DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

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

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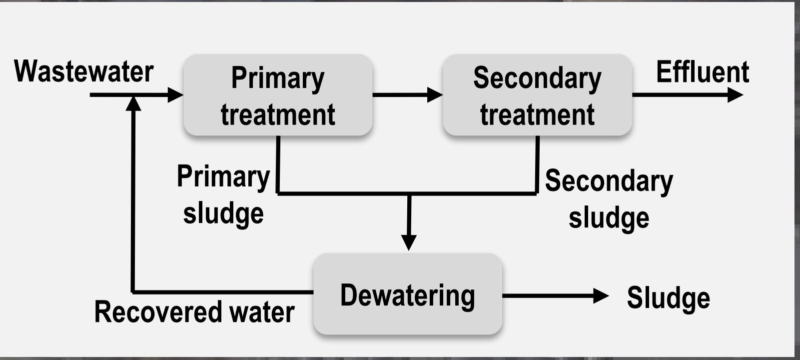
NREL Transforming ENERGY   NC STATE UNIVERSITY

Solid Wastes in Pulp and Paper Industry

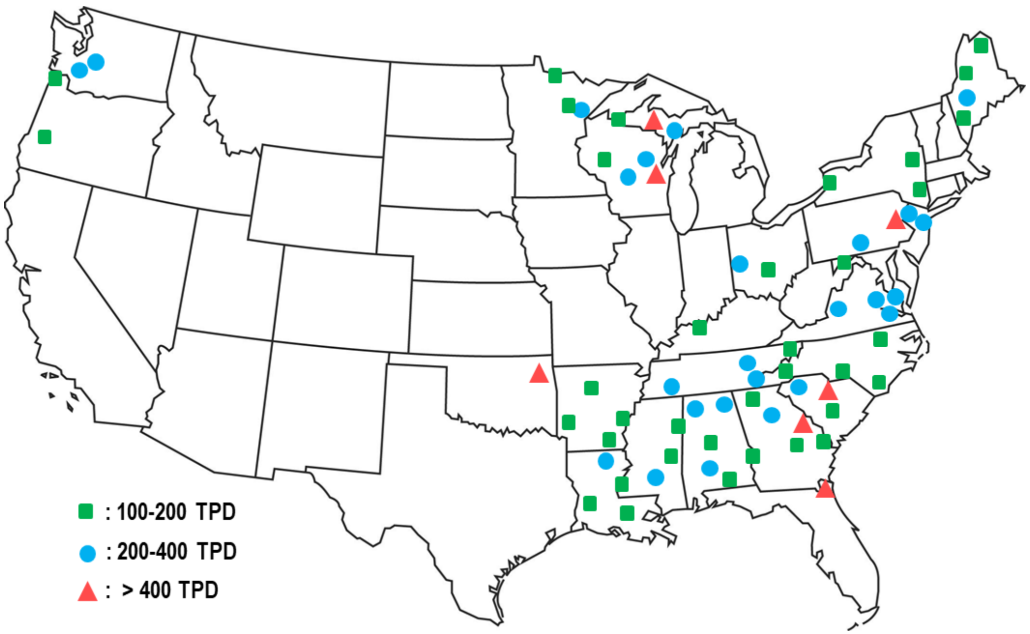
Solid wastes in pulp and paper industry

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

Paper sludge



Sludge Utilization



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)

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

~8MM wet tonne/year (50% MC)
Trucking & landfilling ~ $60/dry tonne
Cost ~ $240MM/year

Project Overview

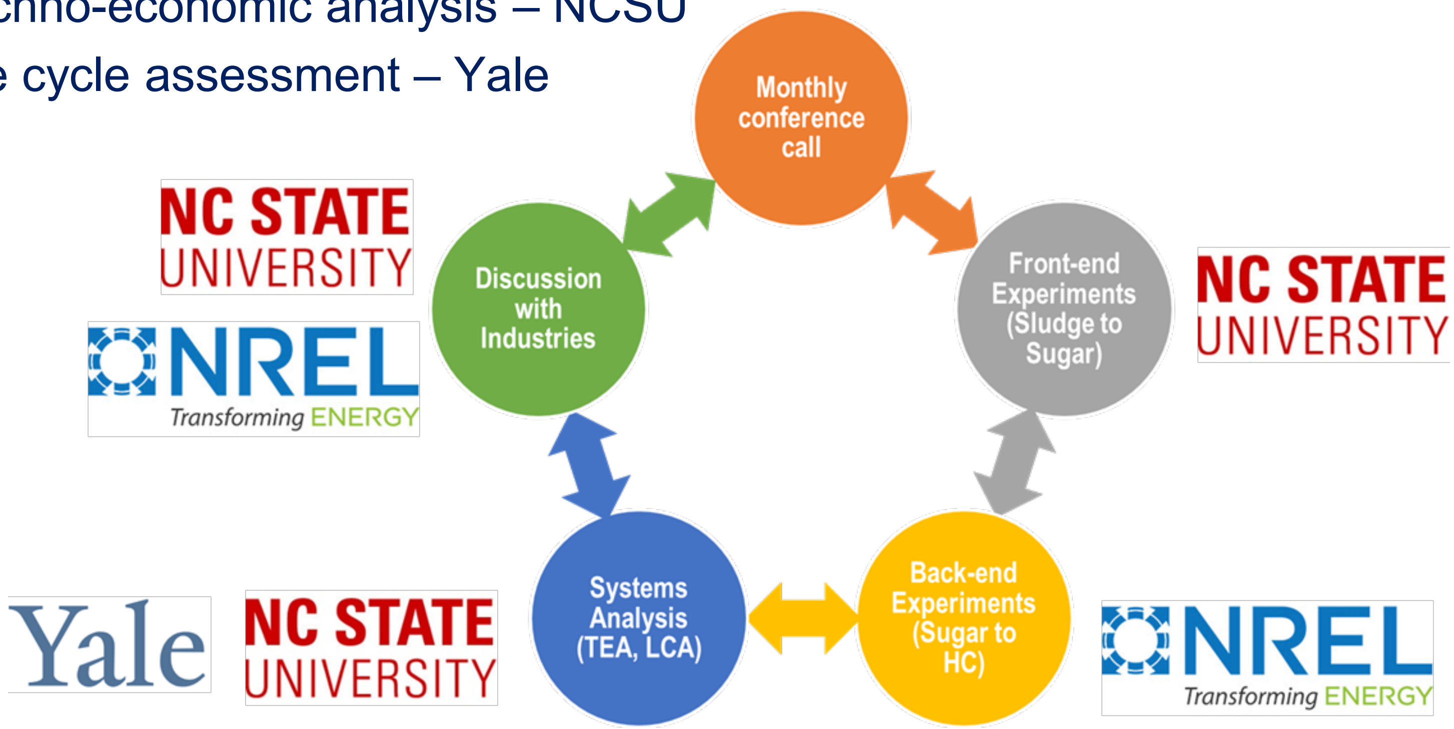
- This project will develop a technology for converting the carbohydrates in paper sludge into a hydrocarbon (HC) biofuel, both economically and sustainably.

	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 jet or diesel fuel Demonstrate a minimum 25% reduction in nLCOD.

