DOE Bioenergy Technologies Office (BETO)
2015 Project Peer Review

Conversion of Lignocellulosic Biomass to Ethanol and Butyl Acrylate

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Where does ADM fit with the IBR?

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- Ensuring a supply of technology for future growth is a priority for ADM Research
- Corn stover utilization may enable continued growth in starch supply while starting a new industry around a currently underutilized material

Quad Chart Overview

Timeline

- BP1 Start Date: January 2010
- BP2 Start Date: January 2011
- End Date: December 2014
- Percent complete: ~100%

Participants

- Novozymes – Fermentation Enzymes
- Andritz – Hydrolysis Reactor
- MATRIC – Process development and engineering for the acrylic acid

Budget: $35.7 MM

- DOE Cost Share: $24.8 MM
- ADM Cost Share: $10.9 MM
- Contingency: $9.0 MM
- 100% of entire budget is complete.

Spent:

FY 10	$	1,978,489
FY 11	$	9,140,411
FY 12	$	16,282,914
FY 13	$	7,486,024
FY 14	$	893,352

IBR Project Overview: Major Objectives

- Validate laboratory results on biomass conversion using acetic acid treatment and conversion of selected streams to fuels and chemicals in an integrated pilot plant
- Demonstrate all plant unit operations
- Demonstrate fermentation of 5 carbon sugars
- Demonstrate catalytic process for butyl acrylate production
- Develop design data for scale up to commercial production
- Complete material and energy balance
- Build data set that will allow accurate capital estimate for full scale facility

Critical Success Factors

Meet or exceeded the project objectives.

An economic and commercial validation to prove viability.

Proving that the new technology performs as predicted.

Project History

2010

- **March 15:** DOE Approval of Plan
- **April 29:** EIR-1 Approved
- **May 28:** Release of Award 1 Funds
- **October:** Purchased Long Lead Equipment – Andritz Reactor
- **October:** Site prepped for building construction
- **October 5:** Project Cost Estimation and Review Application for Award 2
- **October 29:** EIR-2 Approved
- **December:** Construction Permit Approved

2011

- **January:** Building Construction Began
- **January 7:** Operating Permit Approved
- **May 2:** Release of Award 2 funds.
- **May:** Office Addition Started
- **May:** 1100 Process Construction/Commissioning Began
- **October:** 1200 Process Construction/Commissioning Began

