DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

WBS: 2.3.1.209
Catalytic Upgrading of Carbohydrates in Waste Streams to Hydrocarbons

April 6, 2023

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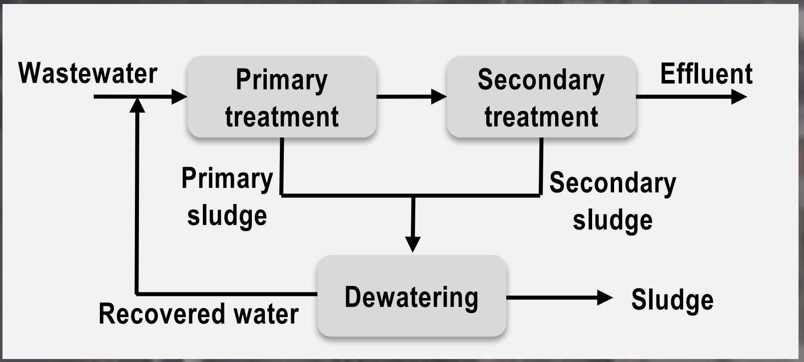
NREL Transforming ENERGY   Yale   NC STATE UNIVERSITY

Solid Wastes in Pulp and Paper Industry

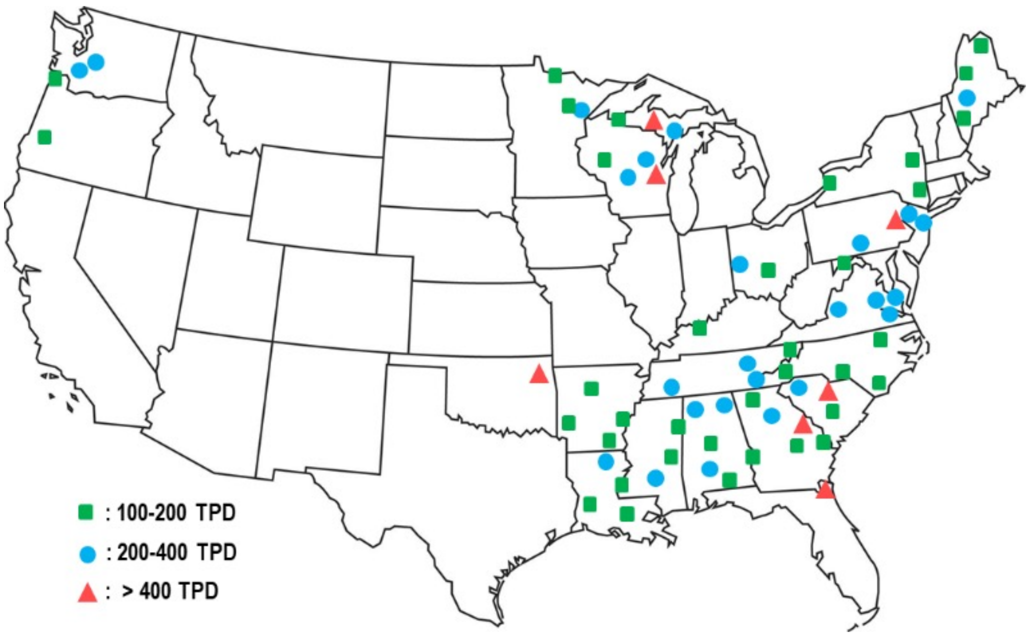
Solid wastes in pulp and paper industry

- Rejects from debarking and chipping operation
- Ash from boiler and furnace
- Causticizing residuals
- Wastewater treatment system
  - Primary sludge
  - Secondary sludge

Paper sludge



Paper Sludge Utilization



Paper products – Packaging, Tissue/towel, Printing/writing

Current practice in US	
Landfill or lagoon	50%
Land application	10%
Incineration	20%
Other beneficial use	10%

Recycled Materials and Byproducts in Highway Applications, National Academies Press (2013)

~8 MM wet tonne/year (50% moisture)
Trucking & landfilling ~ $30/wet tonne
Cost ~ $240 MM/year

Project Overview

- This project will develop a technology for converting the carbohydrates in paper sludge into a hydrocarbon (HC) biofuel, both economically and sustainably.

	Key Milestones & Deliverables
Year 1	Initial verification Develop a mass and energy balance model in Aspen Produce furfural and HMF from paper sludge at 90% and 65% yields
Year 2	Aldol condensation of furans with ketones at 85% yield to intermediates Produce HC via HDO at 80% yield Intermediate verification to produce 50 mL HC Demonstrate a minimum 25% reduction in nLCOD
Year 3	Produce 1.0 L HC for fuel property testing Determine if 75% (GGE basis) of HC can be blended into a jet or diesel fuel Demonstrate a minimum 25% reduction in nLCOD.

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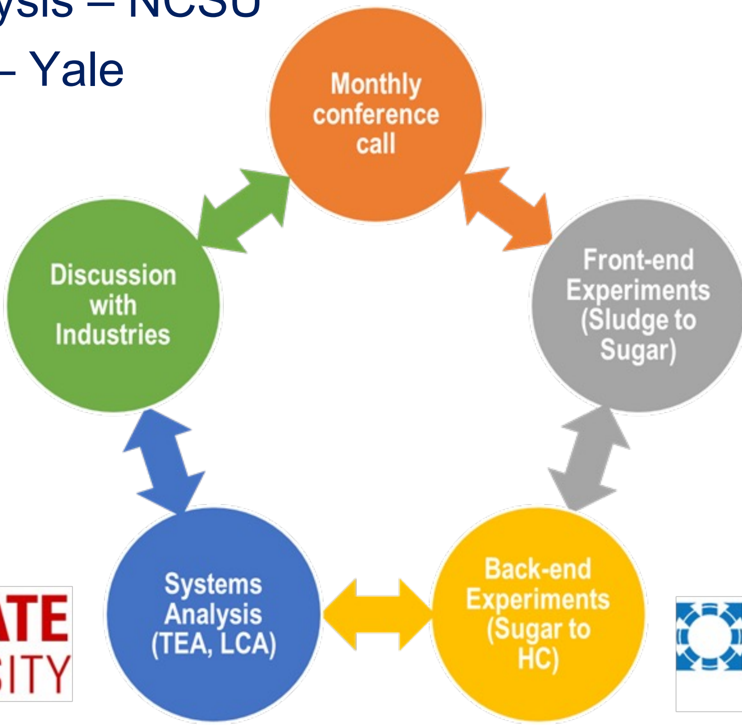
Management: Project Tasks

- Project work breakdown
  - Front-end experimental work (paper sludge to furans) – NCSU
    - Sludge selection, ash removal, enzymatic hydrolysis, dehydration
  - Back-end experimental work (sugars to hydrocarbon) – NREL
    - Dehydration, aldol condensation, hydro-deoxygenation, fuel testing
  - Systems analysis
    - Techno-economic analysis – NCSU
    - Life cycle assessment – Yale



Management: Communication and Risks

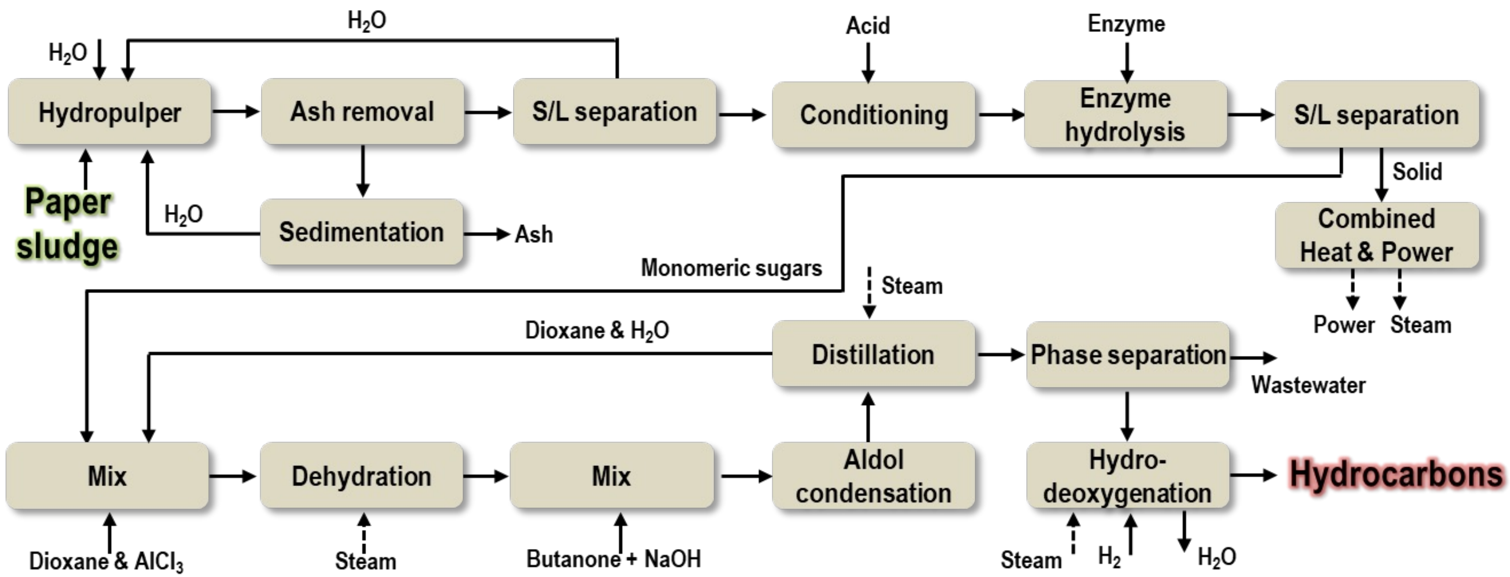
- Communication
  - Contacted 17 paper mills including all major paper producers
  - Monthly conference call between NCSU and NREL
    - Present new results and discuss next work plan
    - Research activities are highly integrated and guided by TEA
  - Quarterly milestone report
  - Regular interaction with the BETO project manager
  - BETO validation: Initial (Aug. 2019, completed), Intermediate (Mar. 2022, completed), and Final (Sept., 2023)
- Risks and mitigation plan