NREL Transforming ENERGY NC STATE UNIVERSITY Yale

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
  - 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), intermediate (June 2021), final (Sept., 2022)

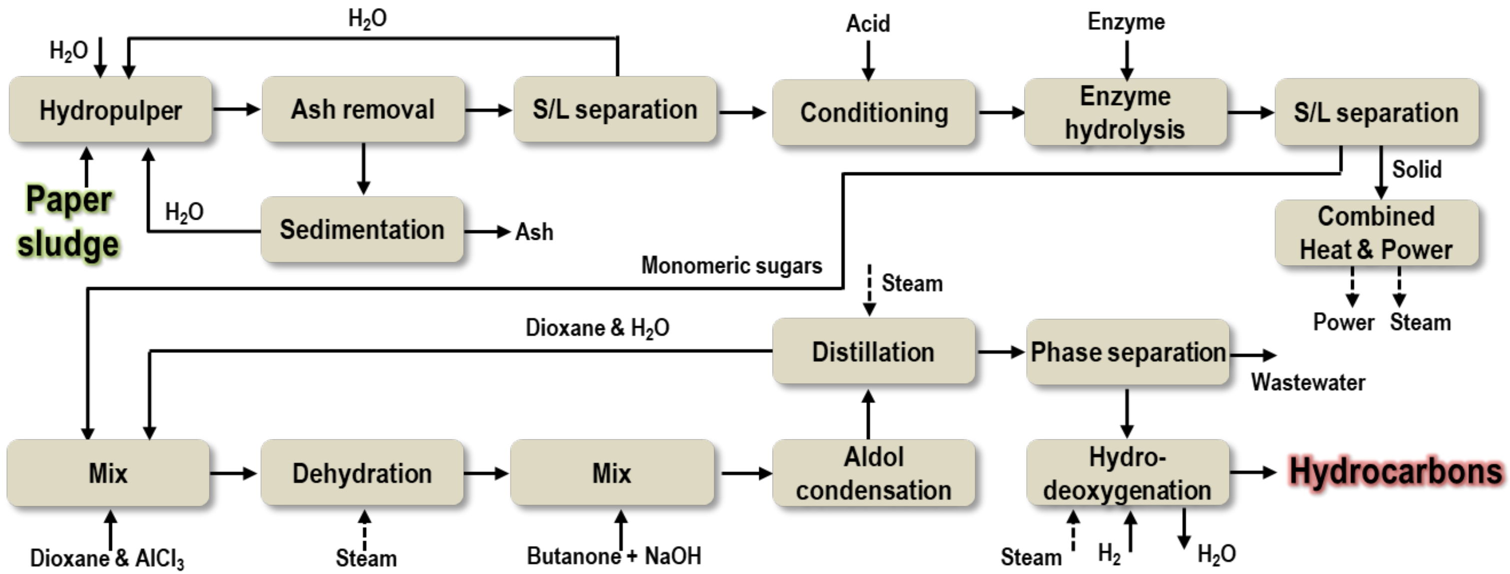
- Risks and mitigation plan

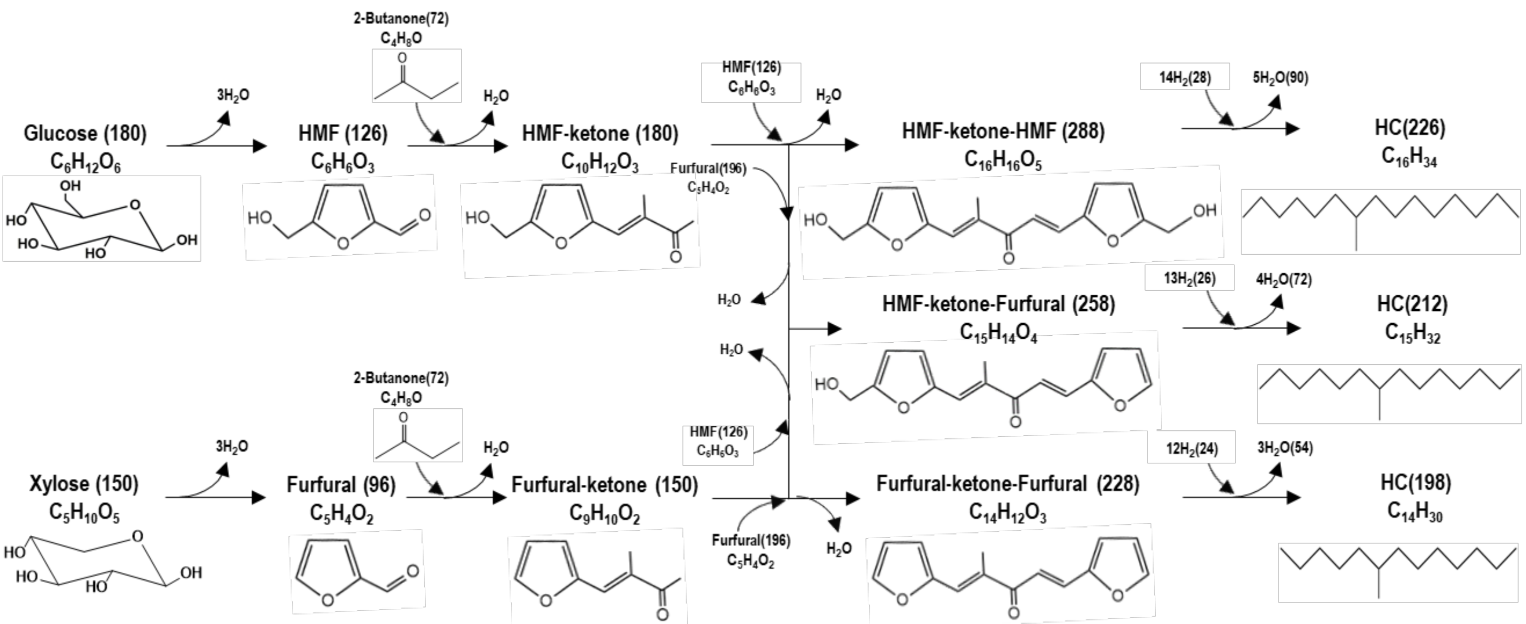
Risk/Barrier	Mitigation plan
High amount of ash in paper sludge	If a single unit (e.g. screening) is not sufficient, multistage unit operation will be developed for ash removal.
Catalyst deactivation due to ash in paper sludge	Characterize used catalysts to identify cause of deactivation and either remove 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.

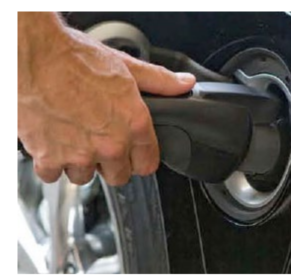
Milestones and Go/No-go

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	3/31/21	Solvent recycle strategies by analyzing distillate and still bottoms	In progress
GN 8.1	Go/No-go: Intermediate verification	06/30/21	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	-
ML6.1	Hydro-deoxygenation	09/30/21	Flow reactor with time on stream >50 h Hydro-deoxygenation >80% yield	-
ML9.1	Enzymatic hydrolysis	12/30/21	Relevant scale enzymatic hydrolysis >2.5 kg sugar production, >64.8% conversion	-
ML9.2	Dehydration and condensation	06/30/22	Dehydration and condensation >1.25 kg intermediate Overall yield >66.3%	-
ML9.3	Hydrocarbon production	09/30/22	Hydro-deoxygenation >85% yield Produce 1.0 L of hydrocarbon product	-
ML10.1	Final verification	09/30/22	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	-