Project History

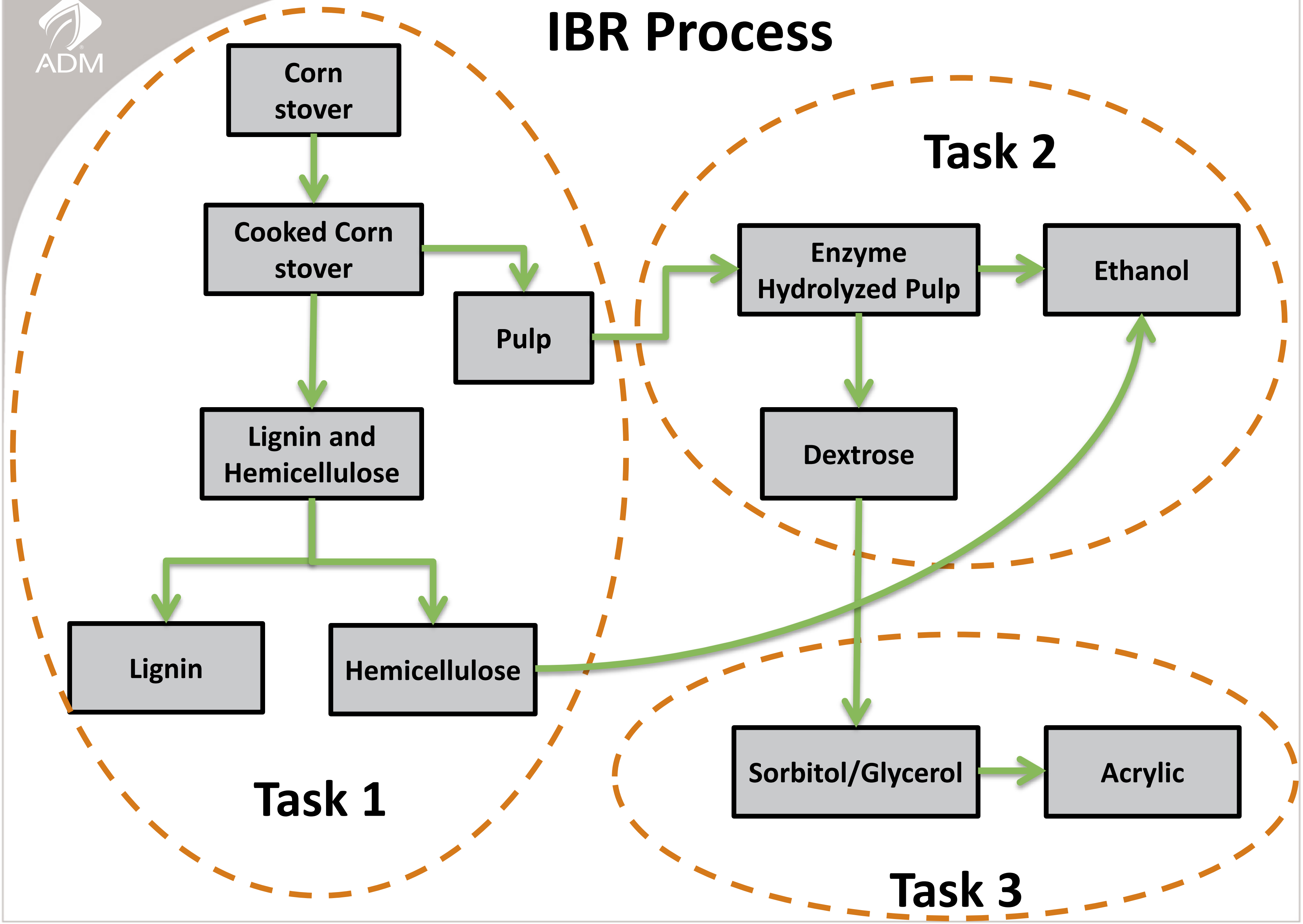
2012 2013

- **February:** 1300 Process Construction/Commissioning Began
- **April:** 1200 Process Construction/Commissioning Ended
- **May:** 1100 Process Construction/Commissioning Ended
- **June:** 1400 Process Construction/Commissioning Began
- **Ongoing:** Extended Run Campaigns

2014

- **Ongoing:** Extended Run Campaigns
- **January:** 1300 Process Construction/Commissioning Ended
- **March:** 1400 Process Construction/Commissioning Ended
- **March 17:** Final Performance Test

IBR Process


Corn stover
Cooked Corn stover
Pulp
Lignin and Hemicellulose
Lignin
Hemicellulose
Task 1
Task 2
Enzyme Hydrolyzed Pulp
Ethanol
Dextrose
Sorbitol/Glycerol
Acrylic
Task 3

Task Issues and Challenges for IBR Process

Task 1

Best design for digester to minimize solvent usage, easy to feed moderately chopped stover, and provide needed shear for breaking apart resistant particles without degrading cellulose fibers.

Best fiber/solvent separation method to minimize solvent usage and provide pulp with minimal acetic acid residue.

Eliminate fiber losses thru the pulp separation process.

Optimal lignin and hemicellulose separation process with efficient acetic recovery.

Task 2

Best treatment steps to maximize dextrose yield and minimize enzyme usage.

Best equipment design for the enzyme treatment. Nature uses intermittent grinding to maximize this step.

Best dextrose residue separation methods or series of process steps

Task 3

Determine what impurities to be removed from process streams for longest catalyst life.

Best way to maximize glycerol yield or at least allow for similar yield as seen on the bench.

