NREL
Transforming ENERGY

Recycling of Dilute Deacetylation Black Liquor to Enable Efficient Recovery and Reuse of Spent Chemicals and Biomass Pretreatment Waste

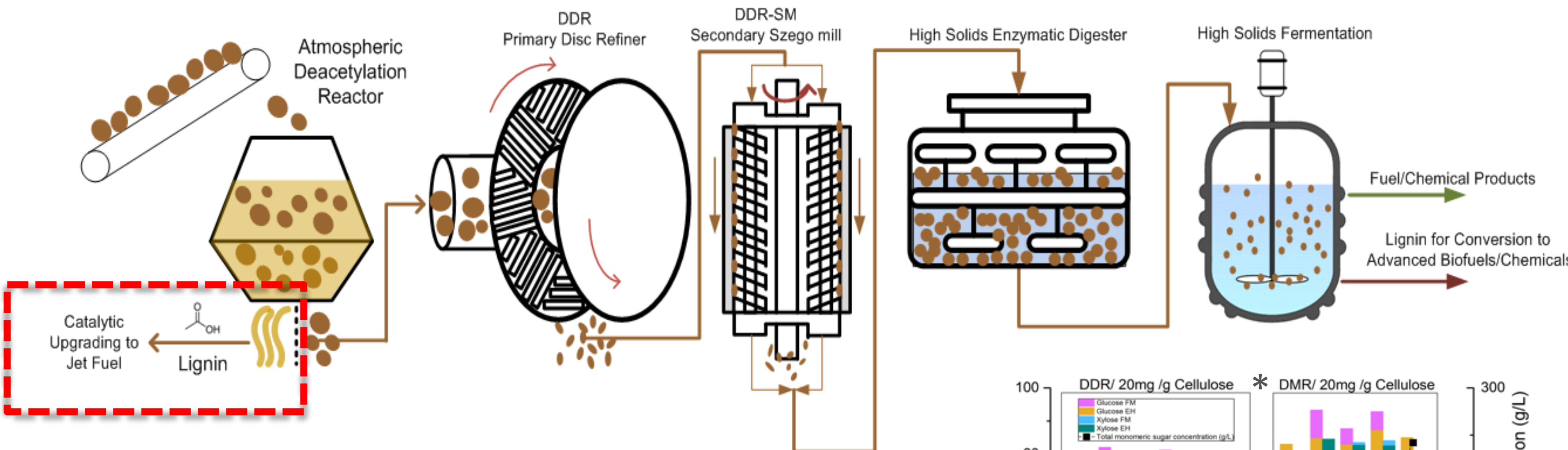
Xiaowen Chen (Xiaowen.chen@nrel.gov)

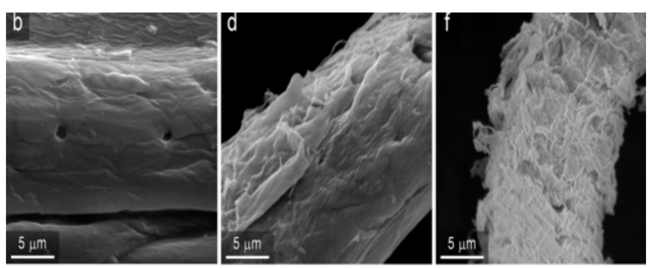
2019 BETO Frontiers in Energy Research special topic webinar

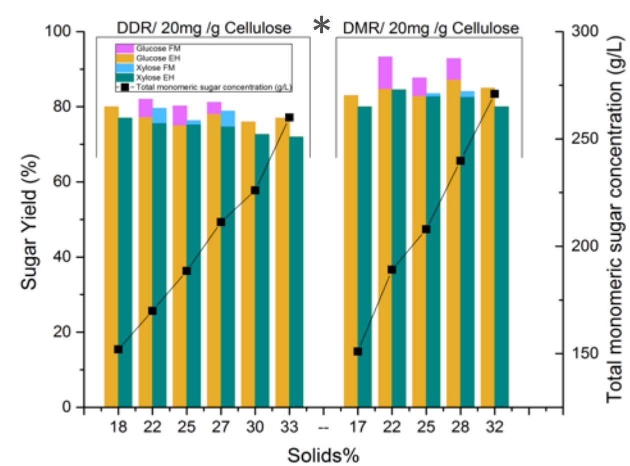
June 20, 2019

Background

Deacetylation and Mechanical Refining Process (DMR)