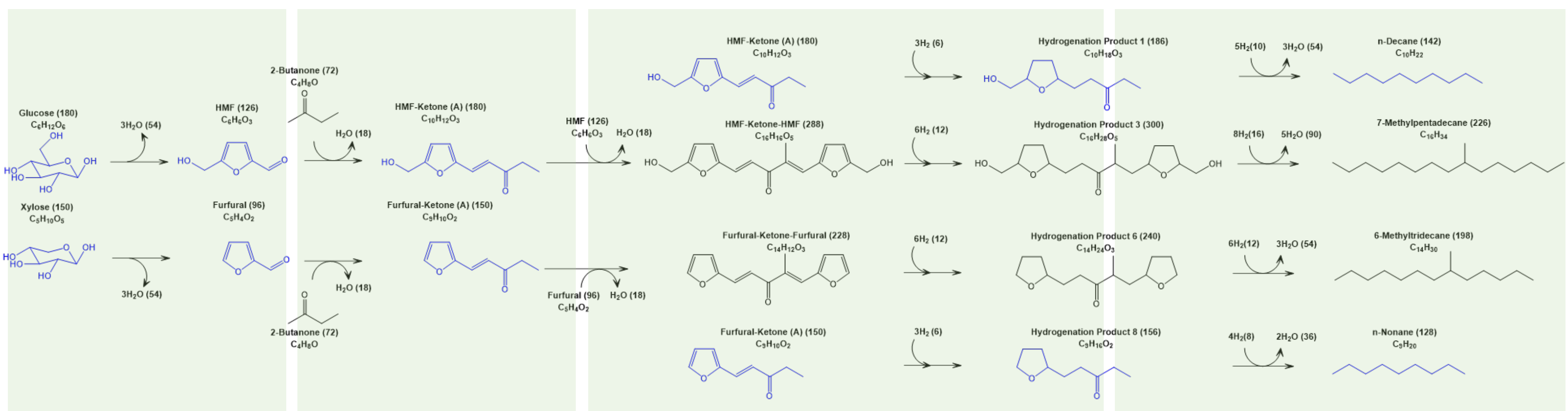
Risk/Barrier	Mitigation plan
High amount of ash in paper sludge	If a single unit (e.g. screening) is not sufficient, multistage unit operation will be developed for ash removal.
Catalyst deactivation due to ash in paper sludge	Characterize used catalysts to identify cause of deactivation and either remove components causing deactivation or design catalyst to be more resistant to deactivation.
Sludge variations between mills	The sludge composition is largely dependent on raw material and papermaking process. The project will exam at least three different sources and develop an optimized solution for each sludge.

Milestones and Go/No-go

Milestone	Topic	Date	Target	Progress
ML1.1	Go/No-go: Initial verification	09/30/19	Confirm the benchmark and assumptions SOPO/budget review	Completed
ML2.1	Preliminary TEA	12/31/19	nLCOD calculation based on the TEA.	Completed
ML3.1	Ash removal	03/31/20	Sludge selection and characterization Ash removal >93%, Carbohydrate retention >65%	Completed
ML4.1	Dehydration	9/30/20	Enzymatic hydrolysis >85% sugar yield Dehydration >69% furan yield	Completed
ML5.1	Aldol condensation	12/30/20	Condensation >85% yield	Completed
ML7.1	Solvent recycle	9/30/21	Solvent recycle strategies by analyzing distillate and still bottoms	Completed
GN 8.1	Go/No-go: Intermediate verification	3/30/22	Produce 50 mL of hydrocarbon product from paper sludge 50% (GGE basis) of HC can be blended into jet or diesel fuel 25% reduction in the nLCOD	Completed
ML6.1	Hydro-deoxygenation	9/30/22	Hydro-deoxygenation >80% yield	Completed
ML9.1	Enzymatic hydrolysis	12/31/22	Relevant scale enzymatic hydrolysis >2.5 kg sugar production, >64.8% conversion	Completed
ML9.2	Dehydration and condensation	03/31/23	Dehydration and condensation >1.25 kg intermediate Overall yield >66.3%	In progress
ML9.3	Hydrocarbon production	06/30/23	Flow reactor with time on stream >50 h Hydro-deoxygenation >85% yield Produce 1.0 L of hydrocarbon product	-
ML10.1	Final verification	09/30/23	Produce 1.0 L of hydrocarbon product from paper sludge 75% (GGE basis) of HC can be blended into jet or diesel fuel 25% reduction in the nLCOD	-

Process Overview





Dehydration **Aldol Condensation** **Hydrogenation** **Hydro-deoxygenation**

Paper Sludge Handling Process

Waste stream from Paper machine

↓

Clarifier

↓

Sludge tank

↓

Press

↓

Storage

↓

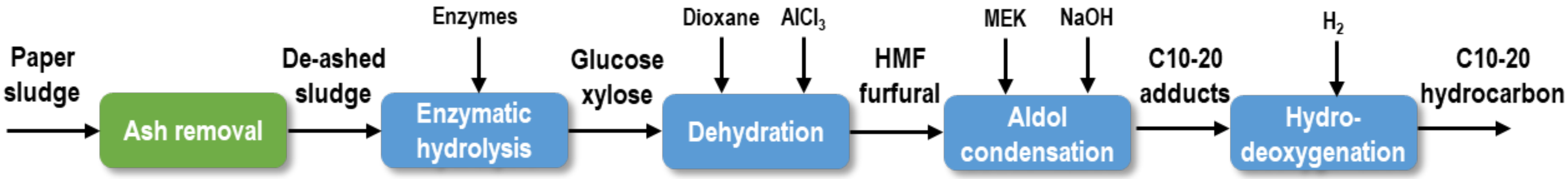
Disposal

Paper Sludge Survey and Selection

Types	Company	Ash, %	Fiber length, mm	Fines, %
Kraft pulp	--	47.2	2.002	17.6
Uncoated freesheet	"D" company	43.7	0.766	30.1
	--	36.7	0.819	19.0
	"C" company	43.2	0.861	29.7
Tissue/ towel	--	57.1	0.809	27.7
	--	42.6	0.754	29.7
Packaging	--	33.3	1.021	33.4
	--	48.8	0.900	27.0
Specialty	--	0.40	0.445	61.6

- 17 companies were contacted
- 11 paper sludges have been received
- Most of work in the project uses the sludge from the "D" company.

Ash Removal from Paper Sludge



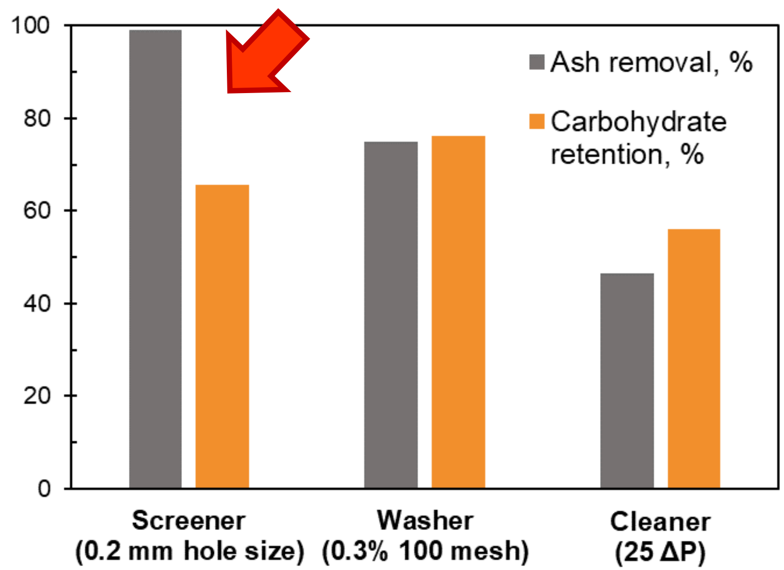
Objectives:

- Remove ash in paper sludge for monomeric sugar production
- Ash removal >93%, Carbohydrate retention >65%
- Characterization of ash remaining in paper sludge