Determine cost of process from glycerol to acrylic.

Additional IBR Challenges

- **Mechanical issues with the Andritz reactor.**
  - **seals, lock hopper, material handling**
- **Screw presses unable to remove pulp fines.**
  - **Added centrifuge step but didn't entirely solve the problem**
- **Extraction of Acetic from C5 stream**
  - **Challenges in C5 fermentation**
- **Distillation size limitations.**
- **Hydrogenolysis to glycerin is low quality and at the low end of the target range.**
- **Glass distillation column failure in the 1400 section.**

Scope Changes

- Stover Fractionation
  - No Major Changes
- Enzymes and Fermentation
  - Half of C6 sugars diverted to chemical usage
  - All C5 sugars will be used for fermentation
- Sugar Conversion to Glycerol
  - C5 was original source of chemical feed
    - Changed to C6 due to purification hurdles
    - Lower yields associated with chemical processing
- Acrylate Production
    - Changed from ethyl acrylate to butyl acrylate for safety and ease of operations

Stover Fractionation Challenges

- Erosion
  - Inlet lock hopper valves where buildup of stover particles behind valve seats has caused gouging
  - Reactor discharge pressure control valves which must cycle in direct contact with stover pulp
  - Transfer lines between high pressure reactor and atmospheric discharge tanks where stover is traveling at high velocity, particularly on pipe bends were outer radii erode fastest
  - Plate in atmospheric tank where pulp first contacts as the steam explosion due to pressure release takes place

Stover Fractionation Challenges

- Non organic material
  - Metal bits of metal found in the bailed stover can cause issues in machinery
  - Residual rocks and dirt from second pass stover is partly to blame for severe erosion issues
- Acid Presses
  - High shear design of our screw presses may have increase the amount of fine fibers in our liquid stream.
  - Alternative designs of presses with lower amounts of shear are being investigated

Fractionation Challenges Overcome

- Stover handling
  - Bridging, compaction, plugging caused many issues early on
  - Proper system cleaining between runs fixed many plugging issues
  - Removal of transitions from large to smaller piping as well as unnecessary edges and shelves in helped alleviate bridging
  - Braces, guards and amp limits for motors to keep dead zones to a mimimum as well as alert operators if non flow was occurring helped stop compaction events

Stover Fractionation Challenges

- Evaporation
  - Fine fiber causes a higher viscosity curve in sugar solutions making concentration more difficult
  - Fiber removal was marginally successful but alternative methods are still being looked at
- Lignin Precipitation
  - Variable quality of lignin due to inconsistency of lignin
  - When allowed to settle lignin conglomerates into hard cake which is difficult to handle
- Acetic Extraction
  - Severe emulsion caused separation issues
  - Solvent degradation due to down time of pilot equipment caused residual acid in final products

Enzymatic and Fermentation Challenges

- **Fermentation**
  - **Residual acids from incomplete extraction and solvent degradation causes enzyme and fermentation rates to be slow or non existent**
  - **High salt concentrations due to natural metals found in stover cause inhibition of both the fermentation and enzymatic processes**

Glycerol Production Challenges

- Sugar Centrifugation
  - High loss of sugar in the heavy phase, in our process this was acceptable only due to fermentation as an outlet in plant scale this may not be feasible
- Hydrogenolysis Reaction
  - Low Glycerol selectivity which makes glycerol as a target product difficult to justify. Coproducts account for majority of yield

Acrylic Acid Production Challenges

- Dehydration
  - Low run time between regenerations causing frequent reactor swings which will be difficult at scale
- Oxidation
  - Acrolein and air integration caused back pressure issues due to localized polymer buildup within mixing equipment

Acrylic Acid Purification Challenges

- Glass Distillation Shared Issues
  - 1 and 2 inch columns were ground glass. Almost impossible to seal due to size of columns and difficulty of alignment
  - Flange material of Teflon was too stiff for good sealing between columns
  - Feed and adapter glass very fragile

