SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

PULP & PAPER
UNIVERSITY OF TORONTO

# Variability in Black Liquor Composition


## Nikolai De Martini

## University of Toronto

***Black Liquor,***
***a wily mistress***
***fluid in its ways.***
***Burning gently?***
***Burning bright?***
***Or exploding into the night?***

# Acknowledgements

- **This presentation draws from the work of:**
  - **Adam Rogerson, MASc, UofT**
  - **Jerry Ng, PhD candidate, UofT**
    - **Professor Yuri Lawryshyn (co-supervisor)**
    - **Andrew Jones (committee member for Jerry)**
  - **Jack Porter (long time proponent of understanding BL variability for improved operation)**

# Sources of Variability in BL Composition

- **Wood**
  - **Species, age, harvest location**
- **White Liquor**
  - **Reduction efficiency, causticity, TTA**
- **Pulping**
  - **Grade, H-factor, white liquor dosage**

# Why Capture Variability with Modeling?

- Objective more stable/efficient operation
- Black liquor inherently difficult for online analysis (significant improvements)
- Modeling can capture lag
  - use of WL/GL analysis
- Can help prioritize operational attention
- Captured variability in process chemistry can help us learn what we do not understand

# Models

- **Dynamic mass balance**
- **Classic time series modeling**
- **Time series neural networks**

# Dyanmic Mass Balance

- Canadian kraft pulp mill
- Campaigns softwood and hardwood
- Model created in CADSIM Plus
  - Modeled full cycle – pulping, brownstock washing, chemical recovery
  - Steps in model fully connected
  - 7-day sampling campaign carried out to help capture transition from HW to SW

# Black Liquor Composition

## Inorganics

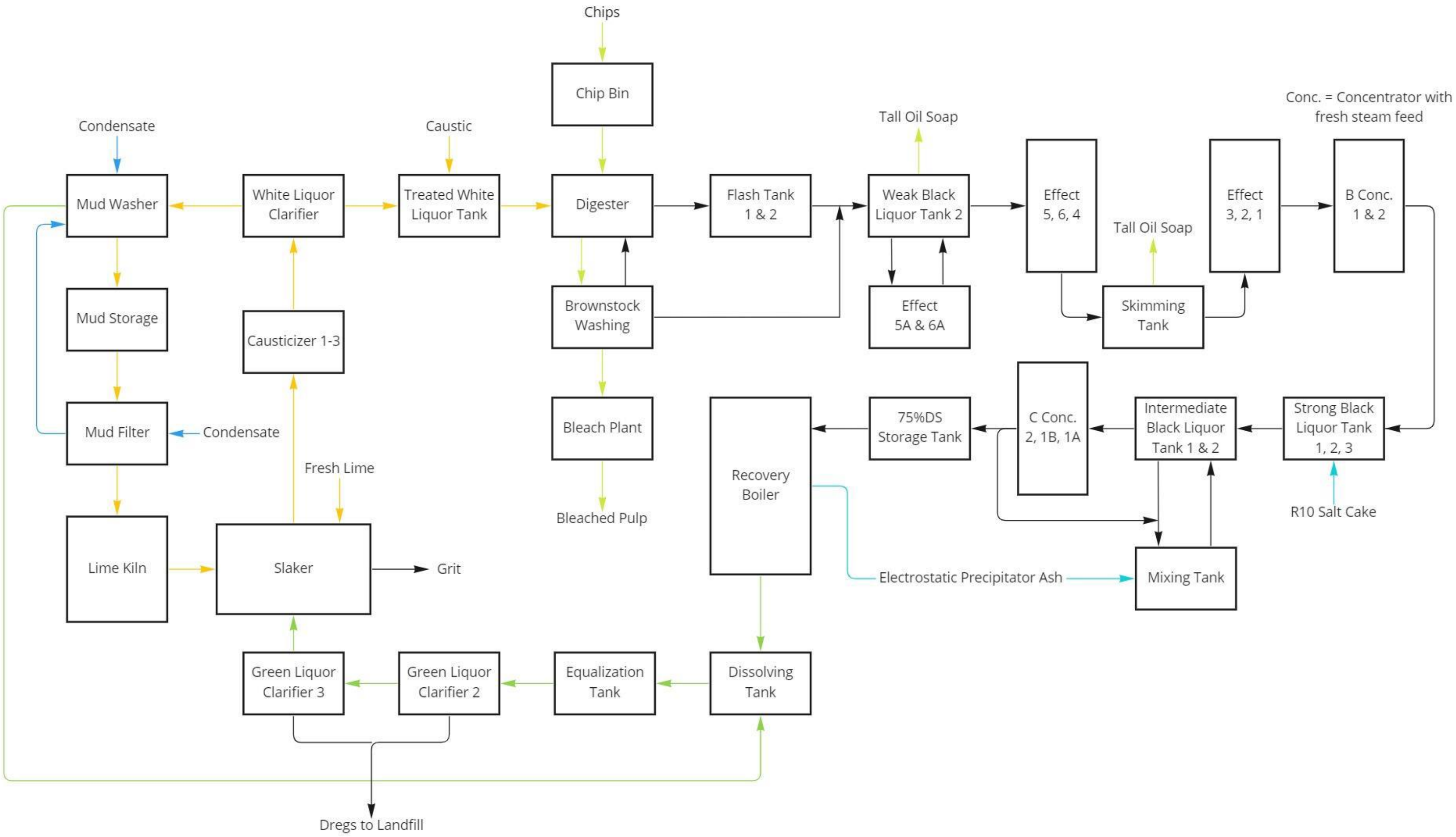
- **Species followed ($Na^+$, $K^+$, $S_{tot}$, $S^{2-}$, $S_2O_3^{2-}$, $SO_4^{2-}$, $CO_3^{2-}$, $OH^-$)**
  - **WL primary source of inorganics**
  - **$OH^-$: $OH^-_{WL}$ + H-Org → $H_2O$**
  - **historical data on WL causticity, TTA, liquor:wood, BL REA established $OH^-$**
- **$CO_3^{2-} = CO_3^{2-}{}_{WL} + CO_3^{2-}{}_{pulping}$**
- **$SO_4^{2-}$ based on historic reduction efficiency**