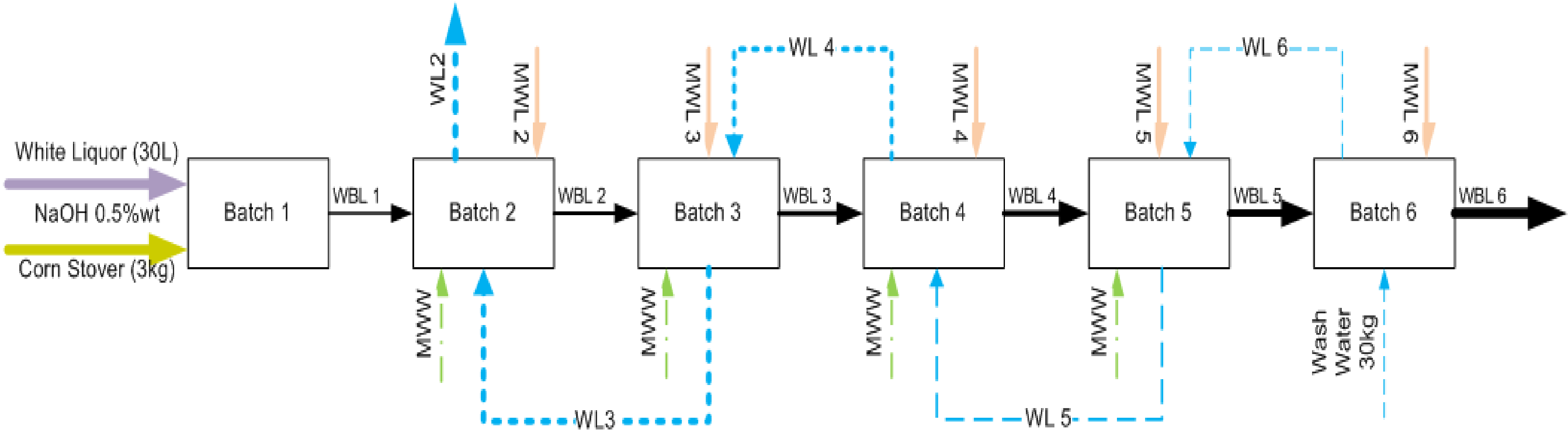


*EH of dilute acid pretreated solids severely inhibited above 17%

Motivation of Black Liquor Recycling

- Recycle of black liquor needed:
  - Recover pretreatment chemicals
    - Key to success!
  - Reduce water/energy/chemical usage
  - Valorize value-added components from biomass
    - Acetate, carbohydrate
    - Lignin and aromatics
    - Potentially potassium and phosphorous
- Current deacetylation is conducted at 8-10% solids
    - Titers are too dilute to be economically valorized
    - Direct evaporation of the black liquor is very energy intensive and may lead to undesired condensation and degradation of valuable chemicals!

Counter-Current Reverse Batchwise Black Liquor Recycling



MWW –Makeup Wash Water
MWL - Makeup White Liquor (NaOH)
WBL - Weak Black Liquor

Positive outcomes

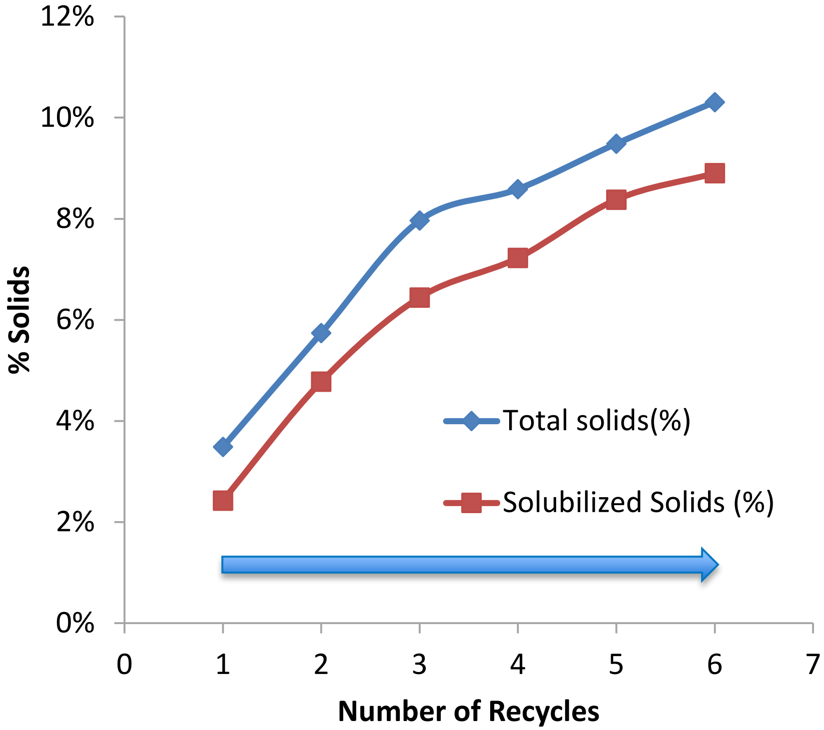
- Lower water/chemical usages
- Higher concentration streams

Possible negative impacts

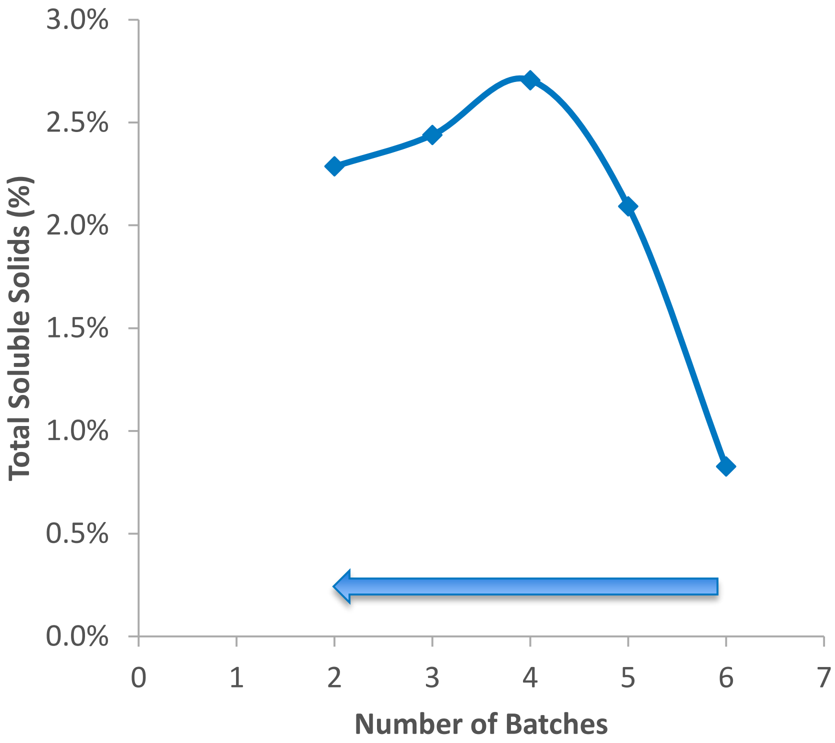
- Black liquor gets too viscous
- Reduced deacetylation effect
- Inhibitors may accumulate in solids that will end up in fermentation