Acrylic Acid Purification Challenges

- Solvent Removal Column
  - Acrylic polymerization due to excessive heat in reboiler section
  - Initial heat exchanger size and style incorrect mostly due to excessive heat loss on small equipment
  - Very fine solids buildup in reboiler section caused pumping issues for such small system
- Acetic Column
  - 1” column caused control problems due to magnification of small changes

Acrylic Acid Purification Challenges

- **Heavies Column**
  - **Small amount of polymerization above feed locations due to localized inhibitor distribution issues**
- **Esterification Reaction**
  - **Solids buildup caused pump issues due to scale of pumps needed.**
- **Vacuum System**
  - **Connection leaks caused excessive vapor entrainment leading to pump corrosion**

Process Targets

Process Yields	Expected	Bench/Pilot	Validation Run
Total Solublized Biomass (%)	50	50	51.7
Cellulose Pulp: Carbohydrate (C6 + residual C5) yield (wt. %)	43	45	37
Lignin/Hemicellulose Stream: Carbohydrate yield (wt. %) – C6, C5	7.5, 20	4.5, 15	2.5, 10
Pentose Fermentation – Total sugar to ethanol yield (wt. %)	42	35	35
Glucose Fermentation – Total sugar to ethanol yield (wt. %)	45	45	43
Hexose Sugar Hydrogenation to Sorbitol (%)	99	99	99.5
Hydrogenolysis and Product Separation (wt.%) – EG, PG, Gly	27, 15, 40	27, 17, 23	17,17,24
Total Butyl Acrylate from Acrylic Acid (%)	99	97	96.8

Laboratory Result Validation - Fractionation

- Demonstrated the ability to split corn stover continuously into the three constituent streams:
  - C6 Pulp
  - C5 Soluble Sugars
  - Lignin solids
- Analytical results of each stream show good comparisons to those produced in the laboratory reactions

Laboratory Result Validation - Fermentation

- **Demonstrated the use of enzymatic reactions to product a high quality six carbon sugar stream.**
  - **Sugar was able to be processed to both ethanol fermentation as well as for industrial chemicals**
  - **Sugar profile of pilot plant material was very similar to that produced in laboratory trials**
- **Limited success of fermentation of five carbon sugar stream. Ethanol production was achieved but purification was more difficult than laboratory testing showed.**

Laboratory Result Validation - Chemicals

- Demonstrated all catalytic reactions including hydrogenation, hydrogenolysis, dehydration, oxidation and esterification
  - Sugar Hydrogenation conversion and selectivity proved very similar to lab reactions
  - Yield of glycerol in the pilot plant surpassed that of continuous laboratory reactors and purification for further processing was successful
  - Demonstrated the ability to produce a bio based acrylic acid through dehydration and oxidation from corn stover feed stock.

Operational Validations

- All unit operations outlined in the final design have been demonstrated with materials processed from corn stover through the IBR equipment
- Demonstration of C5 fermentation has had limited success
  - Difficulties in stream purification are the main cause
- Demonstration of the catalytic process for butyl acrylate production has been successful using a reactive distillation process

