzymes after 10 cycles
  - Reduces cost of enzymes
    - $0.10 per theoretical gallon of ethanol produced
      - Estimate yearly cost of enzymes

Flow diagram

- Ethanol precipitation



Water separation

- Preheat
  - Two steps
  - 200°C
  - 67 million Btu/hr
- Flash drum
  - 1atm

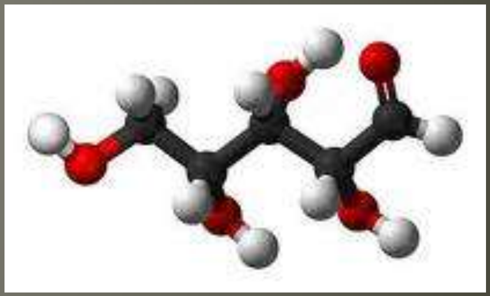
Commercial grade flash drum

Why separate C5 and C6 sugars

- C5 sugars
  - Pharmaceuticals
  - Sweeteners
  - Ethanol
- C6 sugars
  - High-fructose sugars
  - Ethanol
- Market flexibility and stability

Separating C5 and C6 sugars

- Solubility principal
  - Water dielectric constant = 80.1
  - Ethanol dielectric constant = 24.3
- Glucose
  - Stable, less polar
- Pentose
  - Stronger polarity
  - Higher tendency to interact
- Precipitates out at a ratio if 3:1ethanol to solution



Separating C5 and C6 sugars

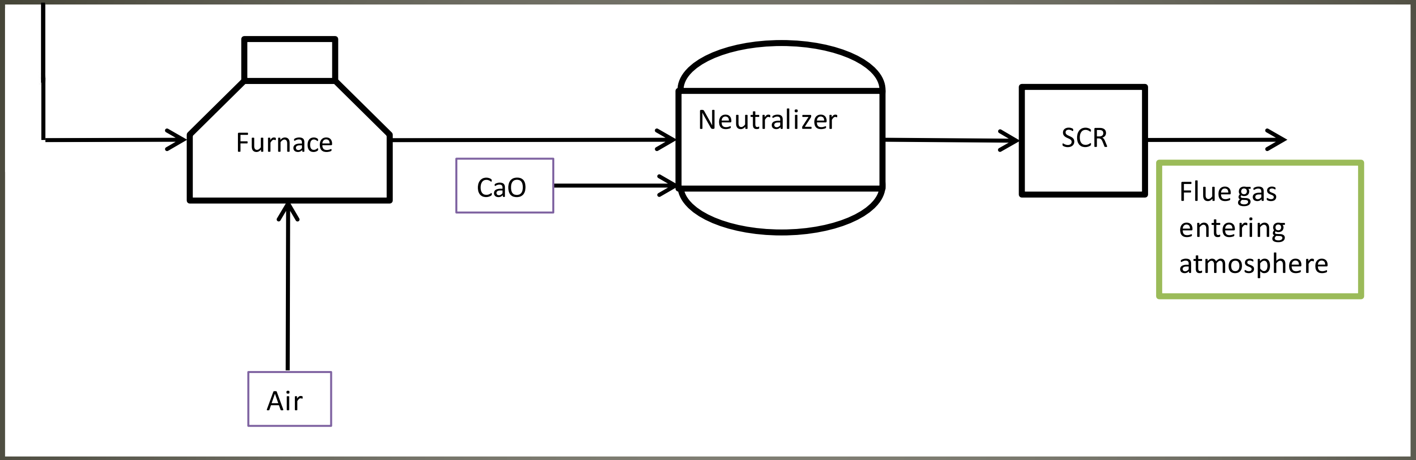
- Precipitation by use of ethanol
  - 80°C
  - 3 to 1 ethanol vs. sugar stream
  - 24 hour residence time
  - 93% C5 precipitation
- Solid liquid separation
  - Continuous separating centrifuge

C5 sugars purity	**93.9%**
C6 sugar purity	**93.9%**

Ethanol recycle

- Ethanol recovery
  - Preheat using water recycle
  - 180°C
  - Flash drum
  - 1 atm
  - 99% recovery of ethanol
- Feed ethanol
  - 222.5 lb/hr

Furnace/Flue gas clean up



- Air fed furnace
- Lime and $CaCO_3$ neutralizer
- Ammonia catalyst scrubber

Furnace/Flue gas clean up

- Furnace
  - 550°C and 5 atm
- Major pollutants
  - NO_2-from air intake
  - SO_2-from burning biomass and leftover H_2SO_4
- Reactions for scrubbers

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$
$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$$
$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$