Number of Recycles	1	2	3	4	5	6
Biomass Loaded (kg)	3.3	3.3	3.3	3.3	3.3	3.3
Dry Biomass (kg)	3	3	3	3	3	3
NaOH (kg)	0.165	0.165	0.165	0.165	0.165	0.165
Initial Water Added (kg)	29.6	-	-	-	-	-
Makeup Water Added in Black Liquor (kg)	-	6.3	6	7.1	5.1	5.6
Initial Wash Water (kg)	-	-	-	-	-	30
Makeup Wash Water (kg)	-	7	7	7	7	-

Solids Accumulation in Black Liquor and Wash Liquor

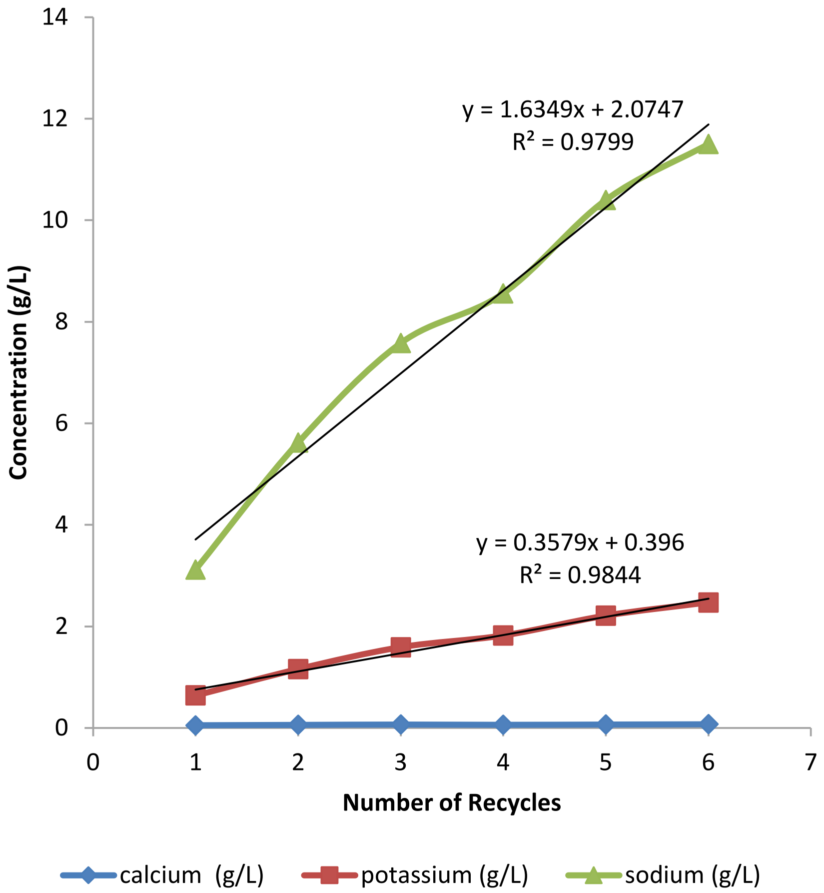


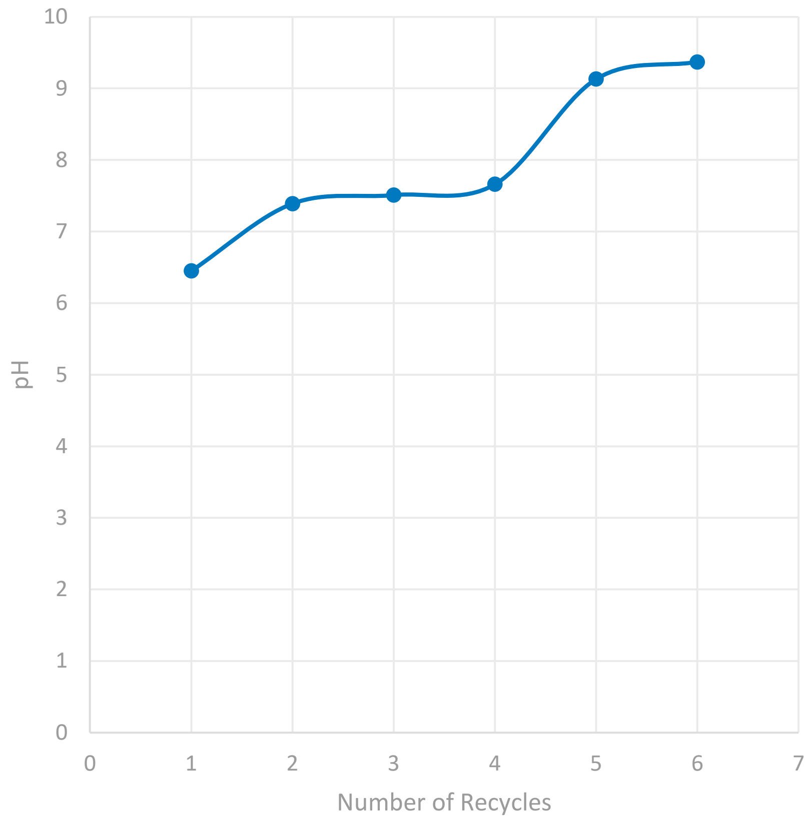
Total solids and soluble solids in the recycled black liquors