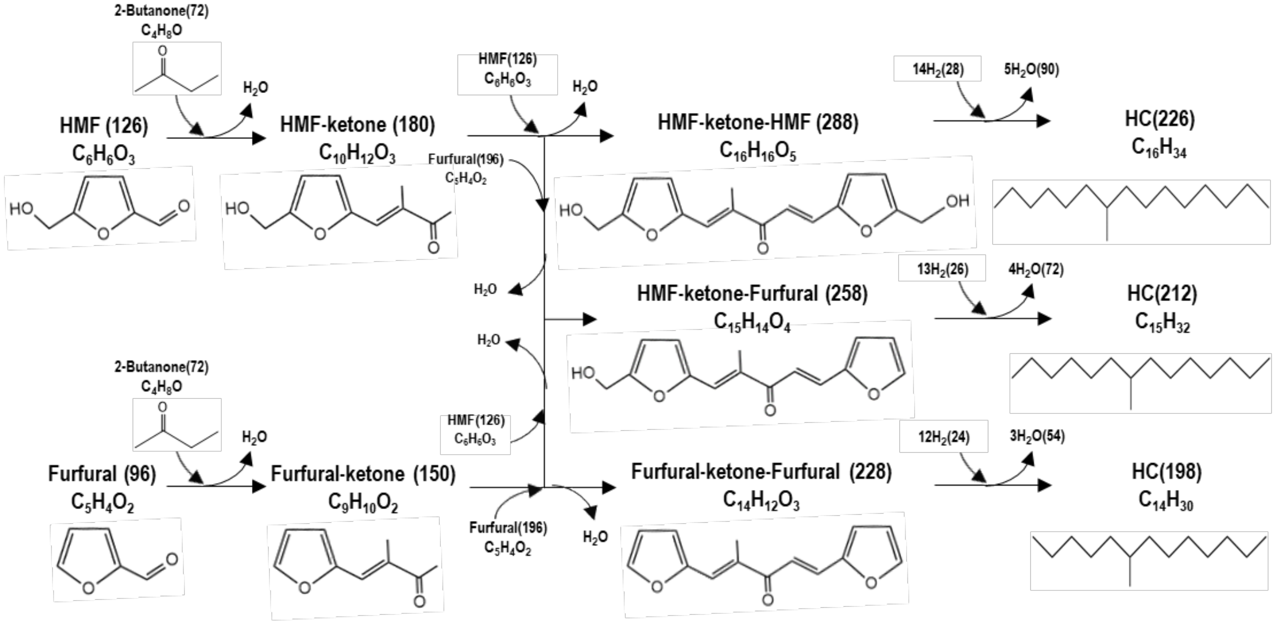
Process Overview

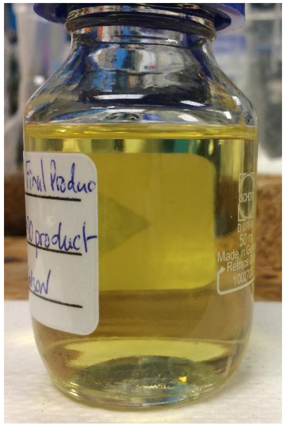




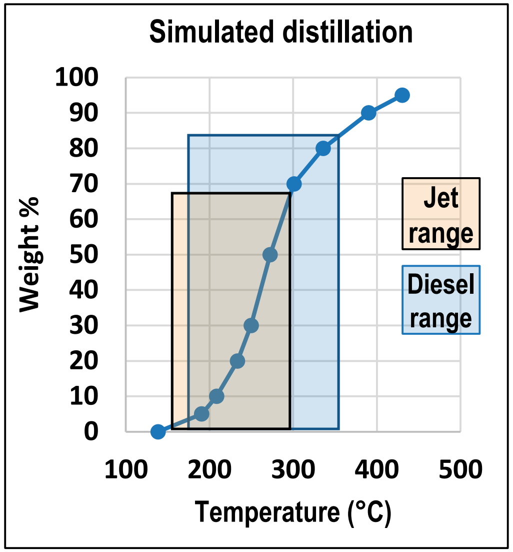


Previous Work: Hydrocarbons from Pure Chemicals





Property	HC Product from HMF/Furfural	Typical US Diesel
Cloud Point (°C)	-64	-40
Density (g/cm^3)	0.828	0.83-0.86
Higher Heating Value (MJ/kg)	43.6	45.6
Energy Density (MJ/L)	36.1	38.5
Cetane Number (AFIDA)	61.5	Minimum 40 Typical 42-45



Project Impact

- In the US, 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.

Process to Produce Paper Sludge

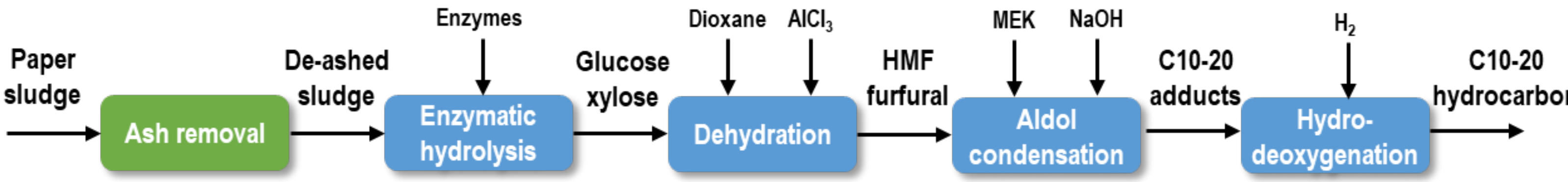
Waste stream from Paper machine
↓
Clarifier
↓
Sludge tank
↓
Press
↓
Storage
↓
Disposal

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
Tissue/ towel	"C" company	43.2	0.861	29.7
	--	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

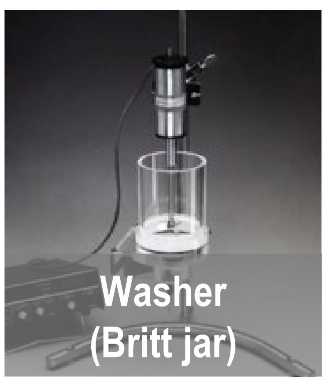
- 17 companies were contacted
- 11 paper sludges have been received
- Most of work in the project uses the sludge from the "D" company.

Ash Removal from Paper Sludge



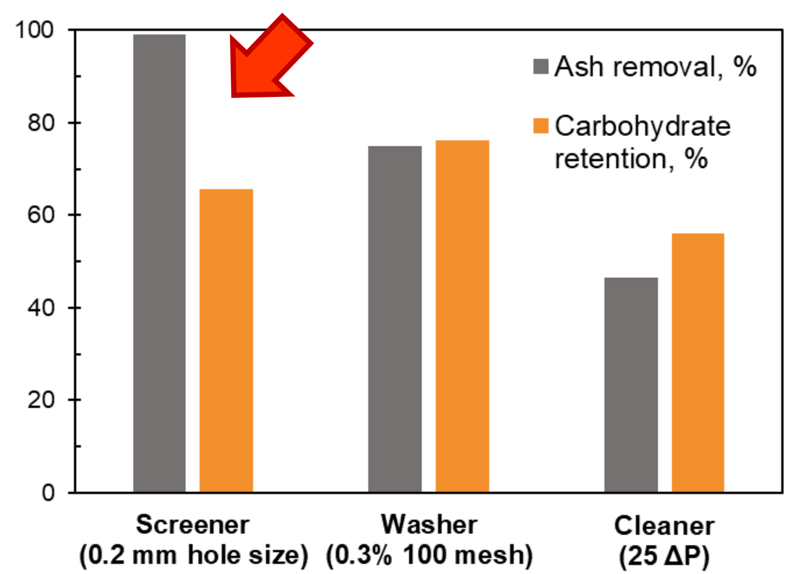
Objectives:
- Remove ash in paper sludge for monomeric sugar production
- Ash removal >93%, Carbohydrate retention >65%
- Characterization of ash remaining in paper sludge

Hole, Slit



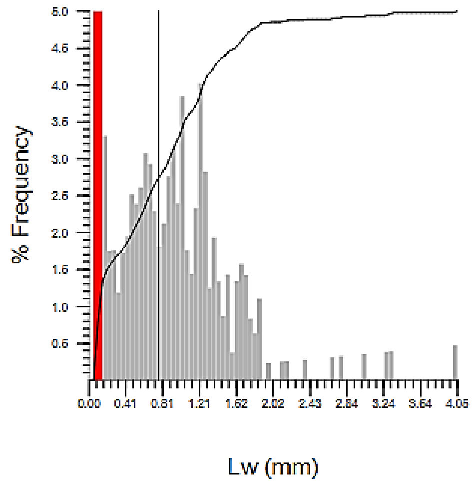
100, 500 mesh

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

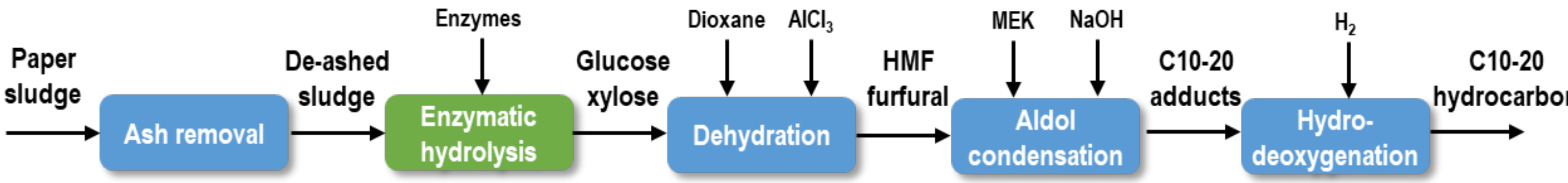
Component	Ca	Al	Mg	Na	S	P	Fe	K
Amount, %	94.7	0.5	0.7	1.6	0.7	0.7	0.2	0.2