# Black Liquor Composition
## Organics

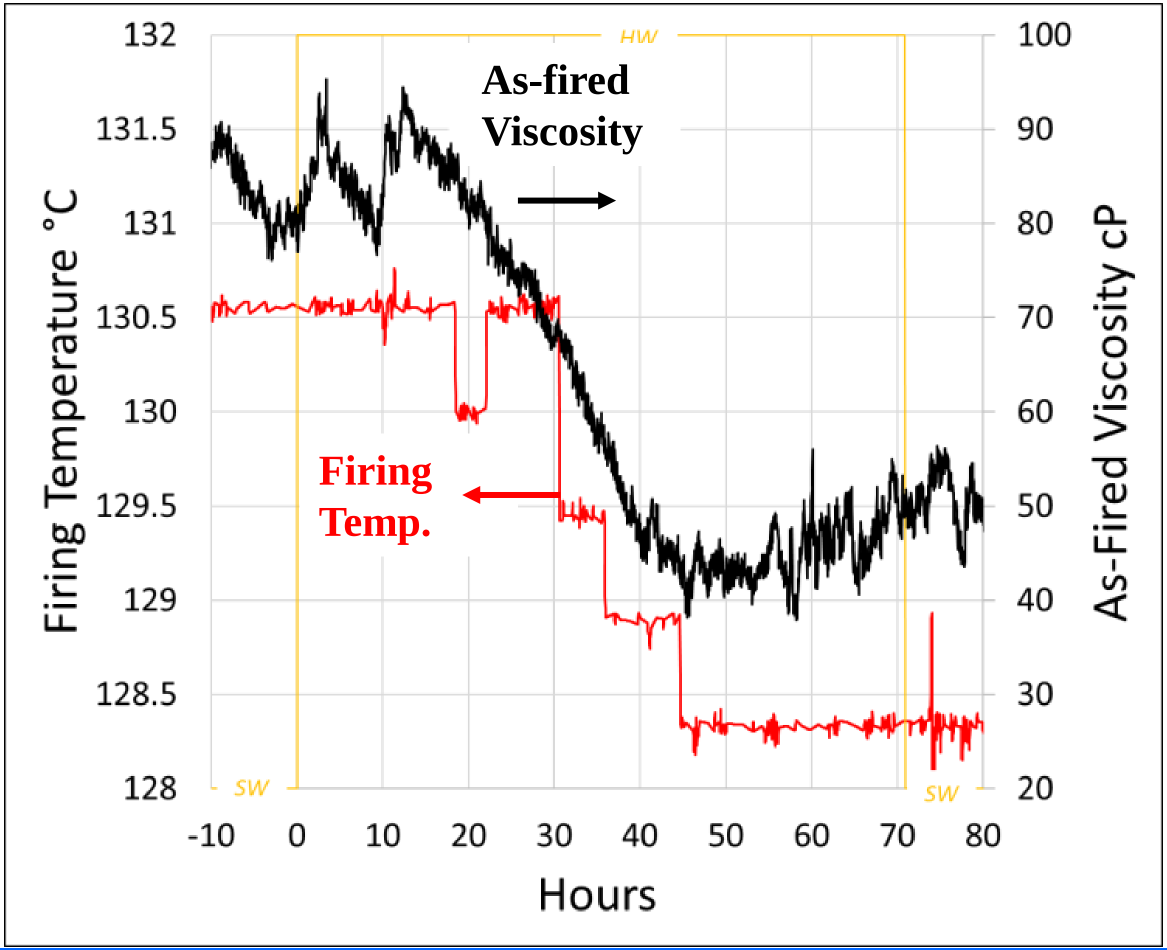
- Organics grouped as SW or HW
  - Yield defines mass of dissolved organics
  - Organics defined as SW or HW
    - Following species (lignin etc. easily added)
  - Both mass and charge followed
  - Soap separation based on sampling campaign