Hole, Slit

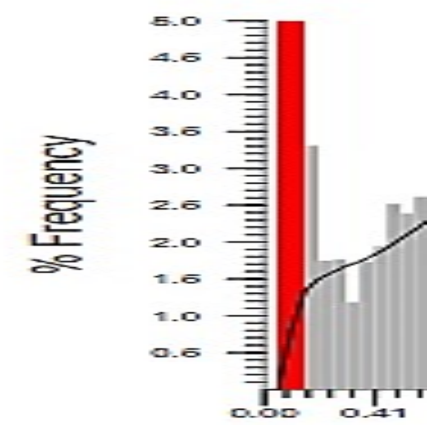
100, 500 mesh

Forward type, ΔP



Paper Sludge Characterization

Paper sludge from "D" company



Length distribution

Fiber Quality Analyzer

Lw, mm	Fines, %
0.766	30.1

Inorganic component

Total 29 elements detected by ICP-MS

Element	Ca	Al	Mg	Na	S	P	Fe	K
Amount, %	94.7	0.5	0.7	1.6	0.7	0.7	0.2	0.2

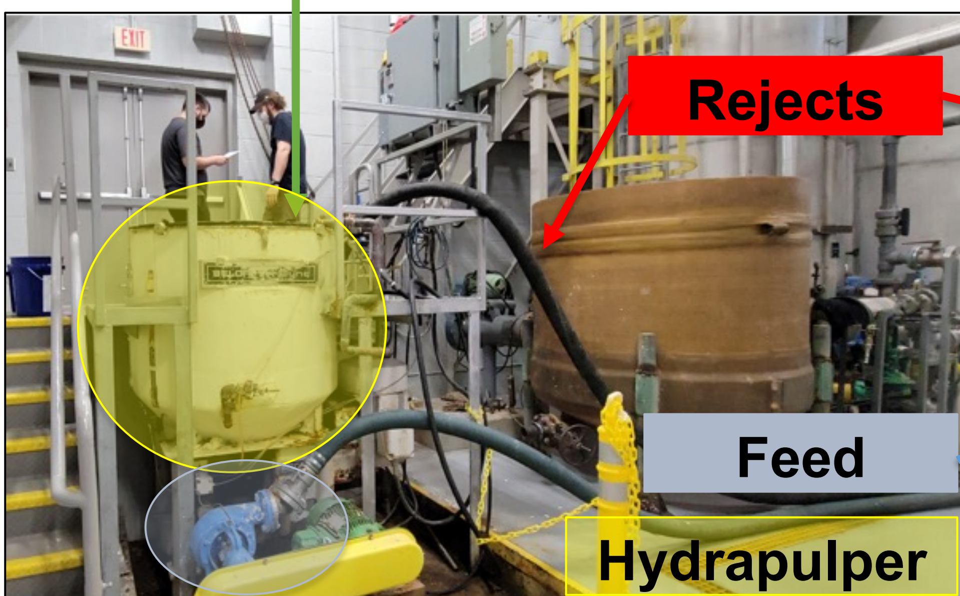
Inorganic components in paper sludge come from **(a) filler (calcium carbonate, Ca),** kaolin/clay (Si, Al)), (b) additives, (c) inks, and (d) wood itself.

Composition analysis

Substrate	Total carbohydrate, %	Glucan, %	Xylan, %	Arabinan +Mannan, %	Ash, %	Lignin, %
Sludge	42.3	30.5	8.5	3.3	43.7	3.1
De-ashed	92.6	75.8	13.2	3.4	1.5	1.5

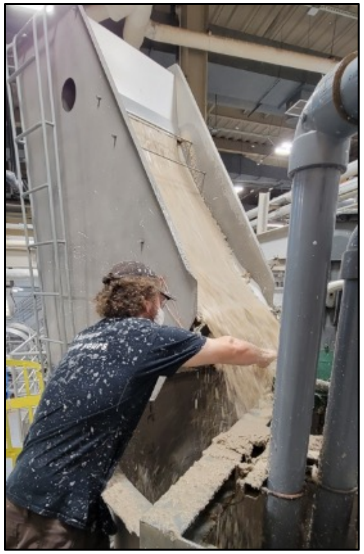
Ash Removal Scale-up

Side-hill screen with
0.5 mm mesh wire



Ash Removal Scale-up

Feed



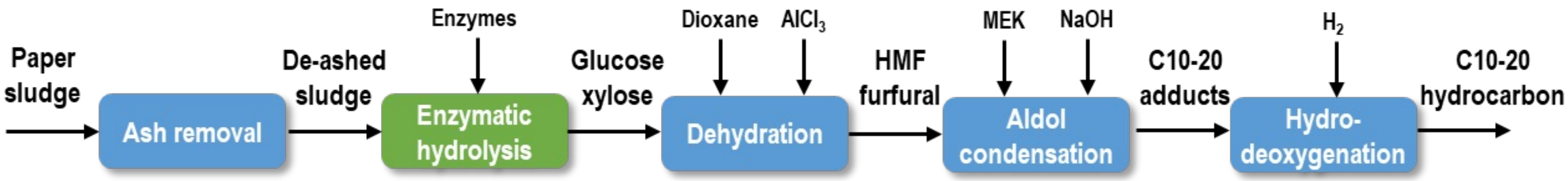
Accepts

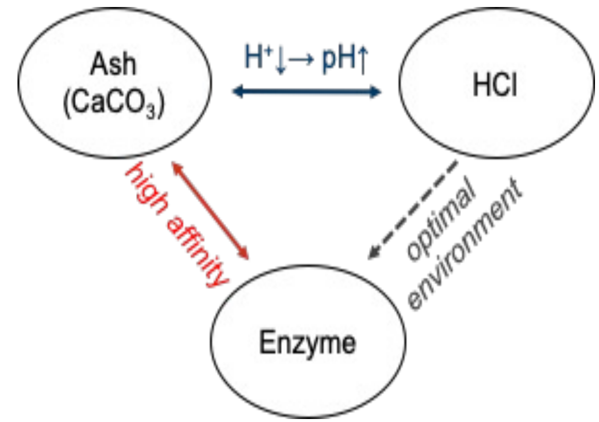
Video: Ash removal operation

Closed Rejects

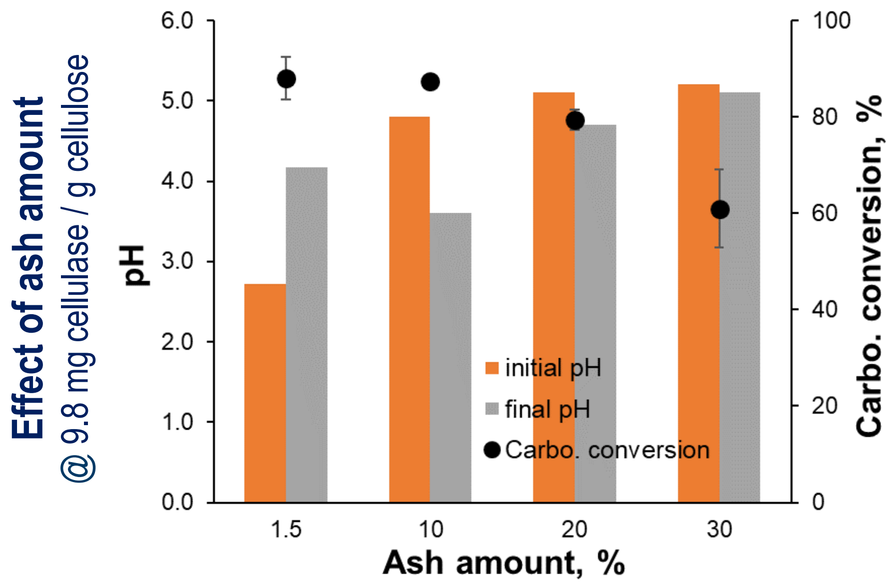
Open Rejects

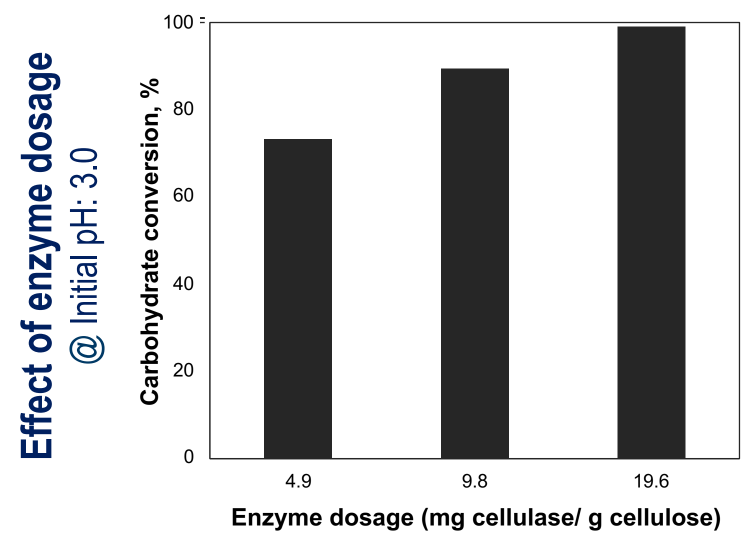
Enzymatic Hydrolysis to Sugars





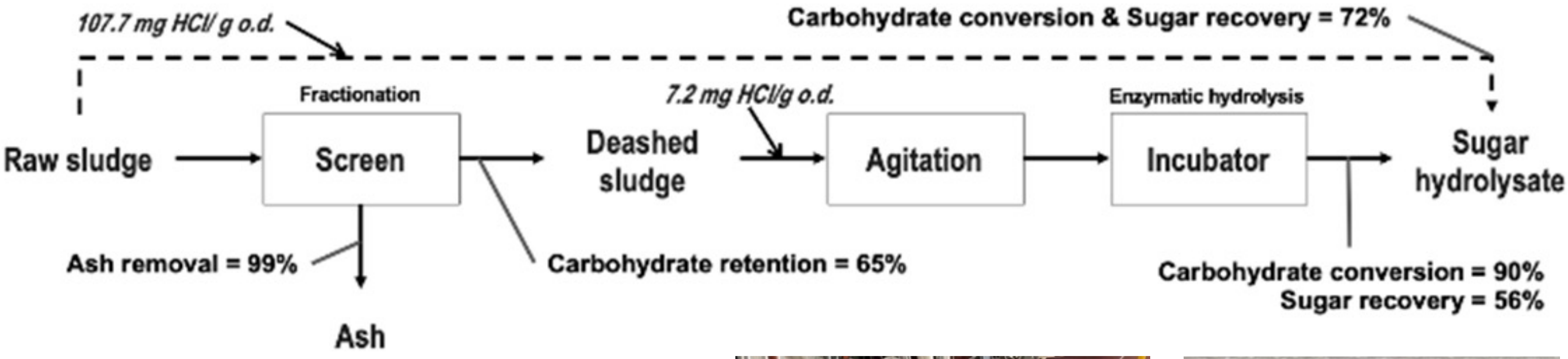
$$CaCO_3 + 2 \cdot HCl \rightarrow CaCl_2 + CO_2 + H_2O$$