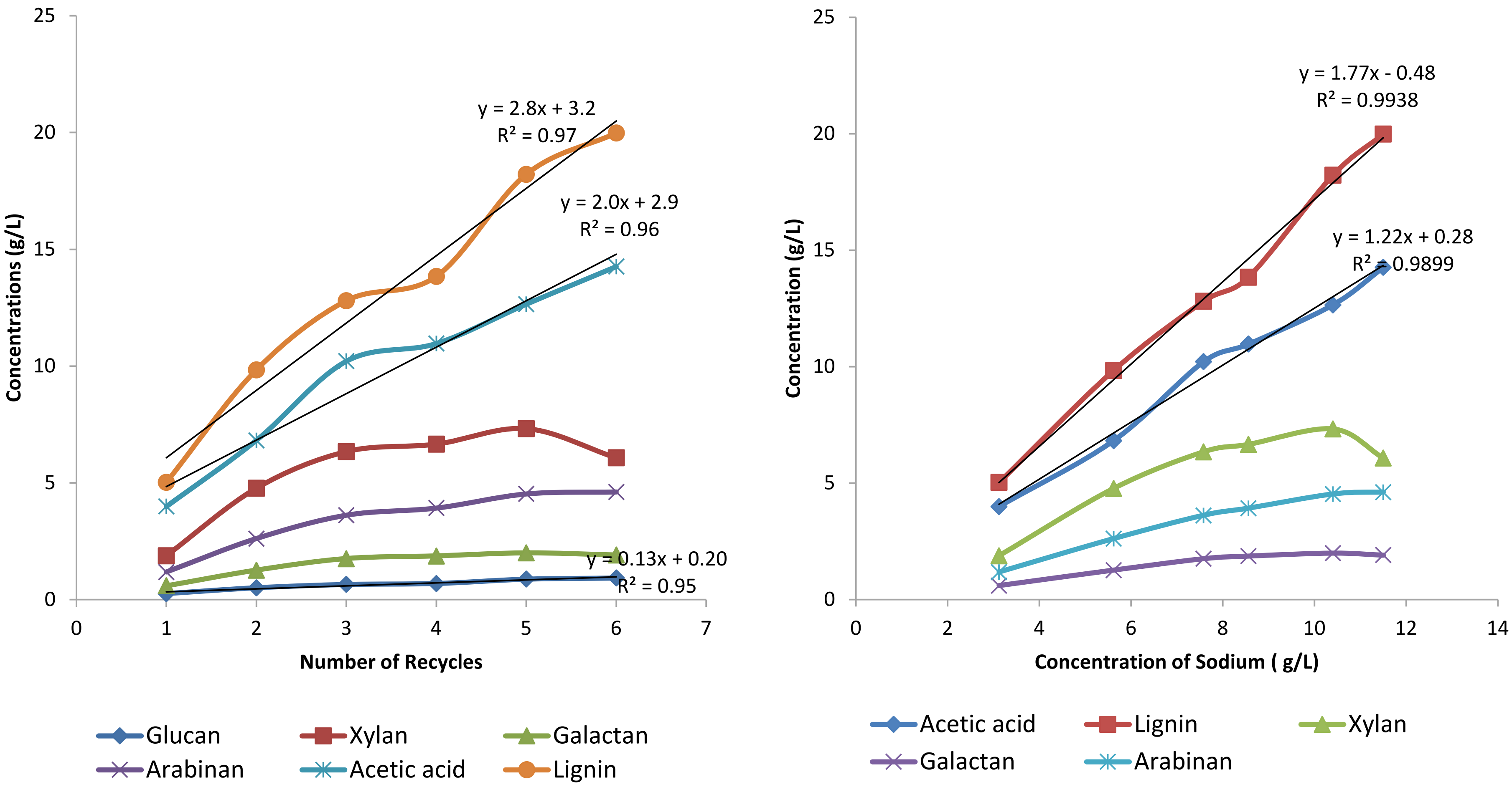
Total soluble solids in the wash liquors