Air pollutants

- Oregon air standards

Pollutant	Average Time	National Ambient Air Quality Standard (NAAQS) Violation Determination[1]	Federal Primary Health Standard (NAAQS) Exceedance Level	State Standard Exceedance Level
Nitrogen dioxide	Annual	Annual arithmetic mean	0.053 ppm	0.053 ppm
Sulfur dioxide	Annual Arithmetic Mean	Not to be exceeded more than once per calendar year.	0.03 ppm	0.02 ppm
	24 hour	Not to be exceeded more than once per calendar year	0.14 ppm	0.10 ppm
	3 hour	Not to be exceeded more than once per calendar year	**0.50 ppm* secondary standard	0.50 ppm

- SO_2- 21.9 ppm
- NO_2- 45.8 ppm

Balances

Substance	IN [kg/hr]	OUT [kg/hr]
Biomass	1764	1243
Cellulose	4105	365
Xylan	1337	149
Arabinan	75	9
Mannan	202	3
Galactan	89	1
Lignin	2428	1712
Glucolignin	3	2
Xylolignin	3	2
Manolignin	3	2
Galactolignin	3	2
Arabinolignin	3	2
Furfural	0	4
H_2SO_4	1024	9
CaO	28139	27702
$CaSO_4$	0	1061
Cellobiose	100	70
Cellulase	100	70
Glucose	0	3917
Xylose	0	1241
Arabinose	0	70
Galactose	0	96
Mannose	0	216
Ethanol	101	100
N_2	17705	18086
CO_2	0	3744
O_2	5376	1668
NO_2	0	4
NH_3	426	55
SO_2	0	3
$CaCO_3$	450	189
Ca^{2+}	0	104
SO_3^{2-}	0	208
H_2O	76484	77796
TOTAL	**139919**	**139905**

Major products

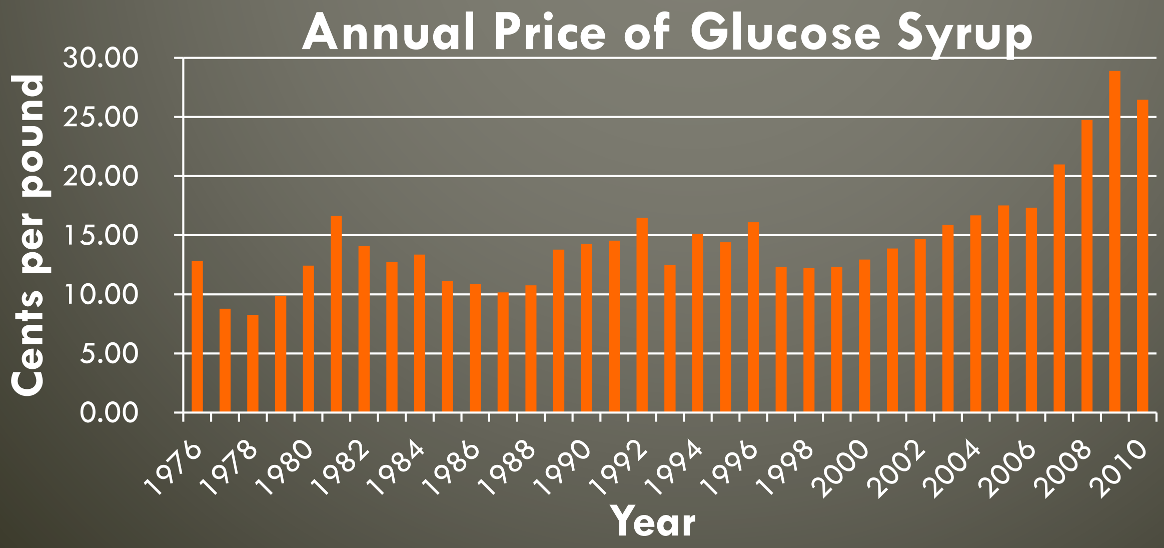
- Energy balance
  - 65.4 MW needed

Feed pricing

Feed	Cost
Poplar	$38/ton
Lime (CaO) & Limestone ($CaCO_3$)	$72.2/ton
96% Sulfuric acid	$329/ton
Water	$0.9/ton
Ethanol (E100)	$2.10/gal
Ammonia (NH_3)	$521/ton
Immobilized enzymes	$520,000/yr

Product pricing

- Glucose
  - $0.21 per pound
- Arabinose, xylose and other C5 sugars
  - $0.26 per pound