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

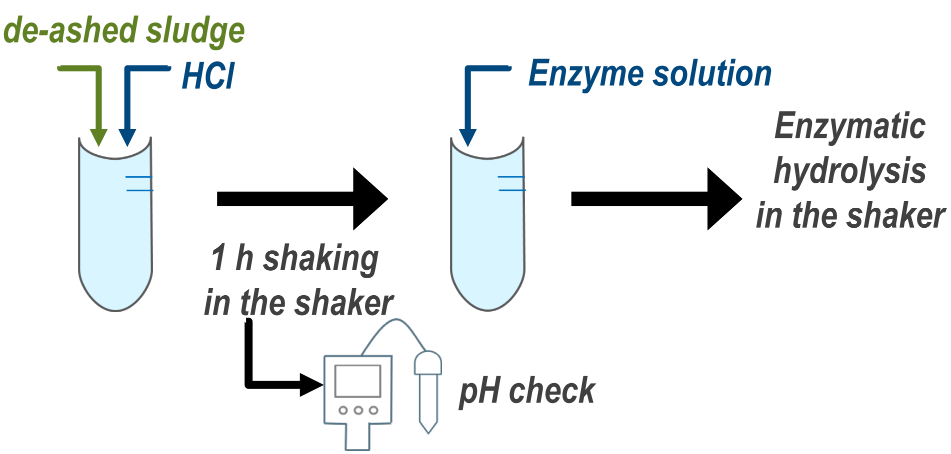
Substrate	Total carbohydrate, %	Glucan, %	Xylan, %	Arabinan +Mannan, %	Ash, %	Lignin, %
Sludge	42.3	30.5	8.5	3.3	43.7	3.1
De-ashed	92.6	75.8	13.2	3.4	1.5	1.5

Enzymatic Hydrolysis to Sugars



Objectives:

- Convert carbohydrate in paper sludge into monomeric sugars
- Use HCl for pH adjustment
- Achieve at least 85% enzymatic hydrolysis with a minimum enzyme dosage



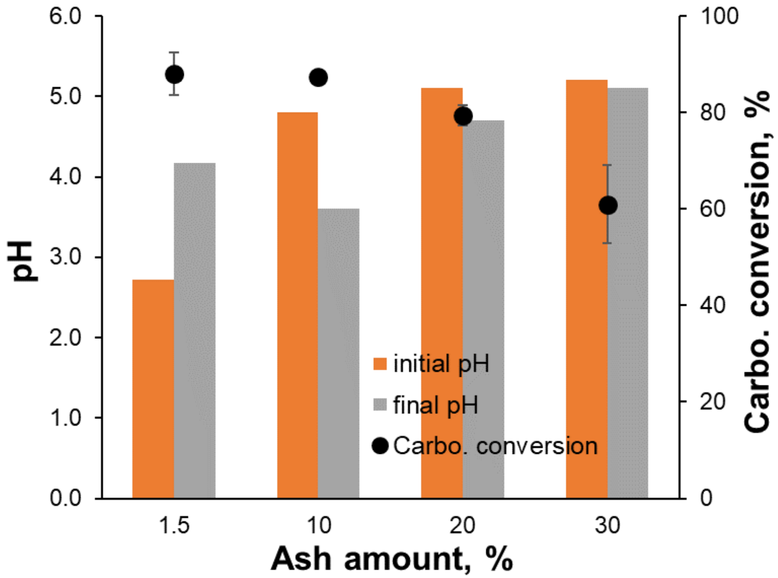
Cellic® CTec2 (Novozymes, USA)
5% consistency, 1 M HCl for pH adjustment
9.8 mg cellulase / g cellulose
Incubator shaker: 50°C, 150 rpm, 96 h

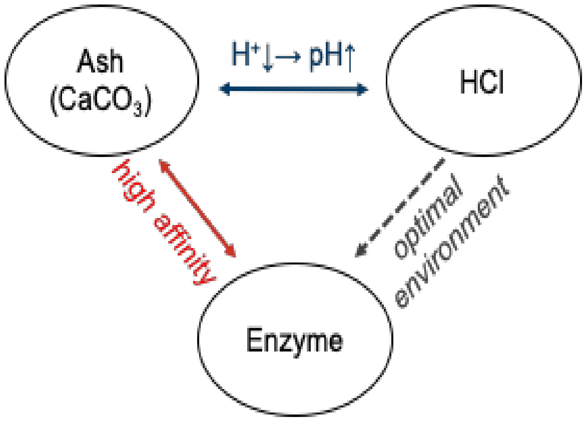
Initial pH	Conversion
3.5	88.2%
3.0	91.5%
2.7	92.6%
2.5	93.4%
2.8	94.9%

Best conversion was found when the initial pH was 2.5 – 3.5

Enzymatic Hydrolysis to Sugars

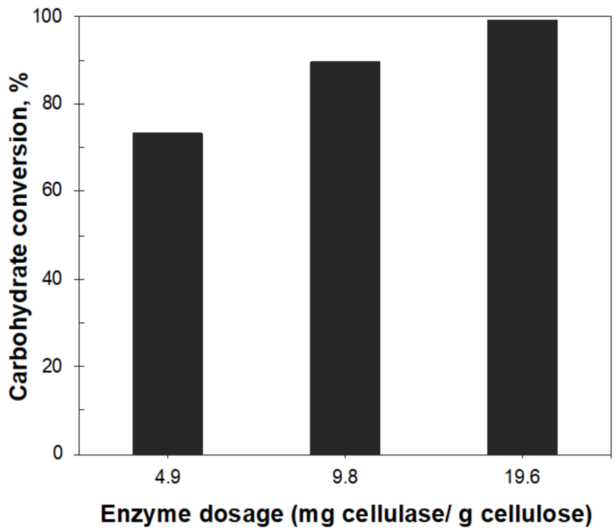
Effect of ash amount
@ 9.8 mg cellulase / g cellulose