Enzymatic Hydrolysis to Sugars

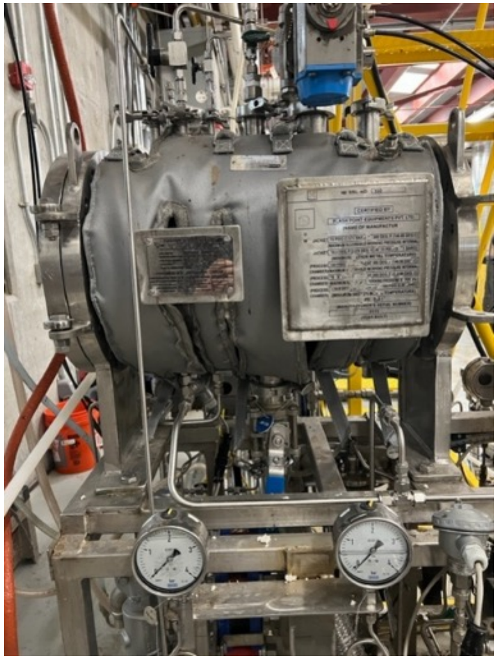
- By adapting the EH process optimized at lab-scale into pilot-scale



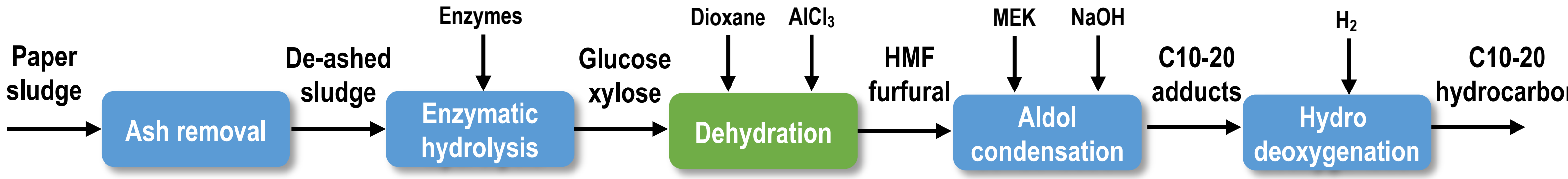
① Higher acid concentration
② High shear application prior to EH

» *To prevent the negative effect of ash on enzyme and buffer pH*

PBR 30 L Reactor

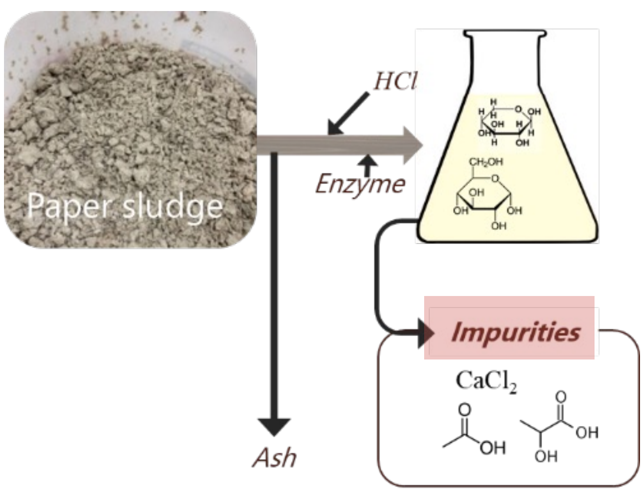


Dehydration of Sugars to Furans



Objectives:

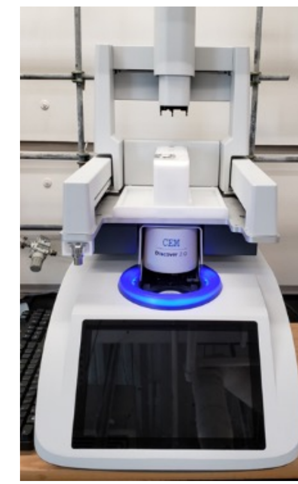
- Produce 1.25 kg of intermediate from sugars derived from paper sludge



① $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

② Organic acid detected (e.g., acetic acid & lactic acid)

- No negative effect of impurities on dehydration was observed.
- Different concentration of impurities affected the catalyst amount ($AlCl_3$).



Catalyst condition		Glucose conversion to product, %	HMF yield, %	Furfural yield, %	Levulinic acid, %	Initial pH
No	$AlCl_3$, mM					
A	10	100	76.1	89.8	1.4	3.0
B	7.5	74.9	6.3	11.6	0	4.6
	20	100	74.5	81.2	0.4	3.3

*A: Sludge 2021 (4% ash), Pulmac masterscreen, Incubator shakers, Concentrated Glucose 65.7 g/L & Xylose 11.4 g/L,

*B: Sludge 2022 (9% ash), Sidehill screen, Paddle reactor, Glucose 71.8 g/L & Xylose 17.1 g/L.

Continuous Production of Furfurals in Flow Reactor

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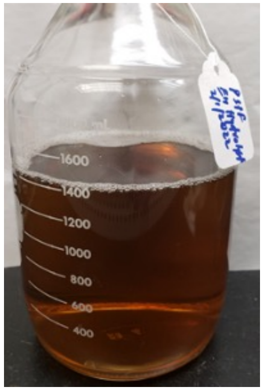
Dioxane: Water-2:1, Temperature: 190°C, Residence time: 7 min
$AlCl_3$ – 10 mM (pH – 3.0), Volume of furfurals produced – 2 L

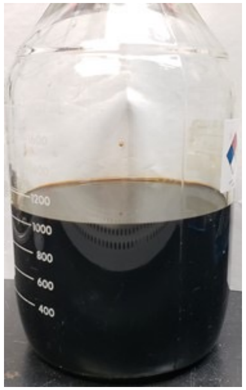
Concentration, g/L	Glucose	Xylose
Pure Sugars	85	18
PStF Hydrolysate		

Yield, %	HMF	Furfural	Combined
Pure Sugars	67	85	70
PStF Hydrolysate			

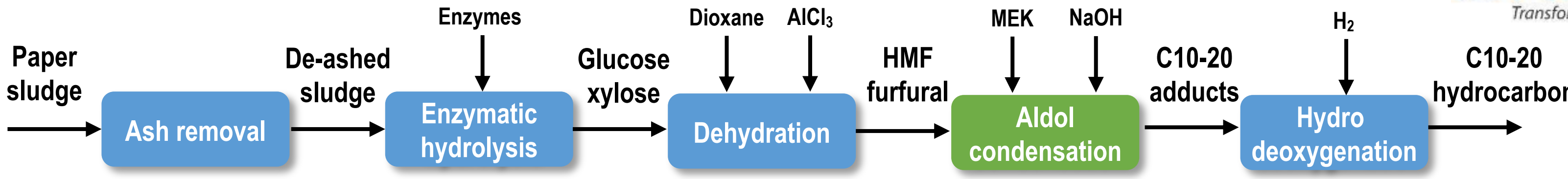


PStF Hydrolysate

Furfurals Solution

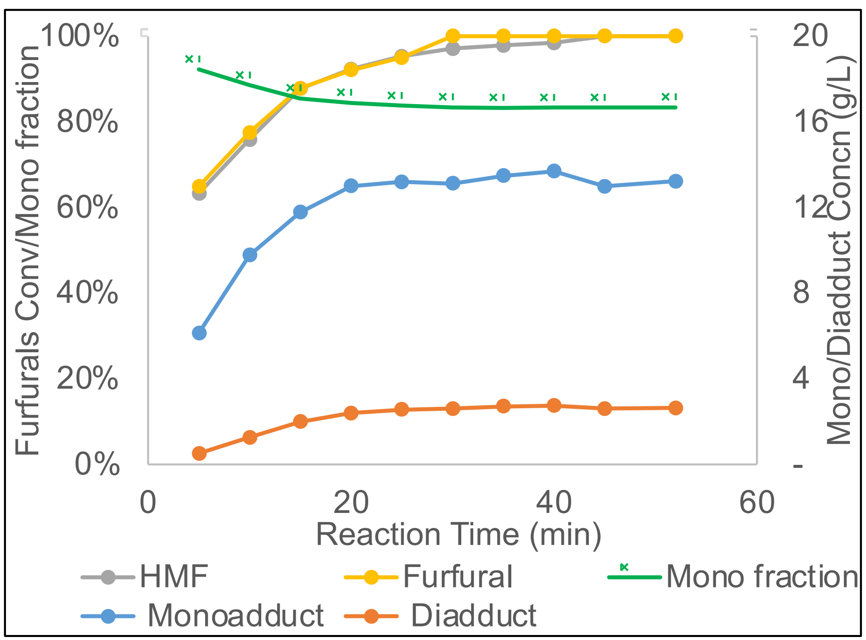


Scaled-up Aldol Condensation to Monoadduct



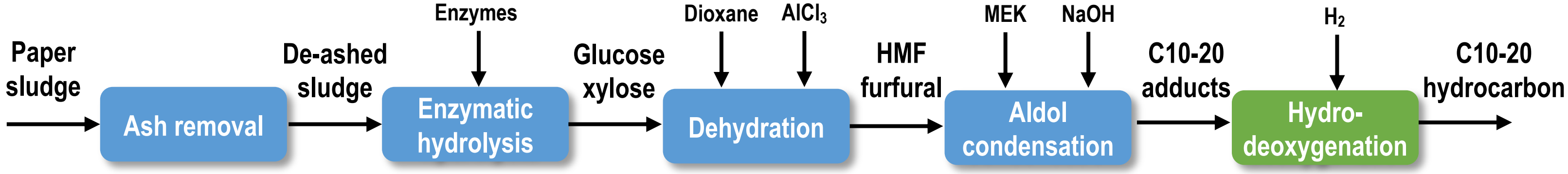
Objectives:

- Change in BETO priorities favoring Sustainable Aviation Fuel over diesel changed our strategy for the aldol condensation to produce more monoadduct than diaddduct
- Produce sufficient aldol condensate for production of 50 mL HC in jet fuel range