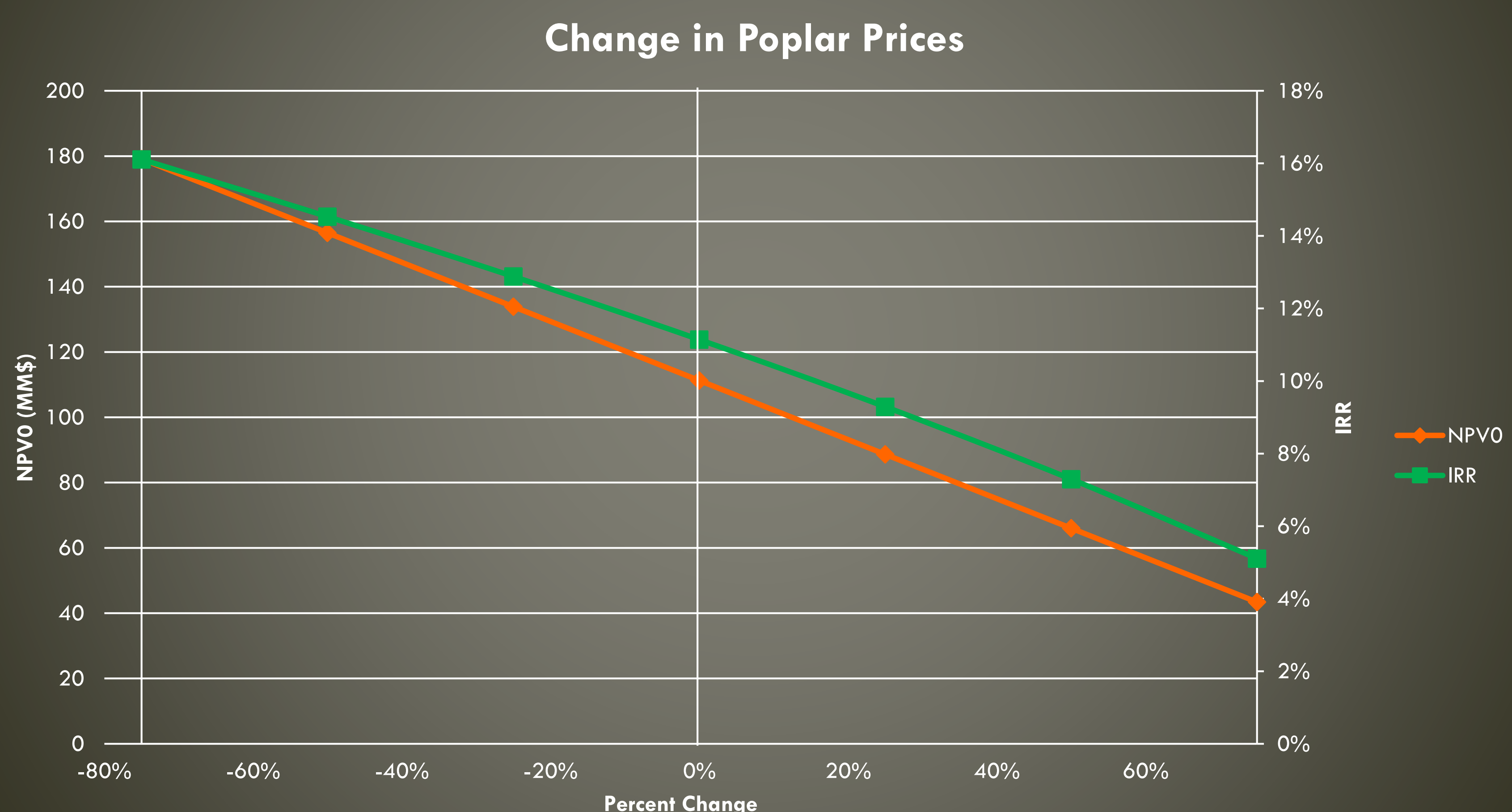
Capital cost

- Purchased Equipment Cost
  - $10.0 million
- Fixed Capital Investment (FCI)
  - 503% installation factor
  - $50.4 million
- 75% capacity for year 1
- 2-year construction period
- 10% discount factor
- 35% tax rate