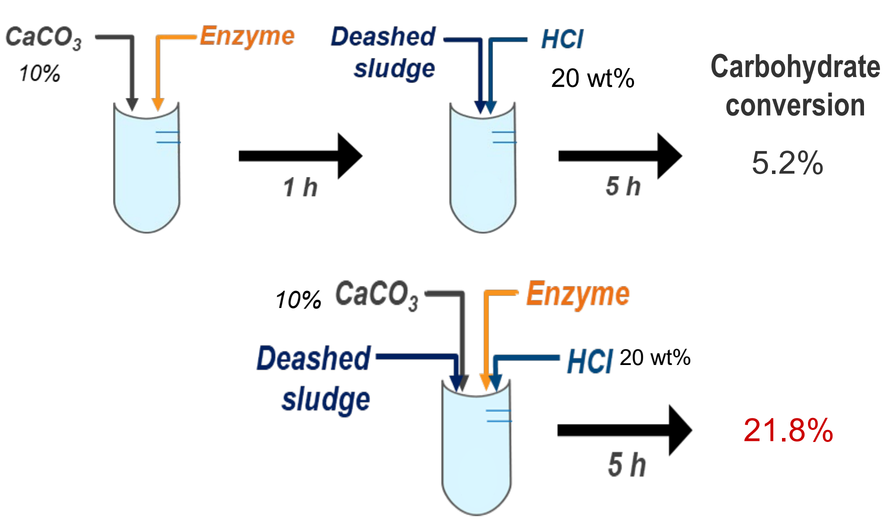


$CaCO_3 + 2 \cdot HCl \rightarrow CaCl_2 + CO_2 + H_2O$

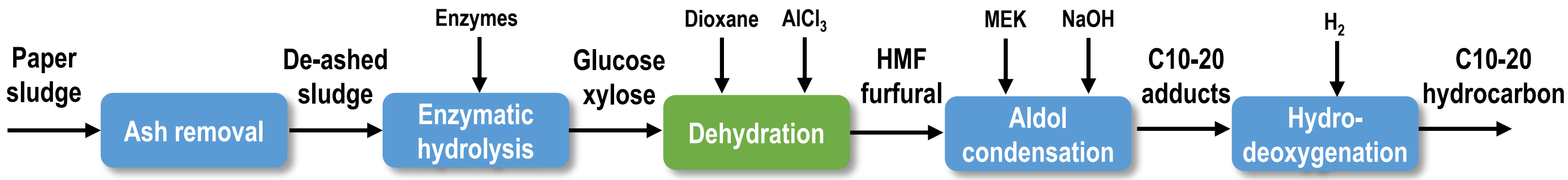
Effect of enzyme dosage
@ Initial pH: 3.0



Affinity between $CaCO_3$ and enzyme



Dehydration to Furans



Objectives:

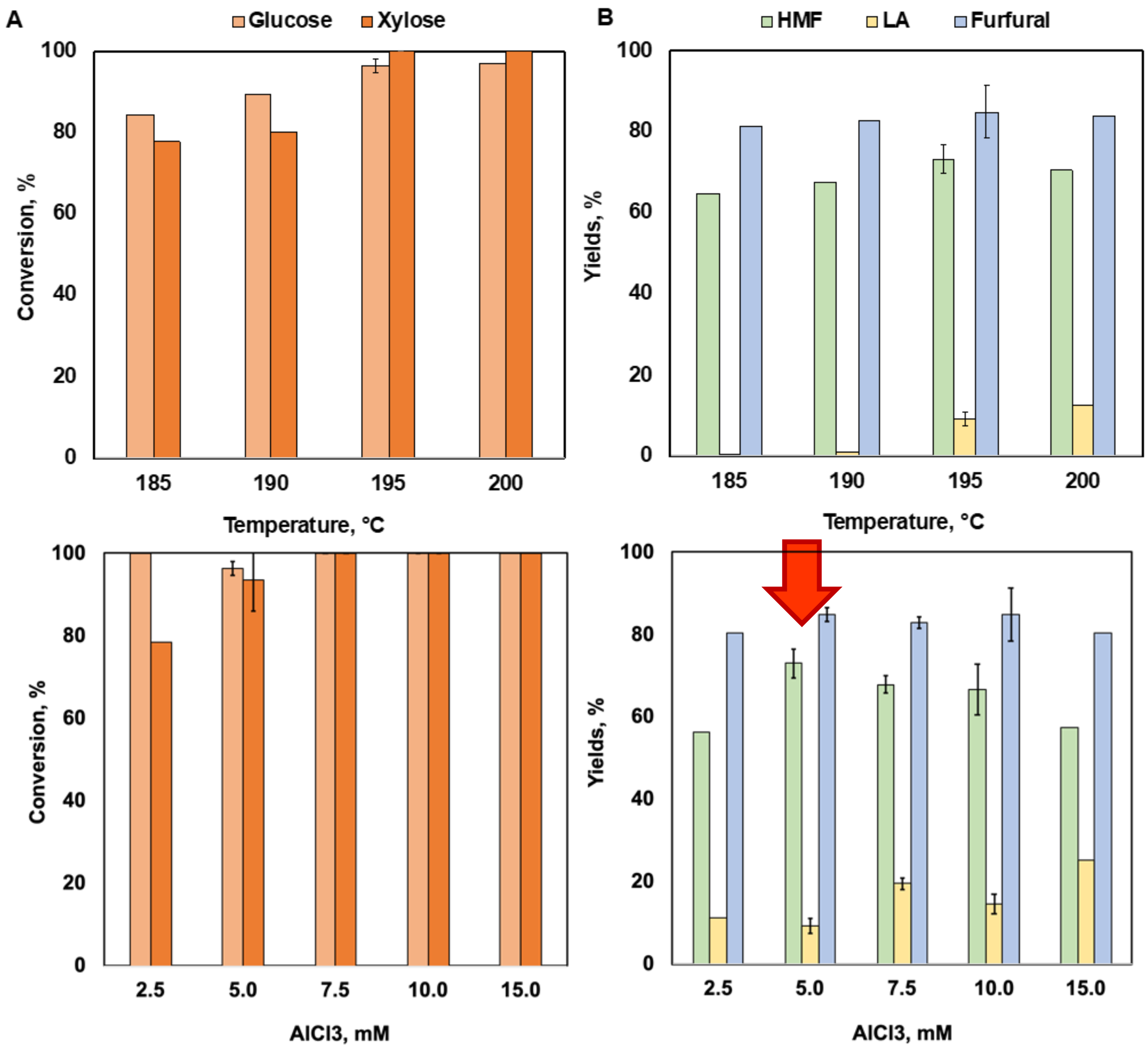
- Verify that sugars in hydrolysates from paper sludge can be converted into furfural and HMF.
- Convert both pentoses and hexoses in paper sludge hydrolysate into furfural and HMF with yields of at least 90% and 65% (Combined yield 70%) of theoretical, respectively.

Sludge-derived hydrolysate: glucose: 29 g/L, xylose: 6 g/L, oligosaccharides: 8%
Solvent: Water:1,4-dioxane (1:2 ratio)
Catalyst: AlCl3, 2.5 - 15 mM
Reaction: 185 - 200°C, 5 min
using Microwave reactor

Dehydration to Furans

Effect of Temperature
@ $AlCl_3$ 5 mM, 5 min

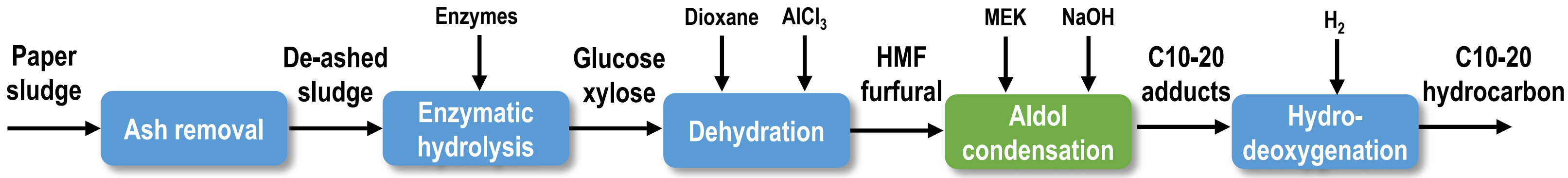
Effect of Catalyst Loading
@ 185°C, 5 min



The increase in temperature results in the increase in HMF and furfural yield, although by-product (e.g. levulinc acid) is produced as well.