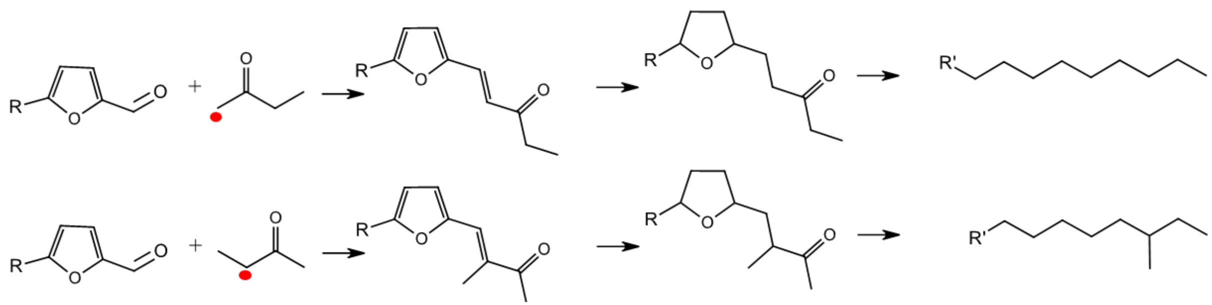


- MEK increased Furfurals:MEK mole ratio 0.49:1
- Scaled-up to 2 L reactions, 80 °C, 50 min,
- 100% HMF/Furfural conversions achieved
- Average isolated adduct yield 73% ± 4%

Hydro-deoxygenation: SAF Production



- Mostly hydrocarbons are C10 from HMF adduct with MEK
- GCMS and NMR indicate that the product contains virtually no oxygenates
- 61% of the product is in the jet fuel boiling range and 67% in the diesel fuel boiling range. Overall more than 75% could be blended into jet or diesel fuel



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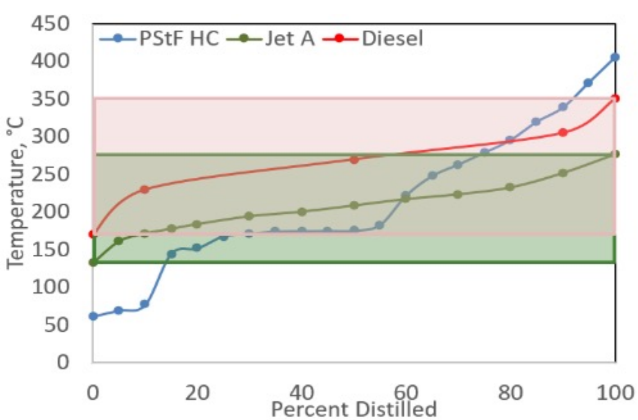
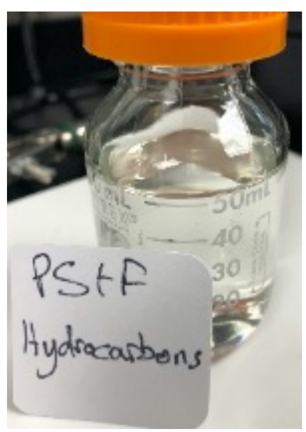




	Our Fuel	JP-5	Jet A
Oxygen content (wt%)	0.059	negligible	negligible
Cloud point (°C)	-48.1	-51	-47
Flash Point (min)	-	60	38
HHV (MJ/kg)	46.7	43	43
Density at 15°C (g/cm³)	0.792	0.81	0.82
Energy density (MJ/L)	37.0	35	35

Techno-Economic Analysis

Objectives:

- Develop a process in Aspen Plus with a detailed mass and energy balance on all unit operations
- Conduct an economic analysis in DCFROR to predict net levelized cost of disposal (nLCOD) and minimum fuel selling prices (MFSP)
- Perform a sensitivity analysis to guide experimental parameters
- TEA goal: 25% reduction in the nLCOD resulting from the technology

1. Data collection for key parameters from the literature
- Unit operation parameters
- Capital cost
- Operating cost

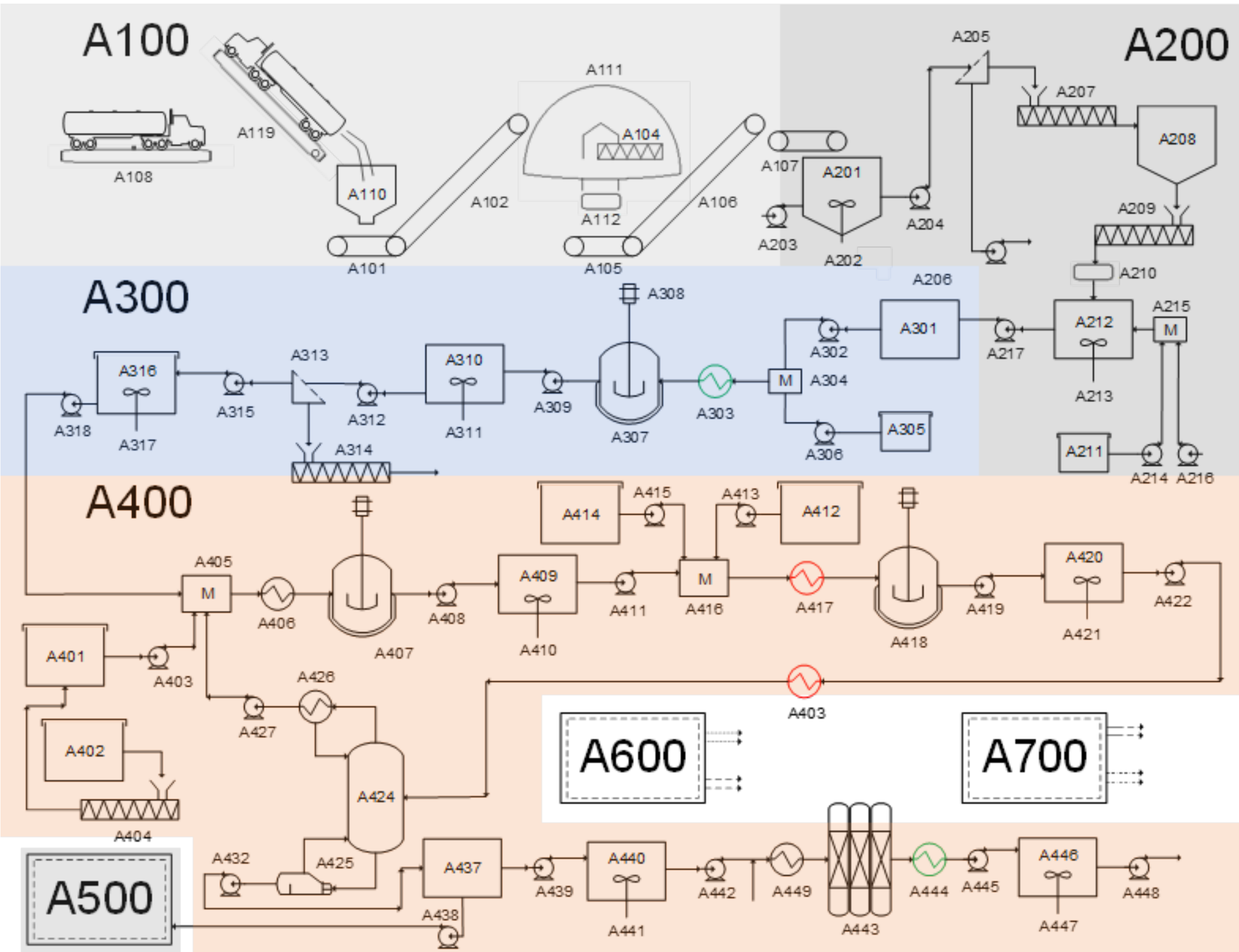
2. Experimental results from the project
- Ash removal, EH
- Dehydration, Condensation
- Others

3. Simulation model of biomass conversion
- ASPEN Plus
- Energy and mass balance

4. TEA model
- DCFROR analysis
- Paper sludge nLCOD
- Hydrocarbon MFSP

5. Sensitivity analysis and case study
- Identify ~30 key parameters
- What-if case study

Mass and Energy Balance



A100 – Feedstock & Handling

Paper Sludge	750 dry tonne/day

A200 – Pretreatment

Carbohydrates Ret.	68.7% ± 1.8
Ash Removal	99.0% ± 0.0

A300 – Enzymatic Hydrolysis

Hydrolysis Temp	50°C
Glucose Conv.	97.5% ± 1.8

A400 – Catalytic Upgrading

1,4-Dioxane : Water	2 : 1 (v/v)
Dioxane/Water Az.	88°C & 81%Diox.