Accumulation of Inorganics and Spent Sodium in Black Liquor



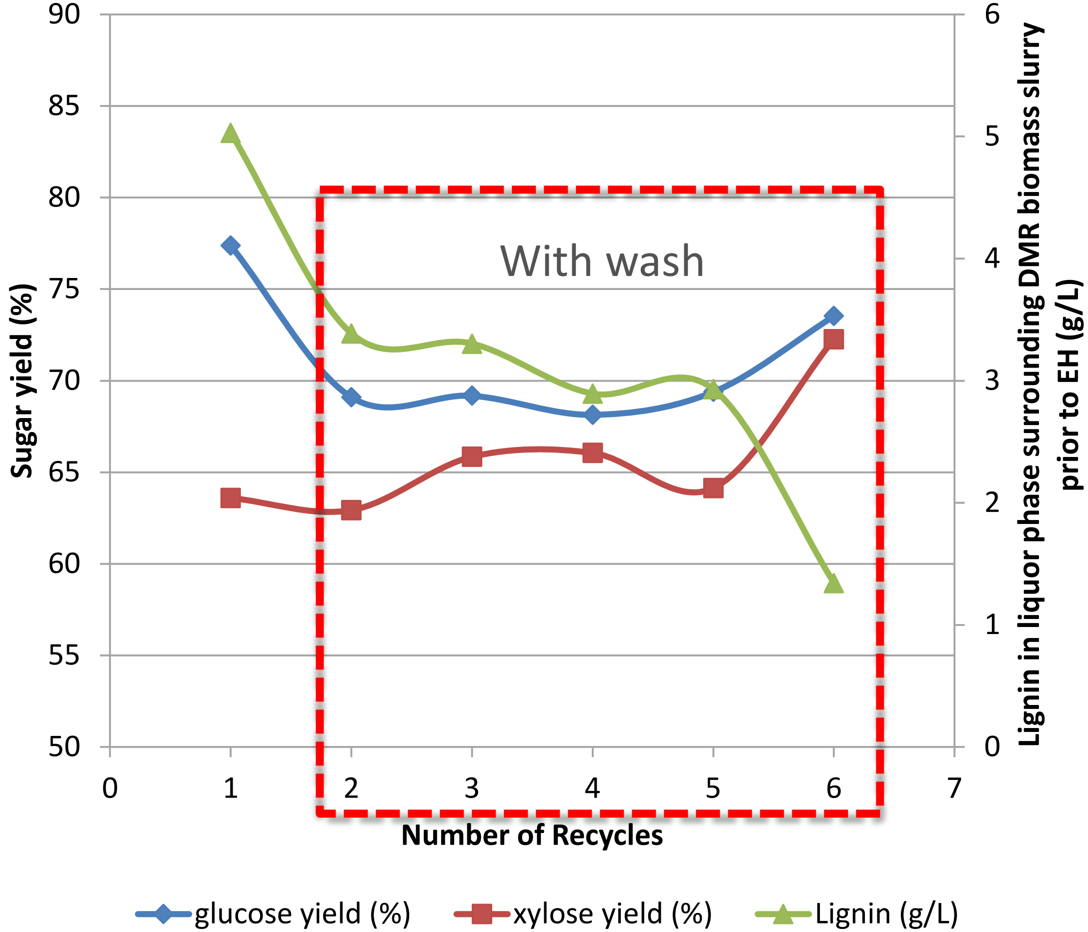


Accumulation of Biomass Components in Black Liquor



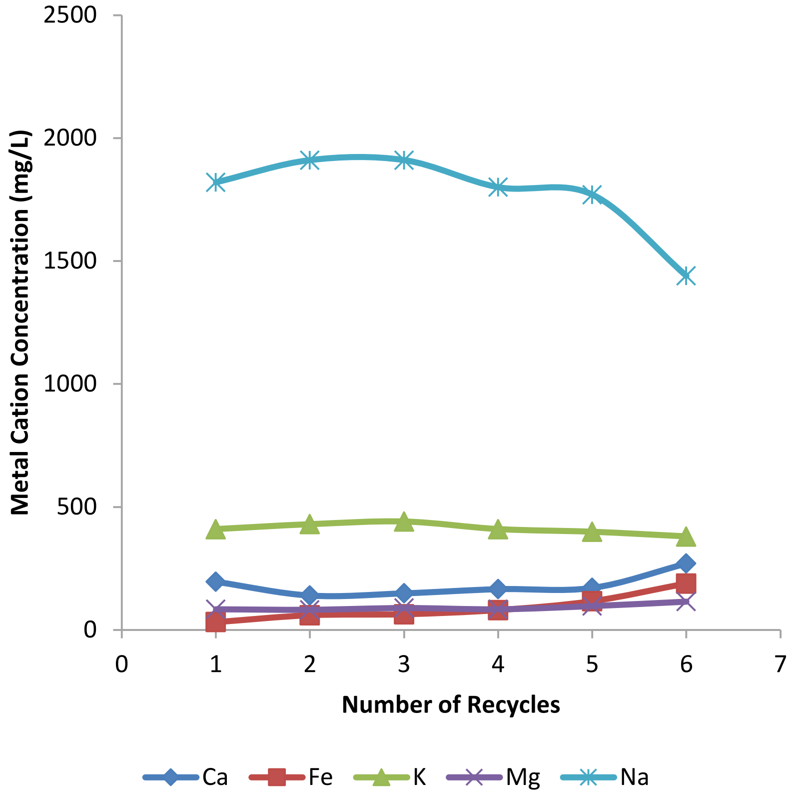
- Lignin and acetate removal is not affected by black liquor recycling and the number of recycles.
- Xylan dissolution is reduced possibly due to adsorption onto solids or oligomer solubility limitations

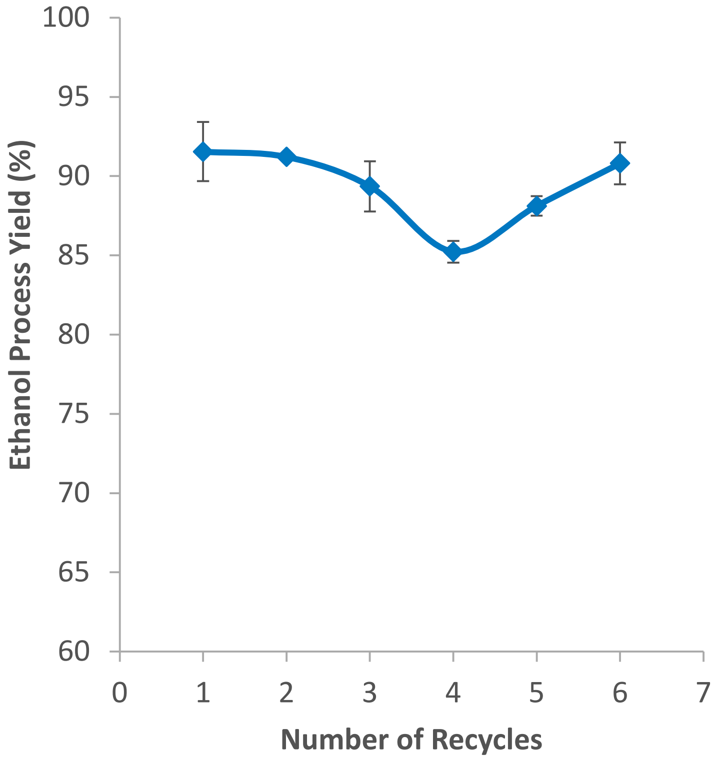
Enzymatic Hydrolysis



- Batch 2-6 (where washing is available) show a reversed trend between sugar yield and lignin concentration
- Batch 1 does not have washing and do not follow the trend
- Sugar yield is lower compared to previous study due to refining issues (more to read in publication)