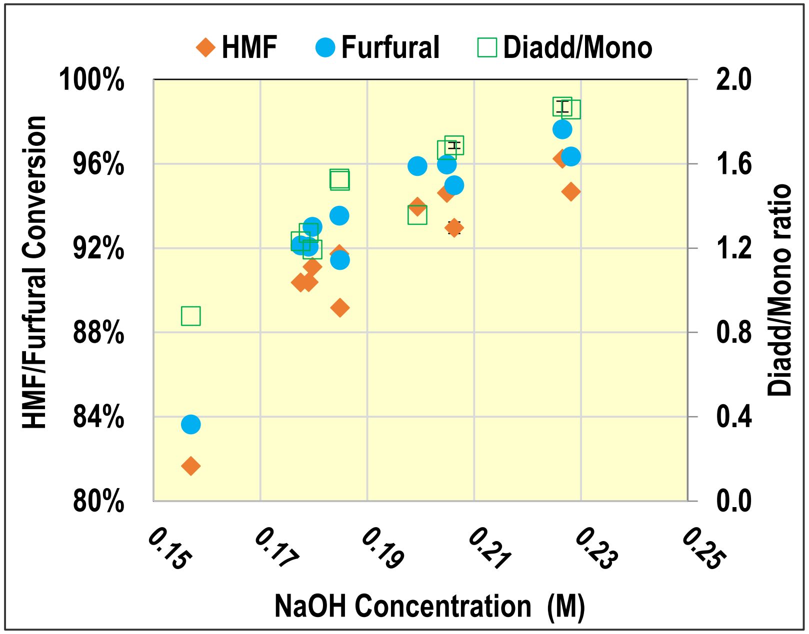
Maximum HMF yield (73%) and furfural yield (85%) were achieved at 5 mM of $AlCl_3$ loading.

Aldol Condensation of Furans to Intermediates



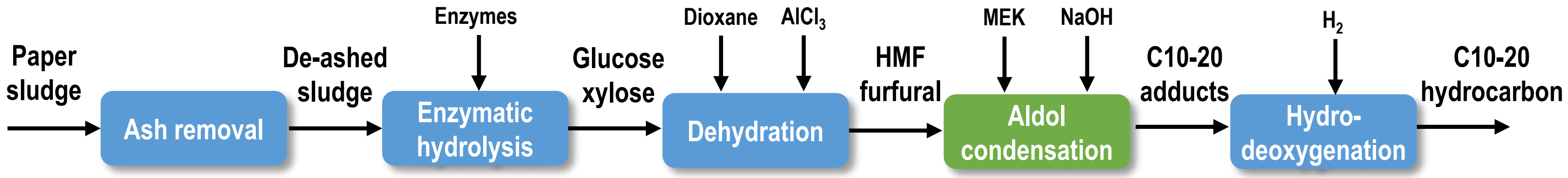
Objectives:

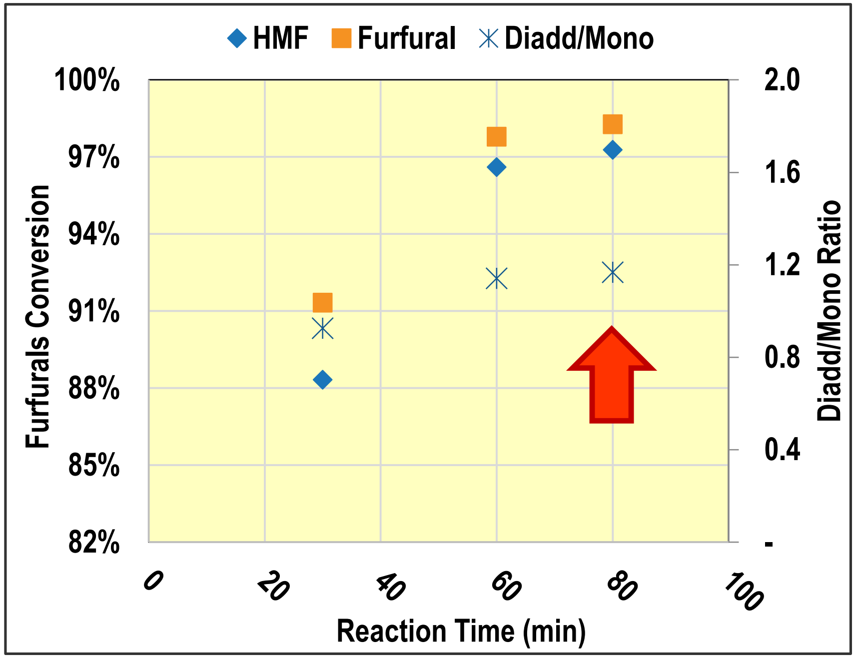
- Verify that furan mixtures can be converted into intermediates with a predominance of C14-C16 molecules from aldol condensations
- Convert both furfural and HMF with a combined intermediate yield of at least 85% of theoretical.



- Small scale screening studies found that paper sludge derived furans took part in the aldol condensation with MEK
- Biggest variable affecting reaction was NaOH concentration
- 60 °C, 60-80 min, Furfurals:MEK mole ratio 2-3.5:1
- HMF/Furfural conversions 95+% achieved
- Diadduct : Monoadduct ratios almost 2:1
- Condensation reactions scaled-up to 100 mL to isolate product and quantify yield