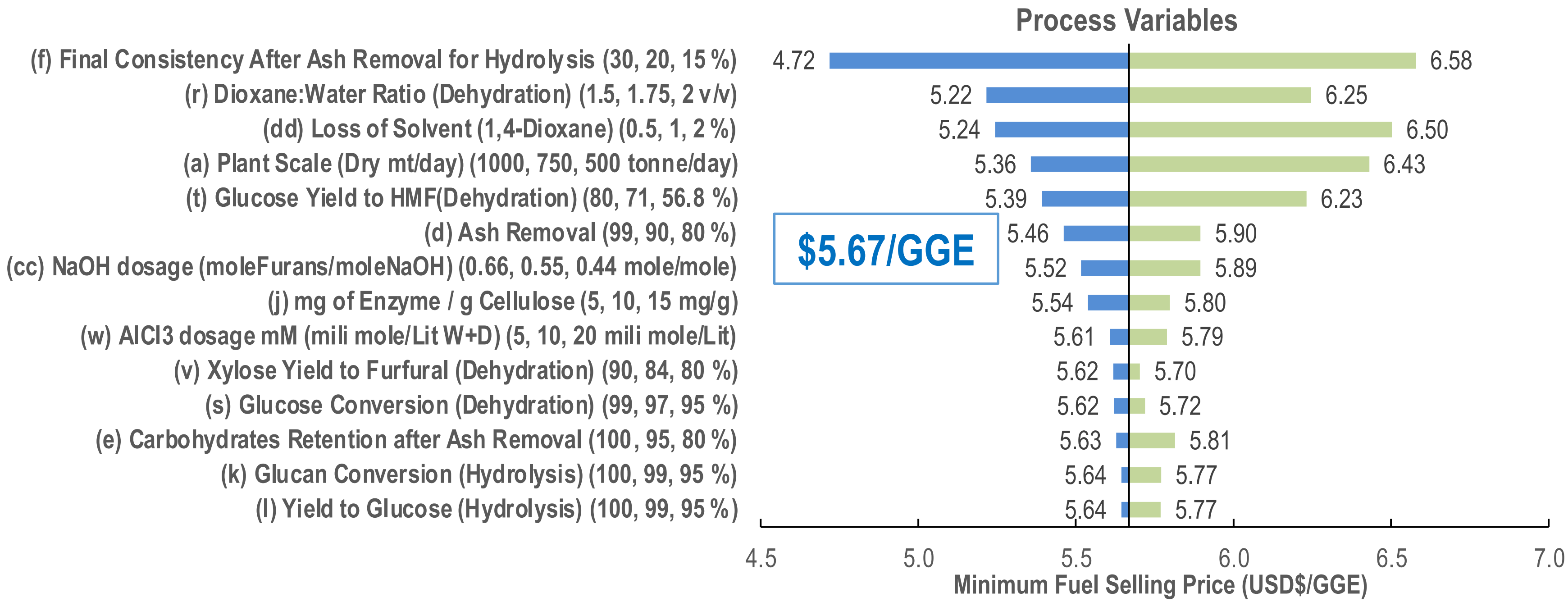
A500 – Waste Water Treatment

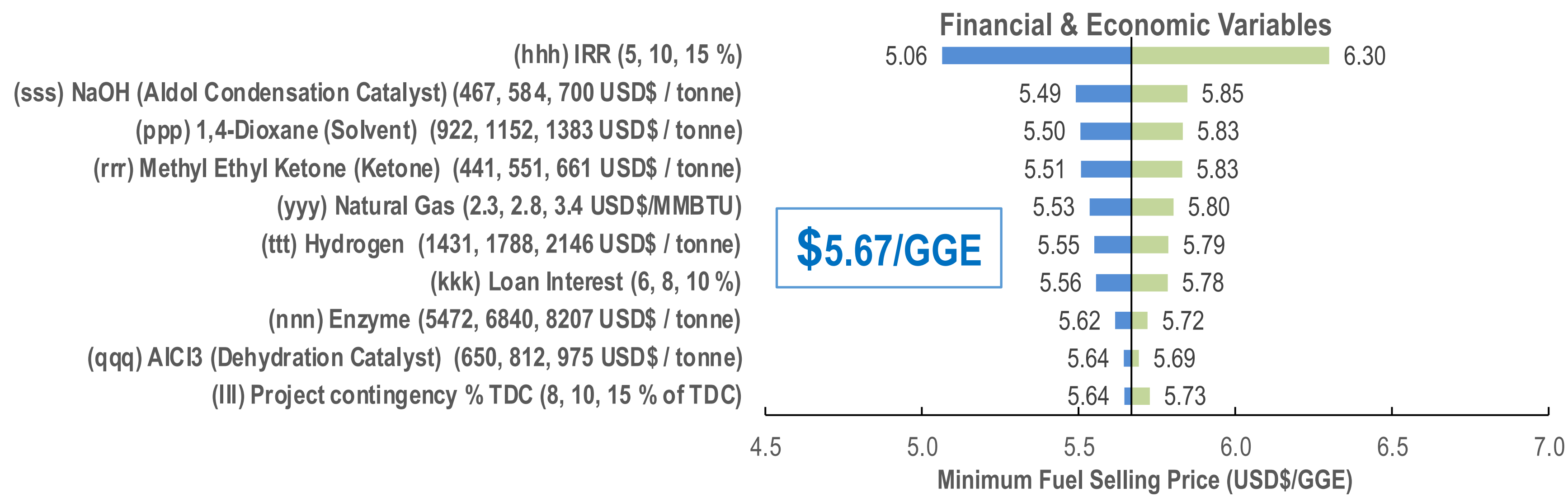
A600 – Heat & Power

A700 – Utilities

aspentech

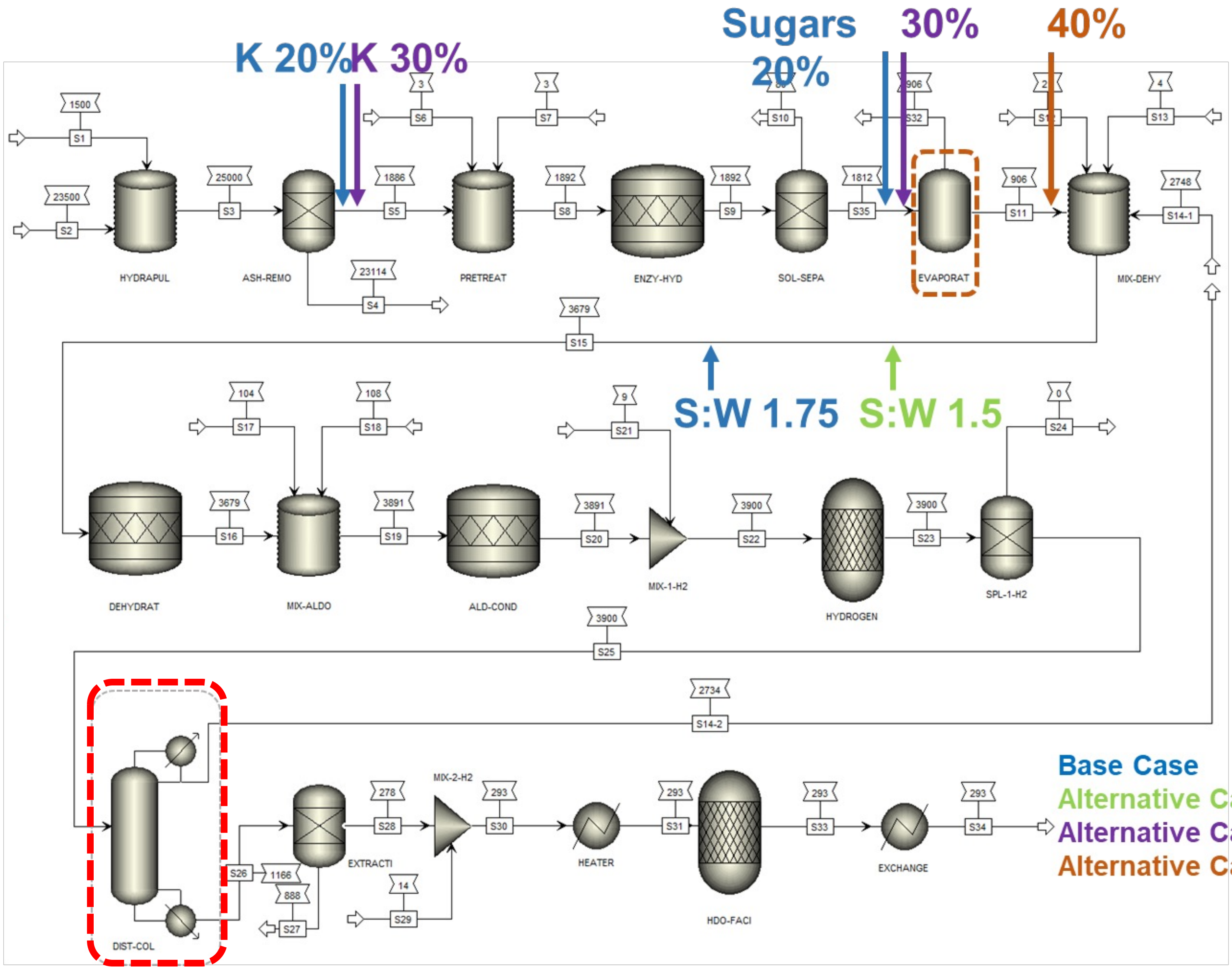
Techno-Economic Analysis: Base Case





Process Improvement I

1,4-Dioxane



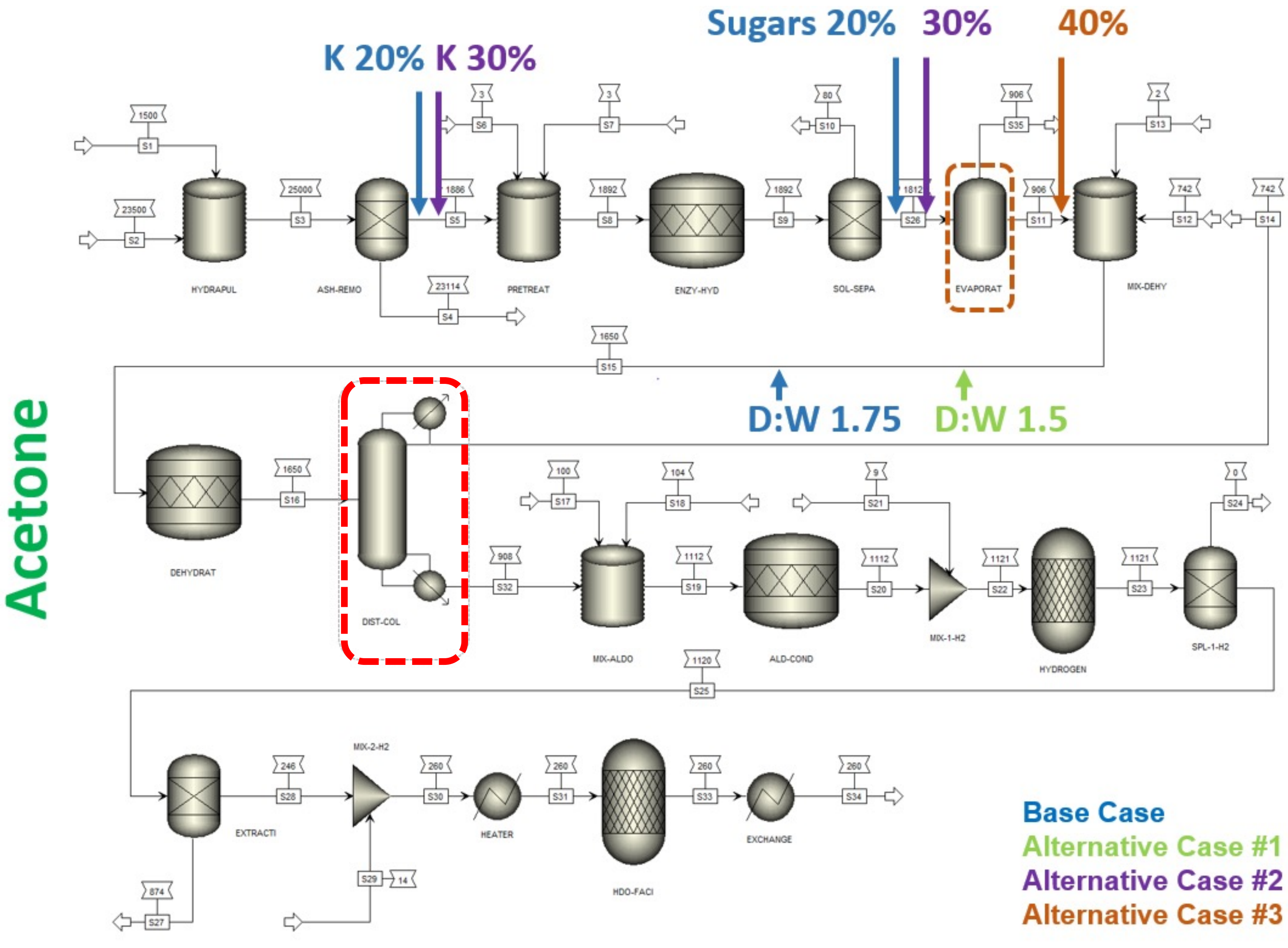
Base Case

Alternative Case #1

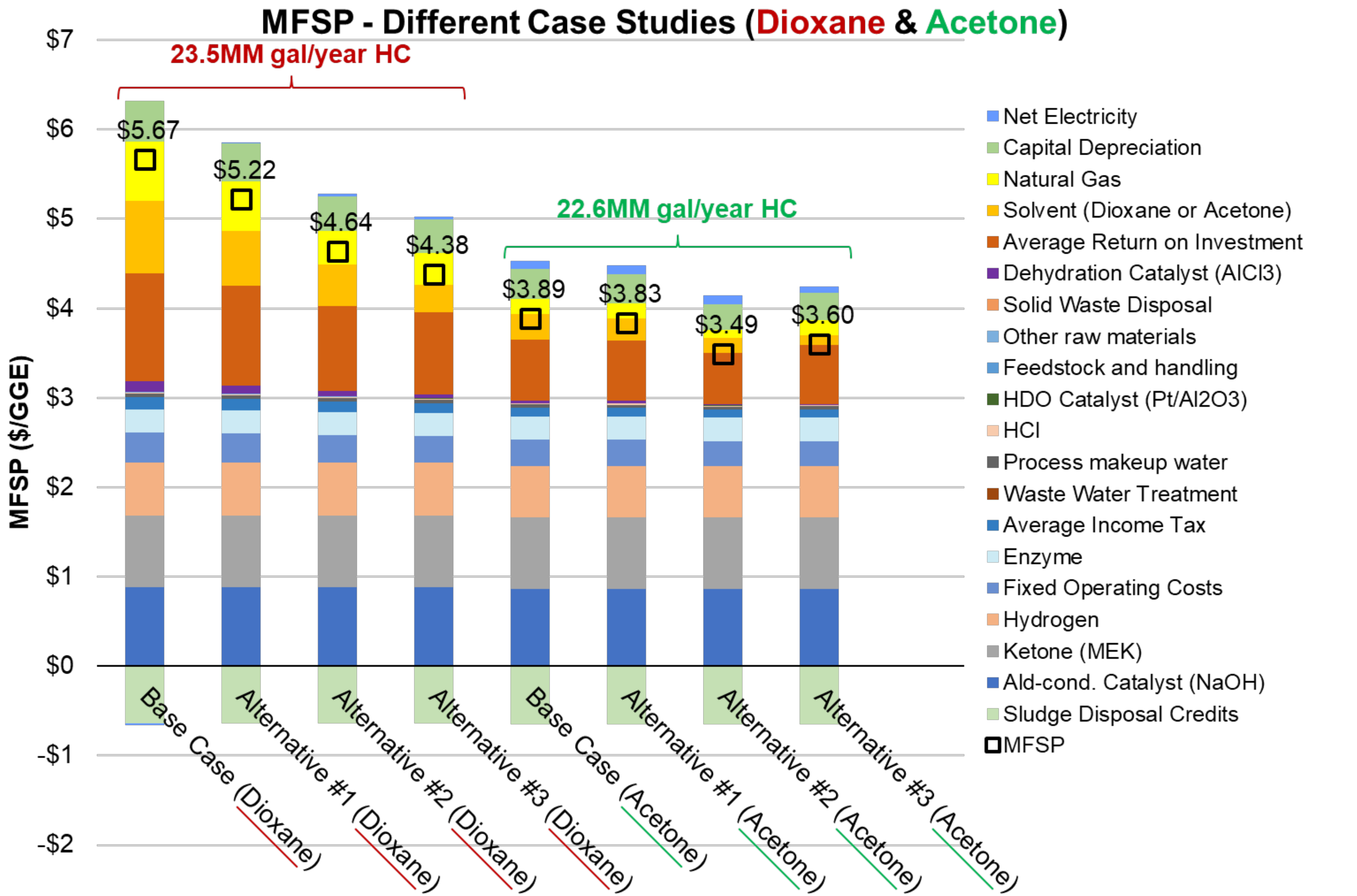
Alternative Case #2

Alternative Case #3

Process Improvement II



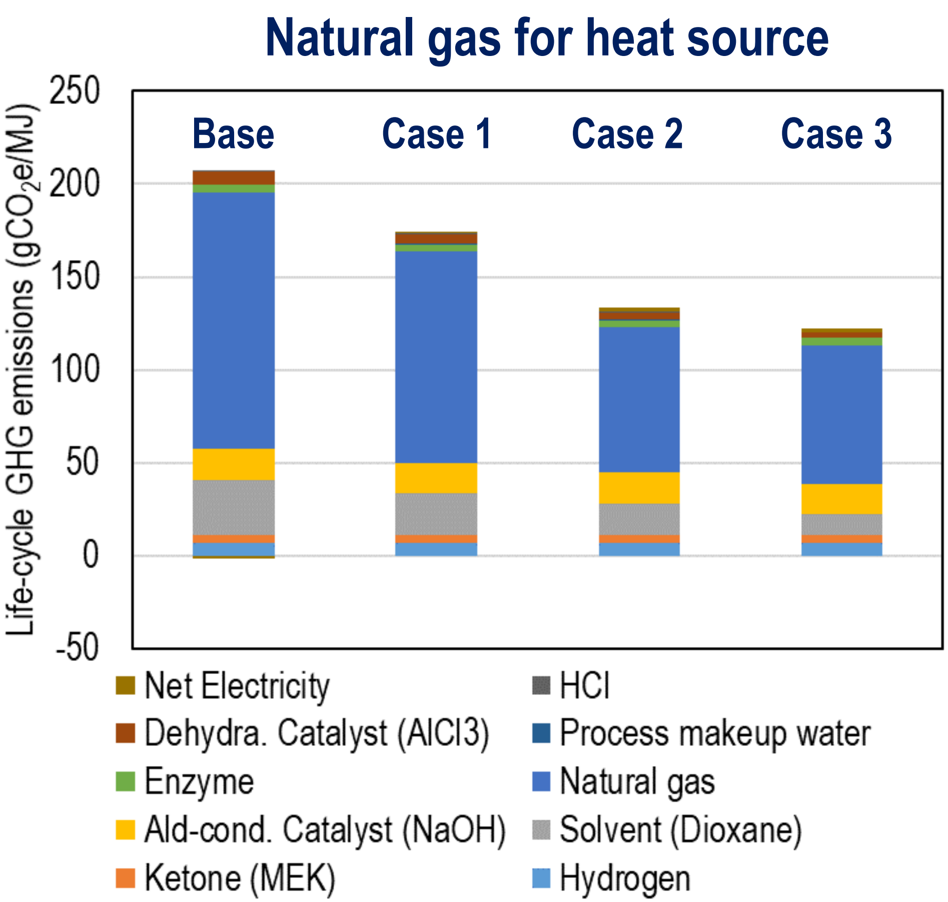
Minimum Fuel Selling Price

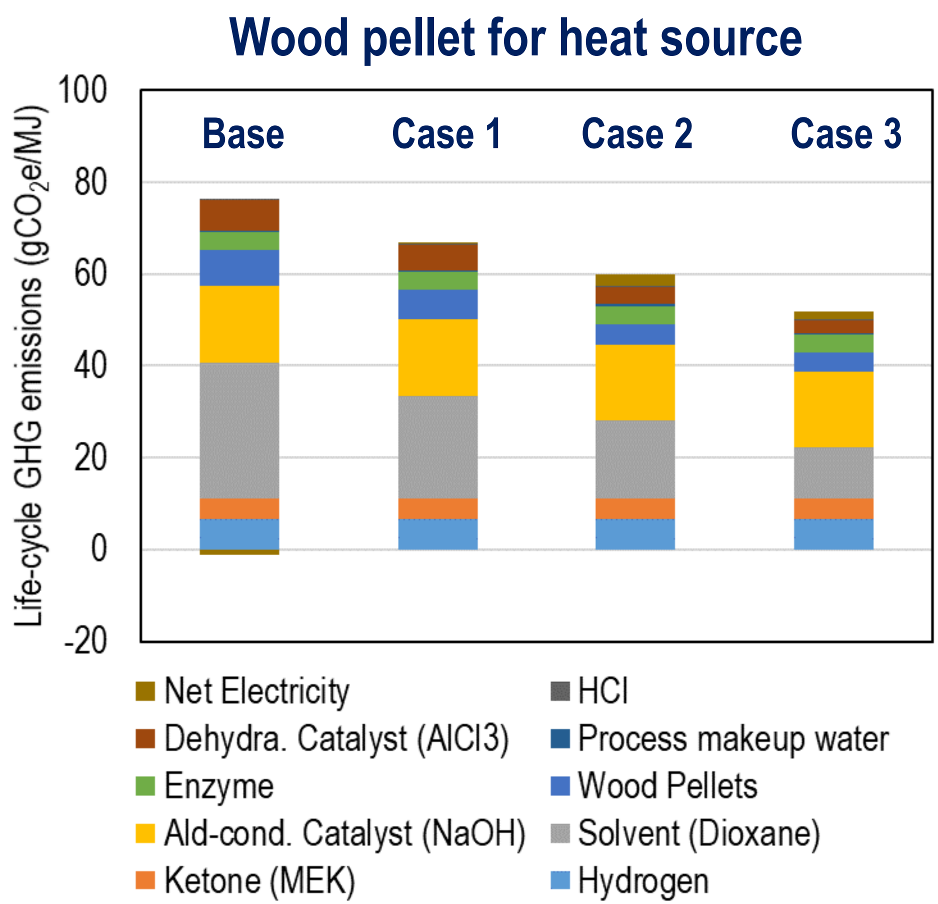


Yale

Preliminary Life Cycle Assessment

openLCA

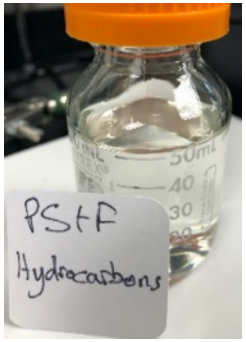




Avoided emissions from landfilling is not included in this analysis, which is expected to be -36.7 gCO_2e/MJ

Summary and Next Steps

- Accomplishments
  - Met the target for ash removal (>93%), carbohydrate retention (>65%), and enzymatic hydrolysis (>85%)
  - Met the target for dehydration (>69%) and aldol condensation (>85%)
  - Go/No-go intermediate verification
    - 50 mL hydrocarbon production from paper sludge
    - Low oxygen content, low cloud point, high energy density



- Project future work
  - Relevant scale demonstration to produce 1L product for fuel testing

- Considerations to further enhance process economics (MFSP)
  - Less water in dehydration (e.g. high solid EH, water evaporation after EH)
  - Increase conversion yield (e.g. dehydration, aldol condensation)
  - Process ash utilization (e.g. cement)
  - Calcium salt recovery (e.g. deicing agent)

Project Impact

- In the US, overall paper production is growing with the demand in packaging and tissue/towel. During these operation, more than 8 million wet tons of paper sludge (50% moisture) are generated annually.
- Most of them are landfilled at an approximate cost of ~$240 million per year, including trucking and landfilling costs.