Ethanol Fermentation





- Fermentation is performed using *rZymomonas*
- Final ethanol titer approximately 60g/L

Evaporation and Viscosity

Key properties of black liquor for conventional Kraft recovery process (combustion to produce energy)

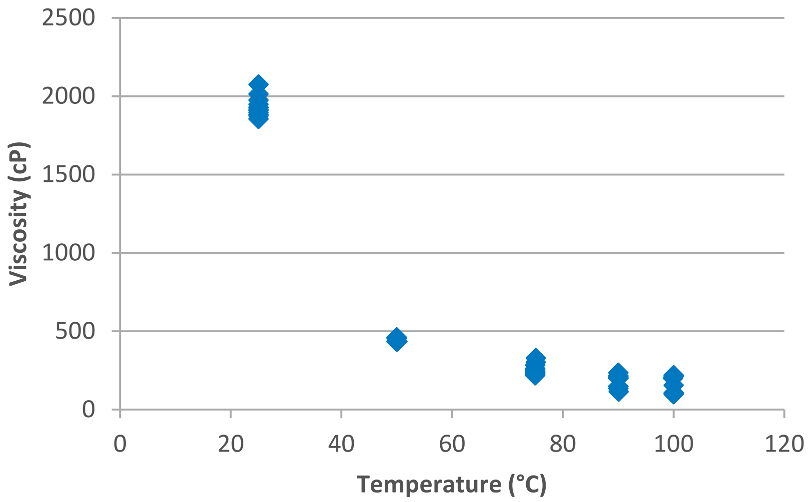
- Viscosity and boiling point rise (BPR)
- Normally combusted at 65% solids

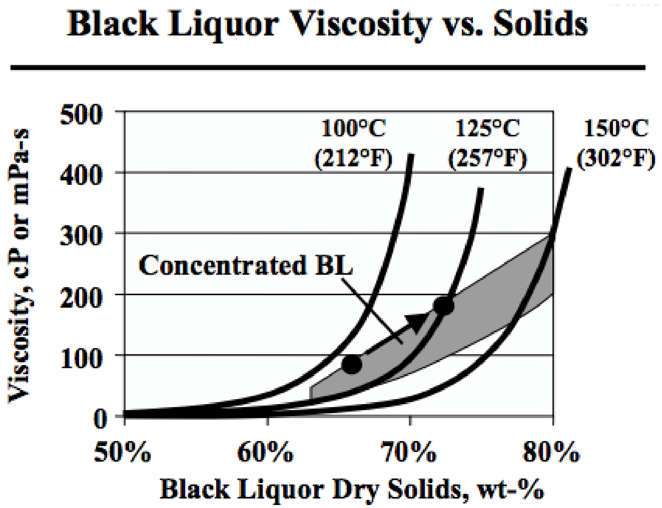
Black liquor concentrated to 65% solids

- Viscosity at room temperature - 2000cP
- Viscosity at 100° C – 154 cP

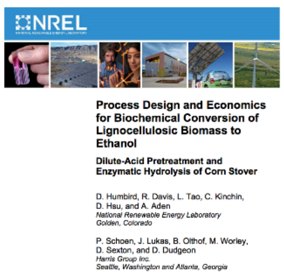
Compared to 65% Kraft black liquor in literature

- Viscosity at 100°C – approximately 100 cP





Techno Economic Analysis


NREL
Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol
Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover
D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, and A. Aden
National Renewable Energy Laboratory
Golden, Colorado
P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, and D. Dudgeon
Harris Group Inc.
Seattle, Washington and Atlanta, Georgia

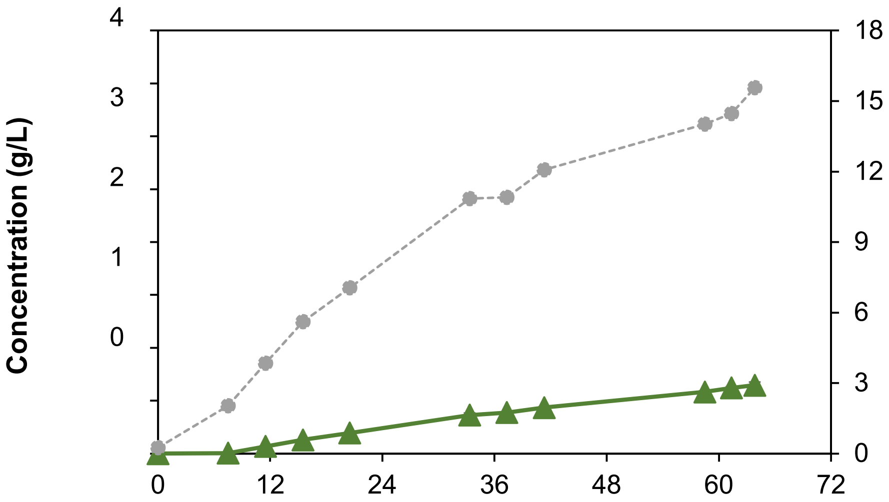
	Without Recycle			With Recycle
Deacetylation (total solids %)	10%	30%	30%	10%
Water for deacetylation (kg/hr)	666,667	166,667	166,667	166,667
Wash water after deacetylation (kg/hr)	0	563,117	0	67,620
Steam for A200 (kg/hr)	58,764	17,266	17,266	14,870
Total water used for A200 (kg/hr)	728,107	748,949	358,054	404,178
MESP ($/gal)	$2.32	$2.27	$2.21	$2.17

With black liquor recycling, we can reduce water usage by ~50% and energy usage by ~75%, thus lowering MESP by 4 to 15 cents per gallon

Valorizing Black Liquor (joint effort with Greg Beckham's group at NREL)