Aldol Condensation of Furans to Intermediates

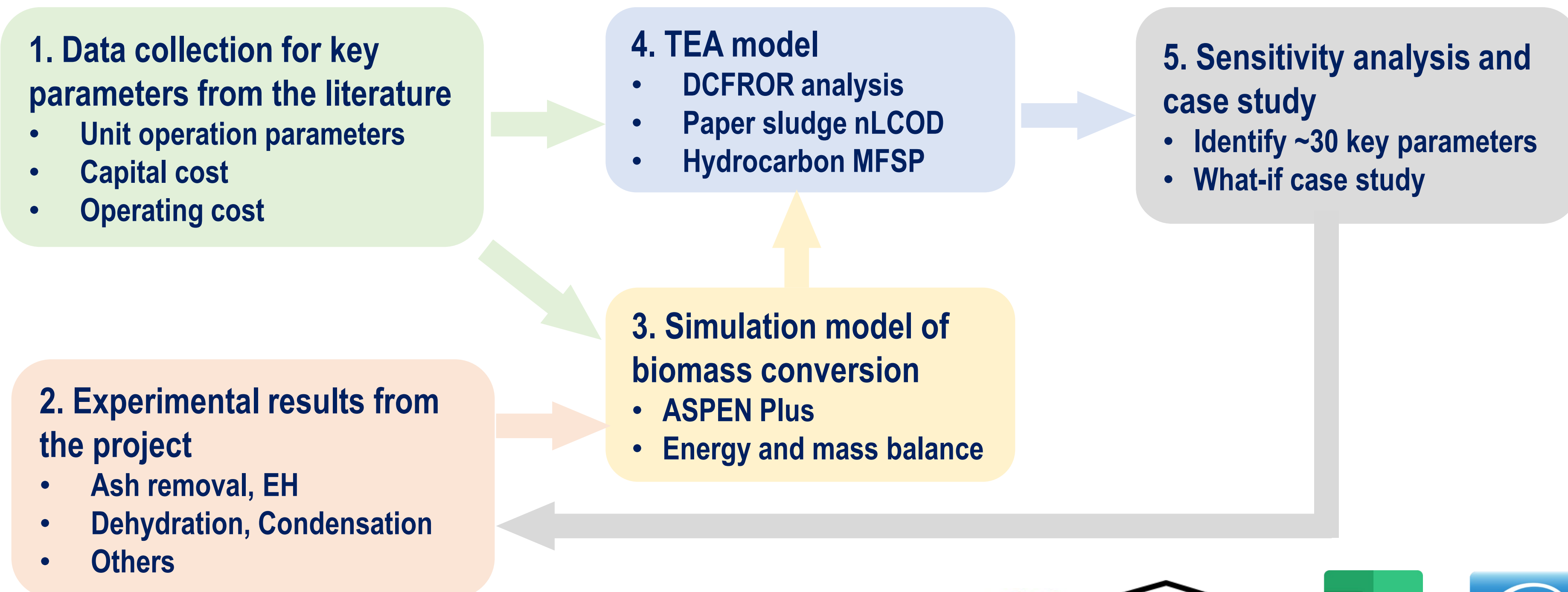




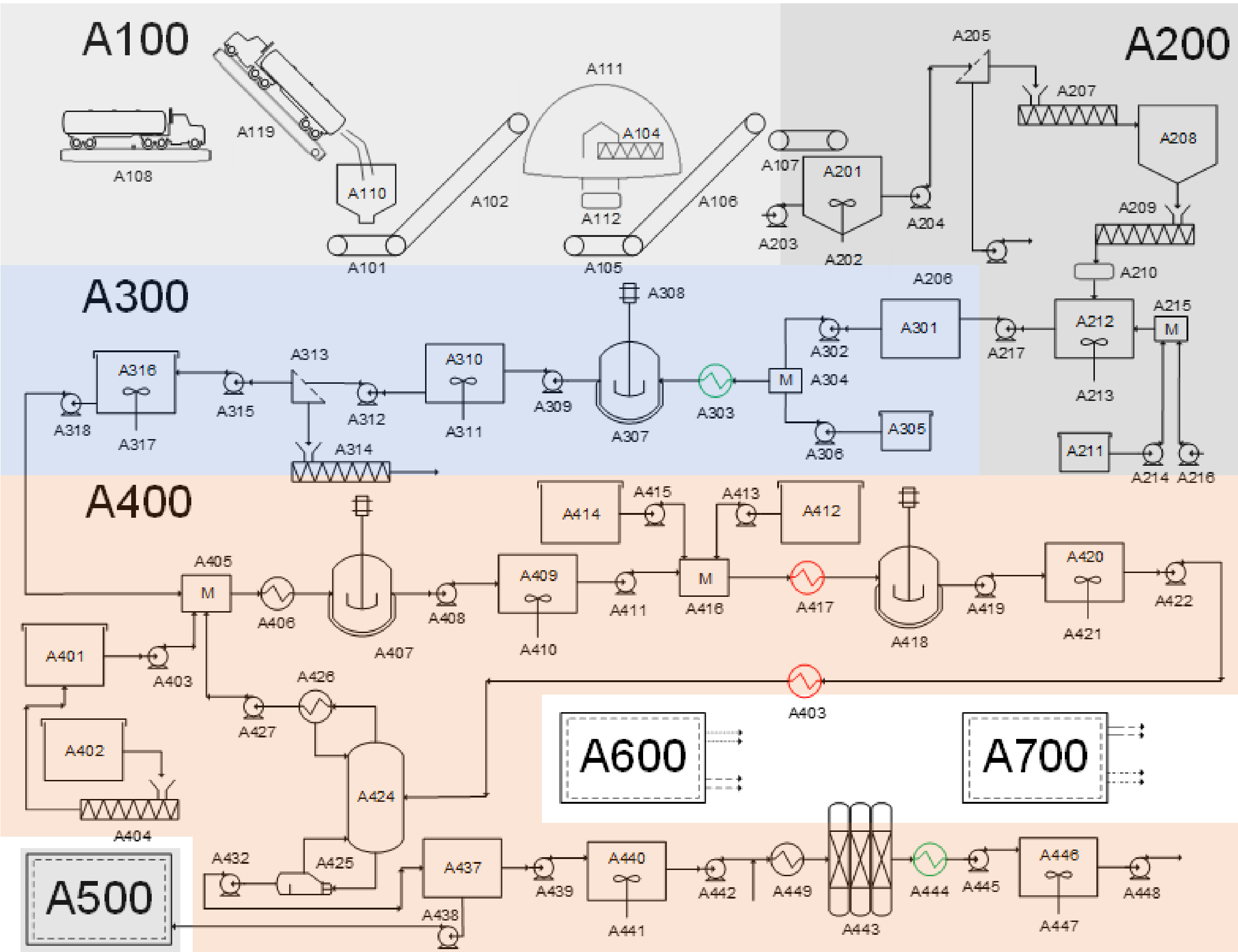
- Aldol condensation product obtained in high yield (88% isolated yield) from paper sludge hydrolysate furans
- Diadduct:Monoadduct ratio 1.17 :1
- 60°C, 80 min, Furfurals:MEK mole ratio 2:1, NaOH 0.20 M