- There are approximately 40 locations, where more than 200 TDP of paper sludge is produced. There is a potential to utilize paper sludge from multiple mills, as many mills are located a close distance from each other.
- Carbohydrate in the sludge could be converted to 150 million gallons of diesel fuel, showing that this project is aligned with DOE's strategy for production of high performance biofuels from waste feedstocks.
- DOE-BETO and other government agencies are interested in working with cost-advantaged feedstock and lessening the disposal cost burdens.

Quad Chart Overview

Timeline
- Project start date: 10/1/2019
- Project end date: 9/30/2023

	Expenditure (Start – 12/31/2022)	Total Award
DOE Funding	$1,826,676	$2,475,807
Project Cost Share	$619,597 (CS 25.3%)	$623,004 (CS 20.1%)

Project Partners
- DOE National Renewable Energy Laboratory
- Yale University

Project Goal
The project goal is to develop a technology for converting the carbohydrates in paper sludge, a wet organic industrial-waste stream, into a hydrocarbon (HC) biofuel, both economically and sustainably.

End of Project Milestone
- Produce 1.0 L HC for fuel property testing
- Determine if 75% (GGE basis) of HC could be blended into jet or diesel fuel
- Demonstrate a minimum 25% reduction in the nLCOD.

Funding Mechanism
DE-FOA-0001916 BioEnergy Engineering for Products Synthesis (BEEPS), Topic Area 4 2018

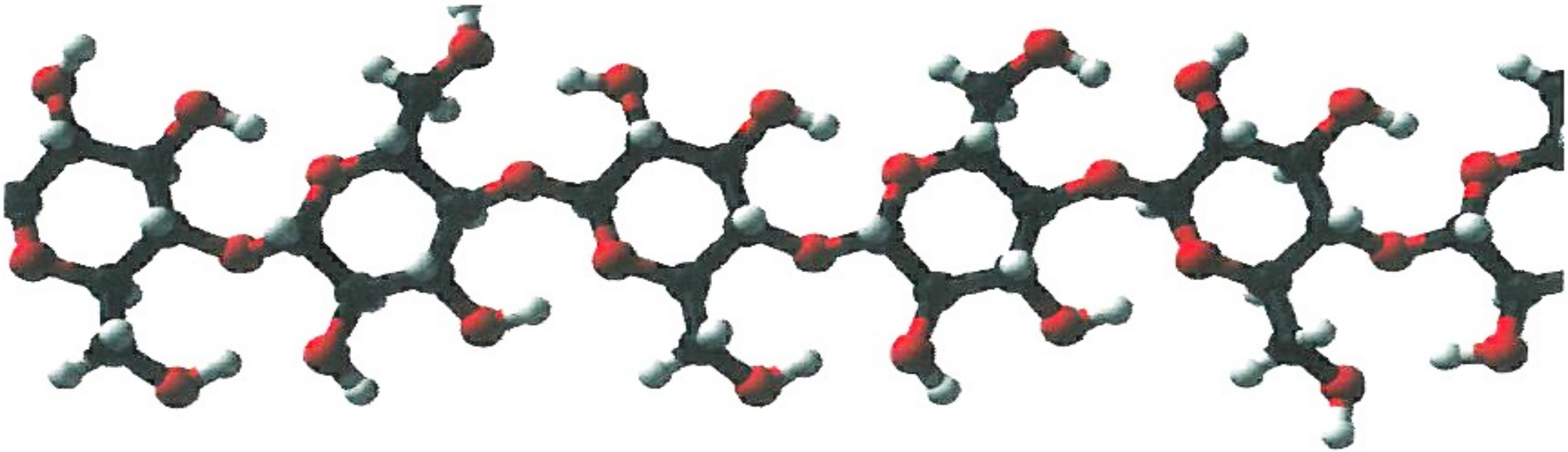
Acknowledgements

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
BIOENERGY TECHNOLOGIES OFFICE

The work is supported by the BioEnergy Technologies Office (BETO), US Department of Energy (DOE) (Award number: DE-EE0008498).

BETO Technology Manager: Beau Hoffman

Additional Slides



Publications and Presentations

- **Publications**