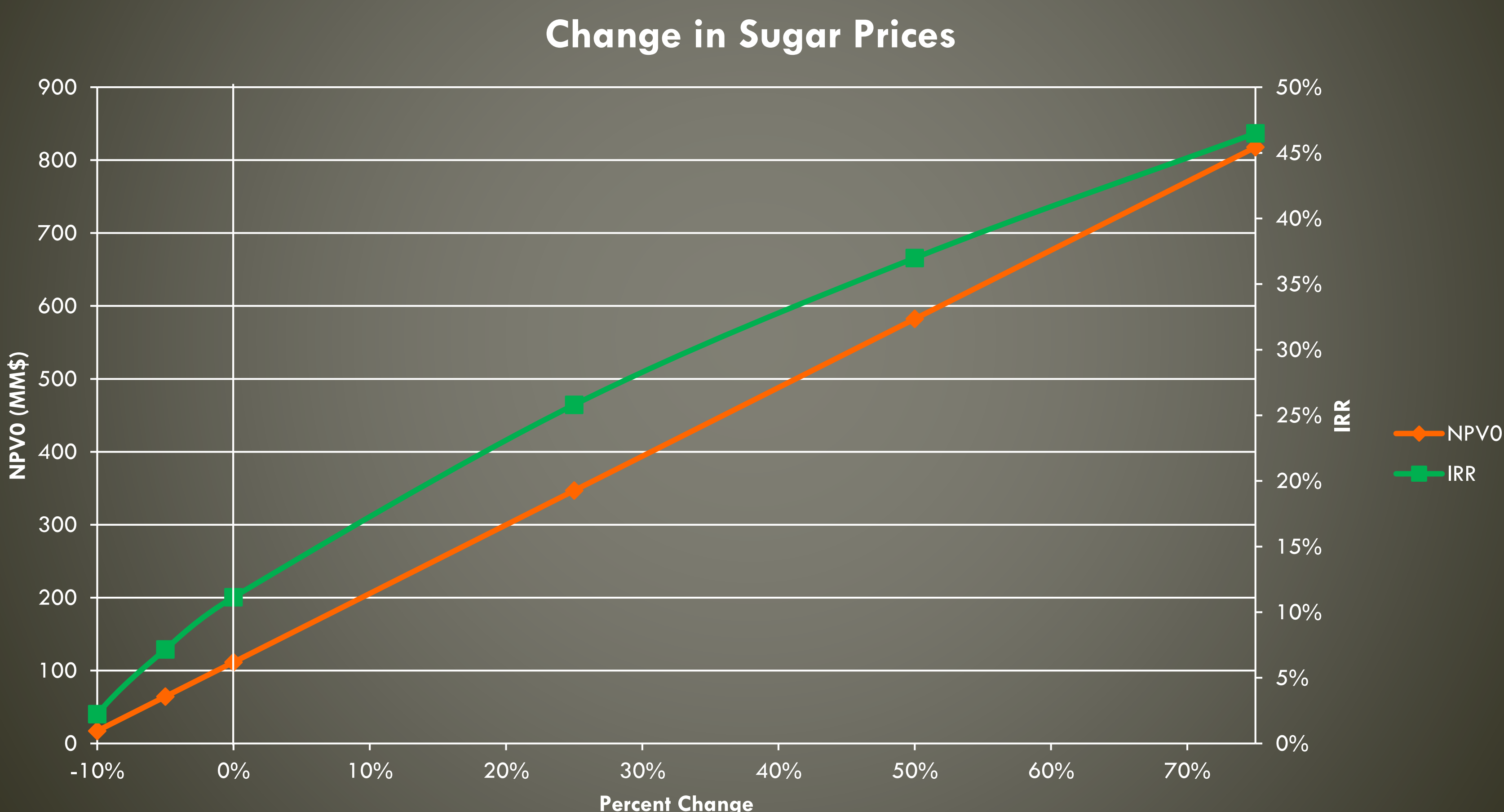
Economics

- Feed cost
  - $9.3 million/yr
- Product revenue
  - $35.3 million/yr
- Net product revenue
  - $26.0 million/yr
- Net present value (20 yrs)
  - $111.3 million (NPV0)
  - $6.0 million (NPV10)
- Internal rate of return
  - 11%
- Payback period
  - 6.95 years

Economic sensitivity



Economic sensitivity



OSHA

- Plant design
  - Physical plant designs
    - Guard rails
    - Heat exposure
    - General work conditions
  - Chemical considerations
    - Storage systems
    - Response kits on sight
    - General worker knowledge
- Emergency considerations

Permitting

- Water pollution
  - Water discharge
    - Small amount of H_2SO_4 and furfural
- Solid disposal
  - Obtain Resource Conservation and Recovery Act (RCRA) permit
    - Regulate waste

Future work

- Produce own enzymes
- Include a fermentation system to produce ethanol directly
  - Research newer, better organisms (i.e. Q Microbe)
- Investigate lowering viscosity of the process stream
- Add a turbine/generator to capture energy

Conclusions

- Positives
  - Good IRR
  - Green technology
  - New technology
- Negatives
  - Fluctuating sugar prices
  - Solids processing facility

Questions??

- Acknowledgments
  - Dr. Patrick Johnson
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Video