Mass and Energy Balance

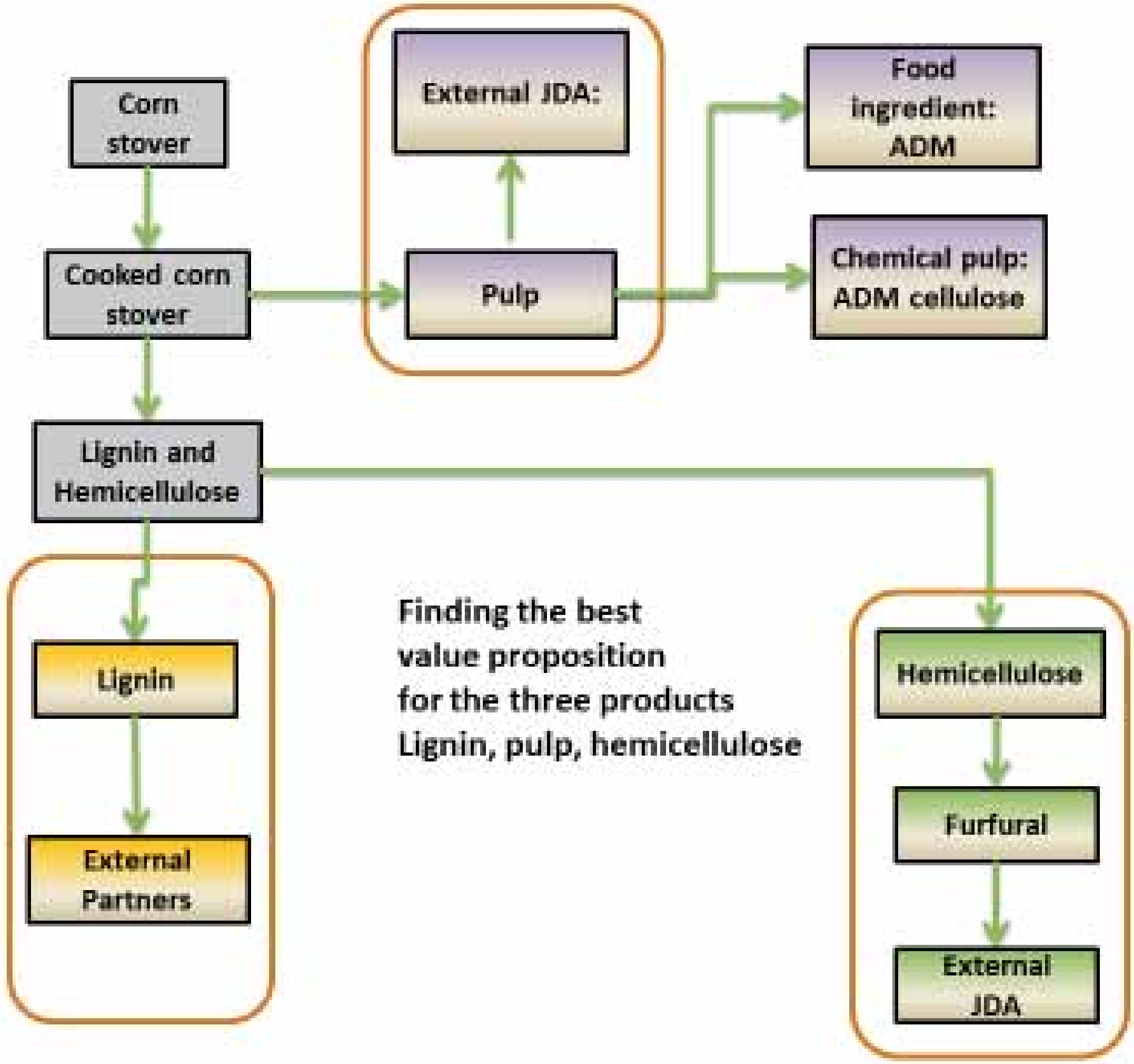
- A complete Material balance has been performed around all unit operations
  - Mass balances have been calculated for all units
  - Conversions, yields and selectivities have also been calculated for all chemical conversions
- Energy balances including heat integration have been limited due to high energy losses associated with pilot plant scale equipment

Assets Utilization

- **Many of the IBR assets are currently being used for internal ADM technology testing. More projects that utilize the equipment are in various stages of implementation**

Off Shoots

- C6 Stream off shoots
  - Food Fiber
  - Industrial Fiber
- C5
  - Industrial Chemicals
- Lignin
  - Industrial Applications


Corn stover
Cooked corn stover
External JDA:
Pulp
Food ingredient: ADM
Chemical pulp: ADM cellulose
Lignin and Hemicellulose
Lignin
External Partners
Hemicellulose
Furfural
External JDA
Finding the best value proposition for the three products Lignin, pulp, hemicellulose