- Converting p-coumaric acid and ferulic acid in the black liquor to muconic acid (Lignin Biological Funneling process)

Lignin feed at high pH
pH= 9
***p*-coumaric = 0.9 g/L**
Ferulic acid = 0.3 g/L

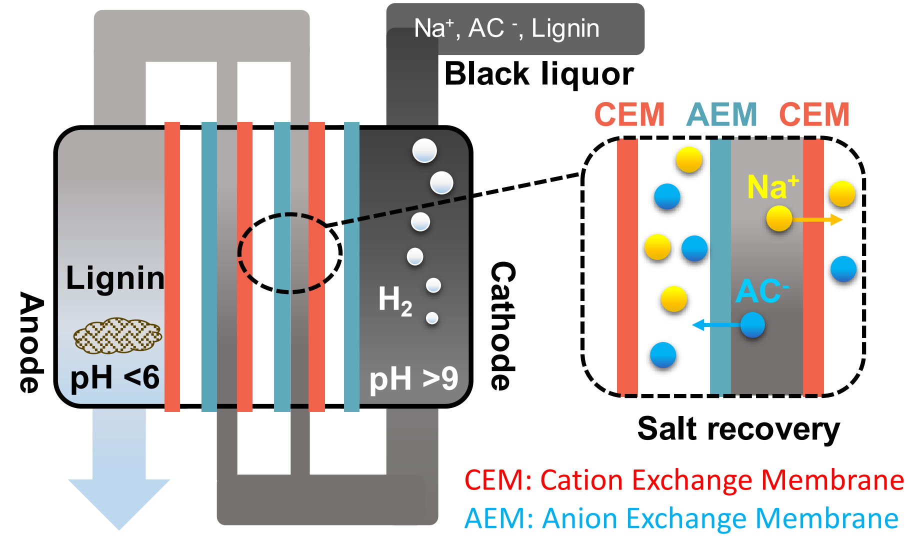


- By recycling black liquor, we could achieve approximately 6g/L p-coumaric acid and 1.5 g/L ferulic acid after 6 recycles

Microbial Electrochemical Technology to Recover Pretreatment Chemicals, Water and Lignin (Joint work with Princeton University)

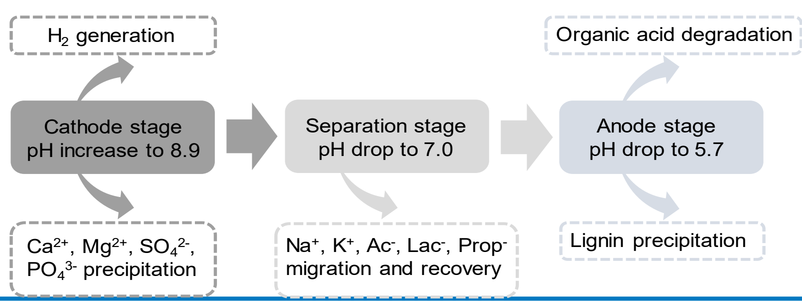
Challenges:

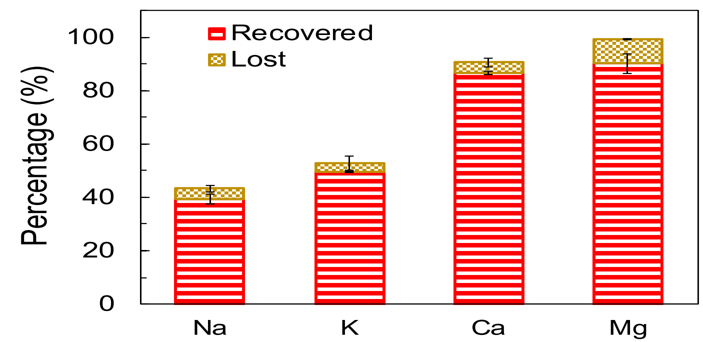
- DMR black liquor
  - Too dilute
  - Valuable and underutilized lignin, organic acids and sodium
- Conventional Kraft process
  - Expensive recovery boiler/lime kiln
  - Burns lignin and other organics
  - GHG, air pollution and LCA issues

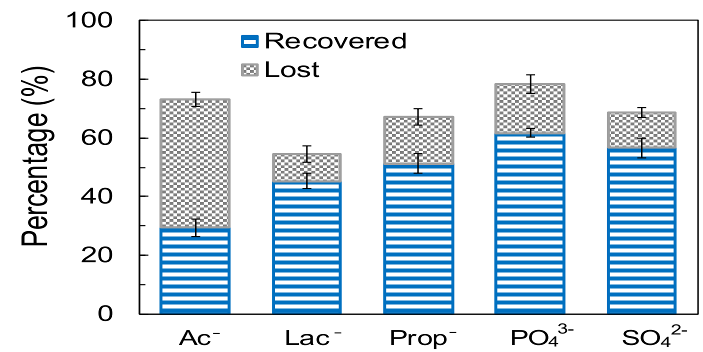


Solutions:

- MET degrades low conc. waste organics
  - Chemical energy -> Electrical potential
  - Salt migration and recovery
- MET precipitates lignin with no added acids







Results:

- Lignin and salt recoveries of ~61.2±2.7% and 92.2±1.6%, respectively.