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



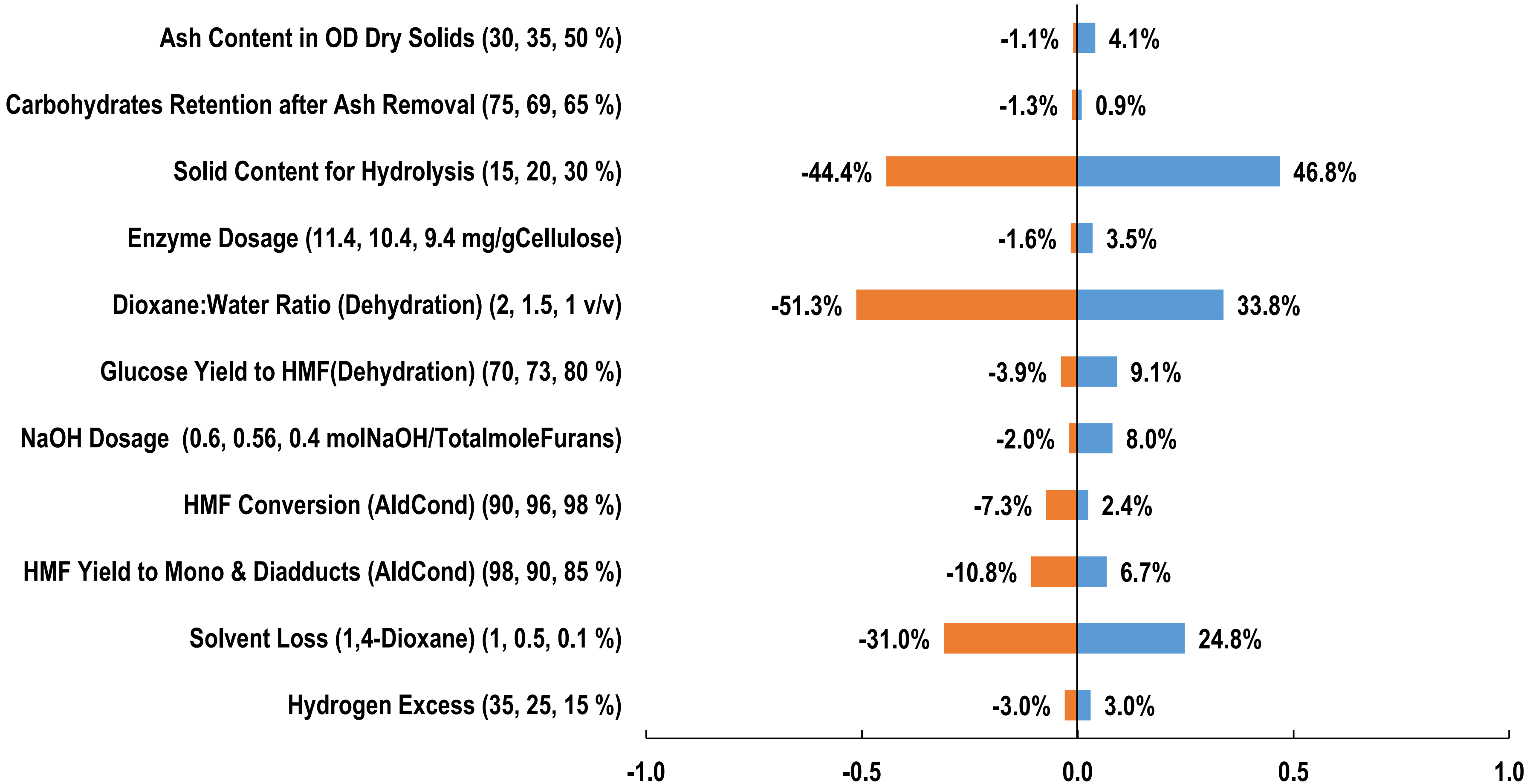
Mass and Energy Balance



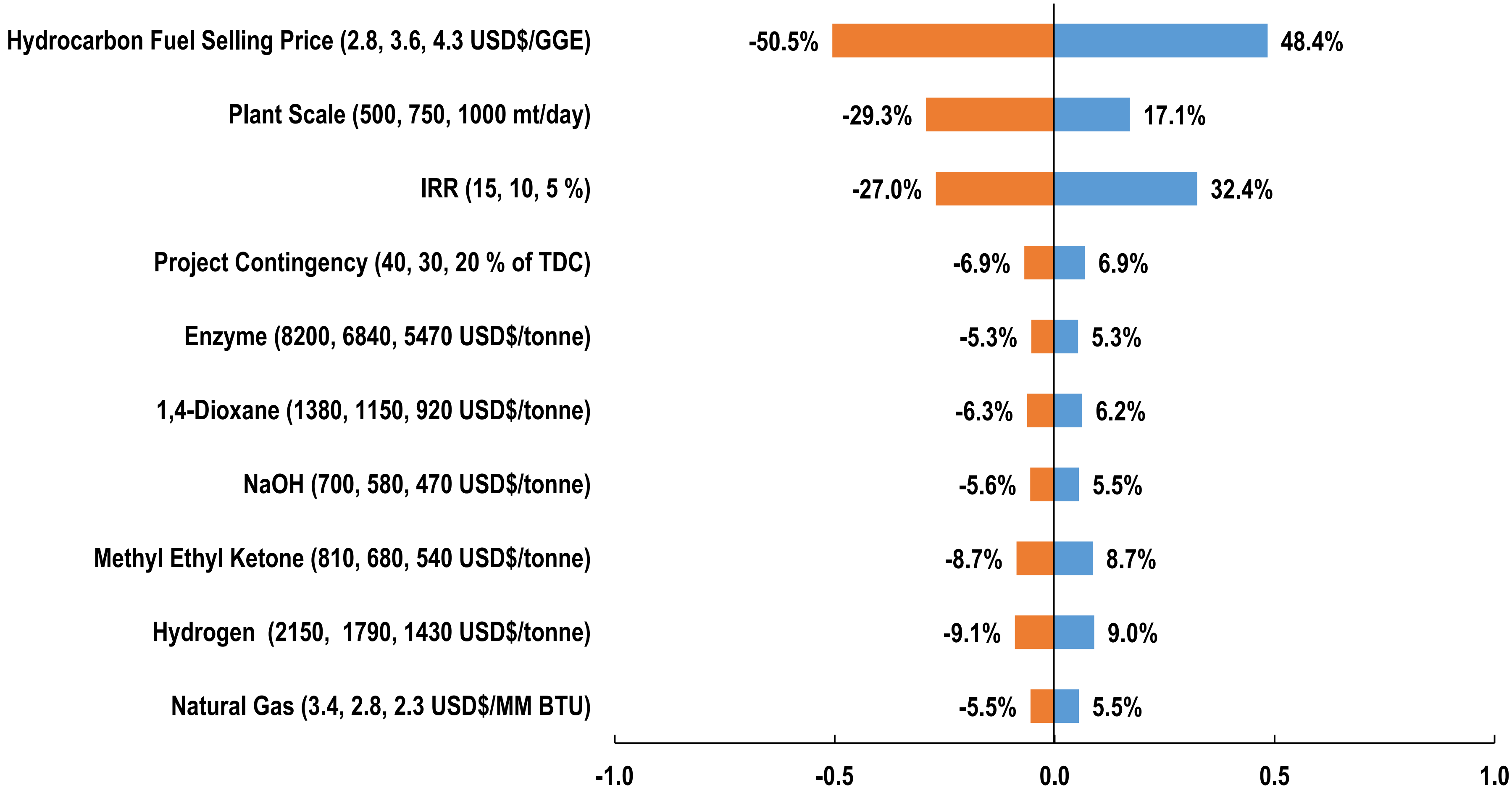
A100 – Feedstock & Handling	
Paper Sludge	750 dry tonne/day
A200 – Pretreatment	
Carbohydrates Ret.	68.7% ± 1.8
Ash Removal	99.0% ± 0.0
A300 – Enzymatic Hydrolysis	
Hydrolysis Temp	50°C
Glucose Conv.	97.5% ± 1.8
A400 – Catalytic Upgrading	
1,4-Dioxane : Water	2 : 1 (v/v)
Dioxane/Water Az.	88°C & 81%Diox.
A500 – Waste Water Treatment	
A600 – Heat & Power	
A700 – Utilities	

aspentech

nLCOD Sensitivity Analysis – Process Factors



nLCOD Sensitivity Analysis – External Factors



Summary

- Accomplishments
  - Met the target for ash removal (>93%), carbohydrate retention (>65%), and enzymatic hydrolysis (>85%)
  - Identified key properties of paper sludge for the process
  - Met the target for dehydration (>69%) and aldol condensation (>85%)

- Project future work
  - Go/No-go verification: 50 mL fuel production from paper sludge
  - Solvent recovery, hydro-deoxygenation
  - Relevant scale demonstration to produce 1L product for fuel testing

- Considerations to further enhance process economics (nLCOD, 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)

Quad Chart Overview

Timeline
- Project start date: 10/1/2019
- Project end date: 9/30/2022

	FY20 Costed (10/01/2019 – 9/30/2020)	Total Award
DOE Funding	$605,513	$2,475,807
Project Cost Share	$337,089 (CS 35.8%)	$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

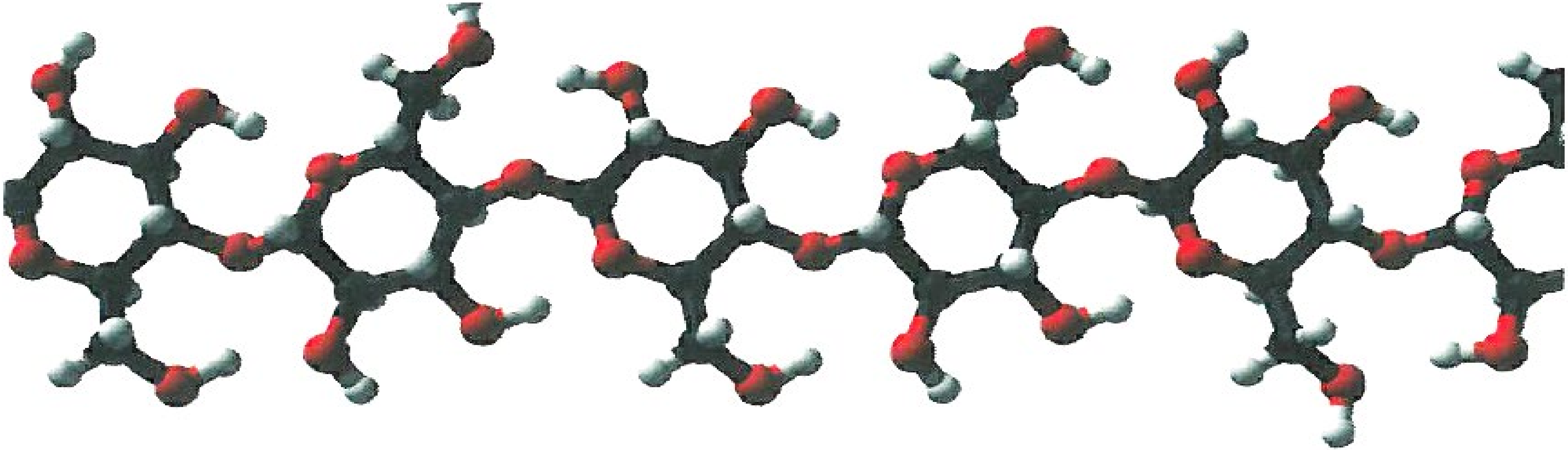
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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



Presentations and Publications

- Conference presentations
  - Techno-economic Analysis of Biofuel Production via Catalytic Upgrading of Carbohydrates in Paper Sludge
    - AIChE 2020 Virtual
  - Valorization of Paper Sludge to Furan Chemicals
    - AIChE 2020 Virtual
- Journal publications
  - Two publications are in preparation