  - H, Park, D, Cruz, P, Tiller, D,K. Johnson, A, Mittal, H, Jameel, R, Venditti, S, Park, Effect of ash in paper sludge on enzymatic hydrolysis, *Biomass and Bioenergy* 165 (2022) 106567
  - H. Park, et al., Valorization of sludge-derived hydrolysate into furan chemicals, In preparation
  - D. Cruz, et al., Dehydration of glucose to 5-Hydroxymethylfurfural: techno-economic evaluation of solvent systems beyond reaction yield, In preparation
  - D. Cruz, et al., From landfills to power aircraft engines: techno-economic analysis of the catalytic transformation of paper sludge into jet fuel, In preparation
  - P. Tiller, et al, Fractionation of cellulose from paper sludge via pilot-scale sidehill screen operations, In preparation
- **Oral Presentations**
  - H. Park, D. Cruz, P. Tiller, D.K. Johnson, A. Mittal, R. Venditti, H. Jameel, S. Park, Effect of impurities on the valorization of paper sludge to furan chemicals, ACS Fall, August 2022, Chicago, IL.
  - D. Cruz, H. Park, P. Tiller, R. Gonzalez, A. Mittal, D. Johnson, S. Park, Techno-economic analysis for the production of bio-based jet fuel via enzymatic hydrolysis and catalytic upgrading of carbohydrates in paper sludge, ACS Fall, August 2022, Chicago, IL.
  - H. Park, D. Cruz, D.K. Johnson, A. Mittal, …, and S. Park, Valorization of paper sludge to furan chemicals, 2020 AIChE annual meeting, Nov. 16-20, Virtual.
  - D. Cruz, H. Park, R. Gonzalez, D. Johnson, S. Park, Techno-economic analysis of biofuel production via catalytic upgrading of carbohydrates in paper sludge, 2020 AIChE annual meeting, Nov. 16-20, Virtual.
  - H. Park, D. Cruz, D.K. Johnson, A. Mittal, …, and S. Park, Effect of ash on enzymatic hydrolysis of paper sludge to produce sugars, 2020 ACS fall, 2020, Aug. 17 – 20, Virtual.
- **Poster Presentations** (provided upon request)

Paper Sludge Handling Process