Chen and Ren et al. Green Chemistry, 2018

Black Liquor Lignin to Jet Fuel*

Challenges:

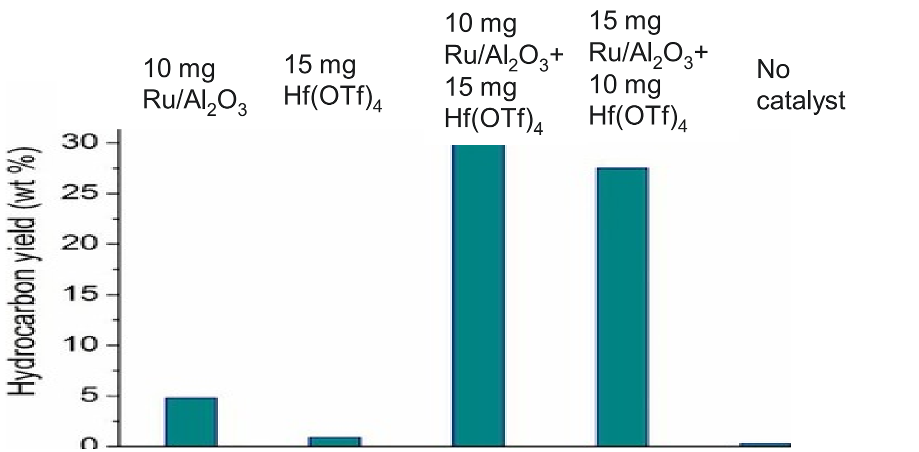
- Lignin's intrinsic heterogeneous robust structure
  - Upgrade/Recovery to single product is very difficult
  - Condensation/Repolymerization
- HDO with acid combined metal as bifunctional catalytic system
  - Most Brønsted acids: less selective
  - Most Lewis acids: water sensitive

Solutions:

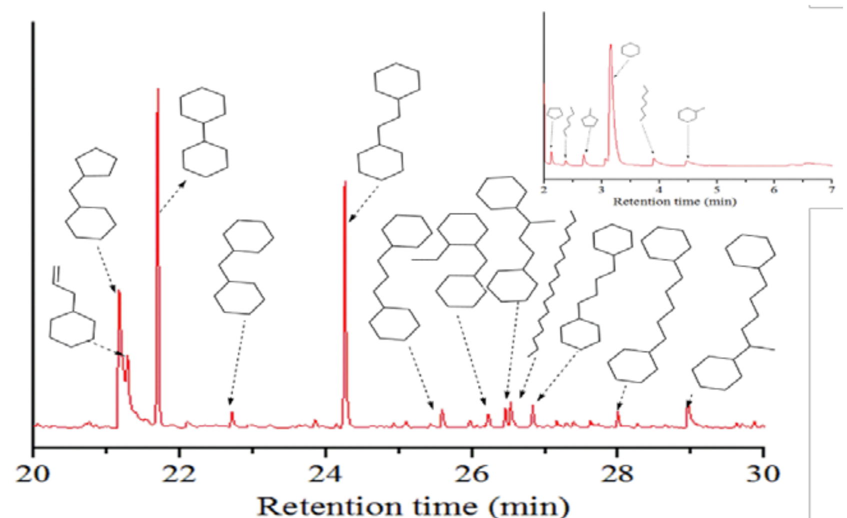
- Super Lewis acid- Metal Triflates
  - Widely used in organic synthesis
  - Water tolerant and thermal stable

Results:

- Near theoretical yields of hydrocarbons were produced from lignin model compounds
- Products mostly alkyl-dicyclohexanes (30%) from lignin in DMR Black Liquor
  - High energy
  - High density



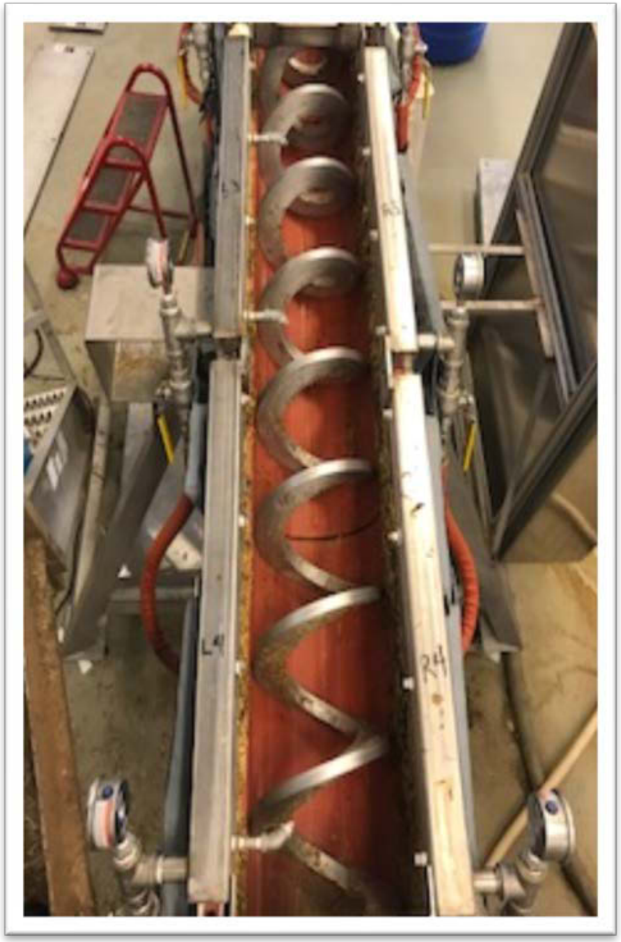
Hydrocarbon yields from DMR lignin in HDO conversion under different conditions. Reaction conditions: lignin (50 mg), *n*-octane (1 mL), *T*=250 °C, *t*=4 h, *P* Hydrogen =4 MPa. in 1 mL *n*-octane containing 10 wt % water as solvent.



*Wang, Yang and Tucker *et al.*, ***ChemSusChem***, 2018, **11**(1)

Future work – from batch to continuous reactor

Continuous Counter Current Inclined Shaftless Screw Reactor



Contact info

- Xiaowen Chen

Email: Xiaowen.chen@nrel.gov

Thank you

www.nrel.gov

NREL/PR-5100-74639

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL
Transforming ENERGY