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

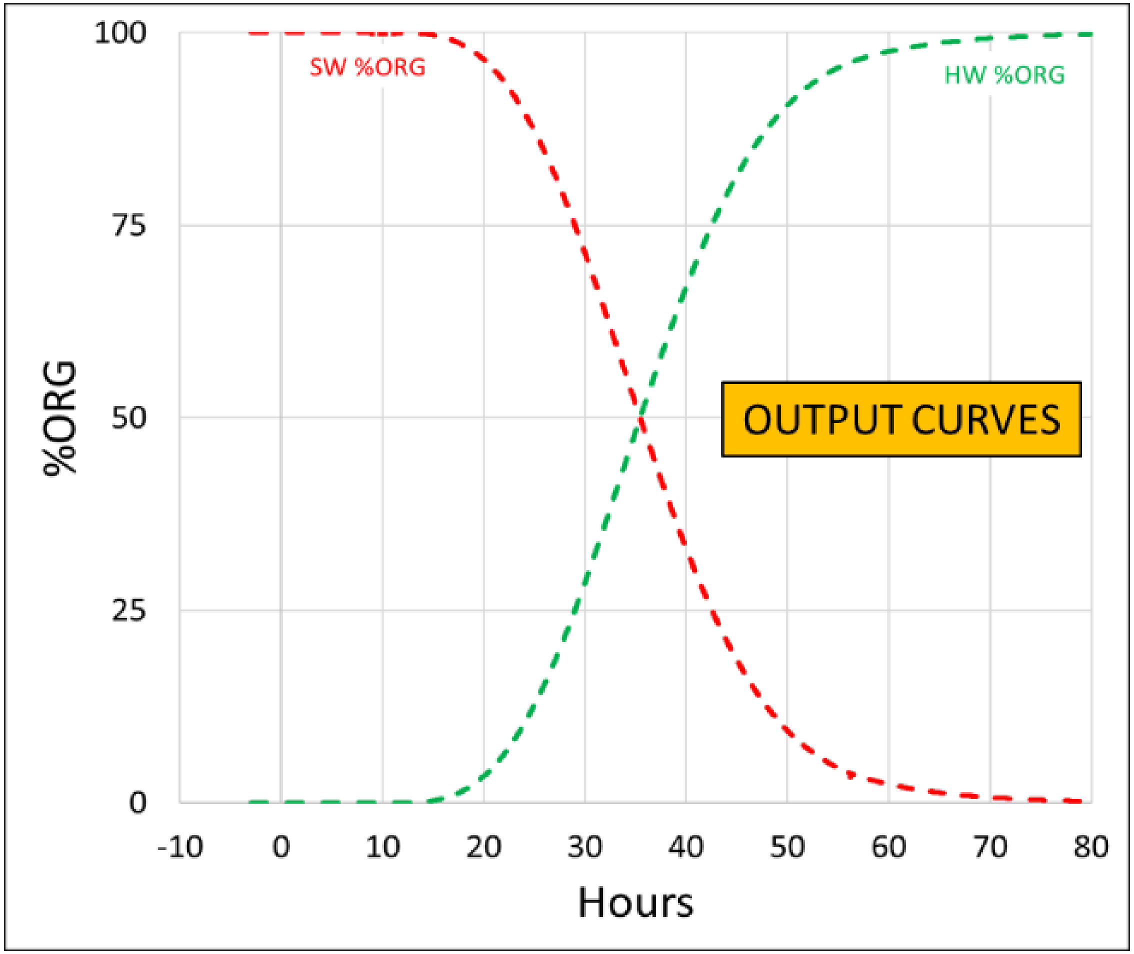
# Model of Mill



# Mill BL Viscosity/Firing Temp SW to HW Transition – Operational Data



# Fraction "SW/HW Organics SW to HW Transition

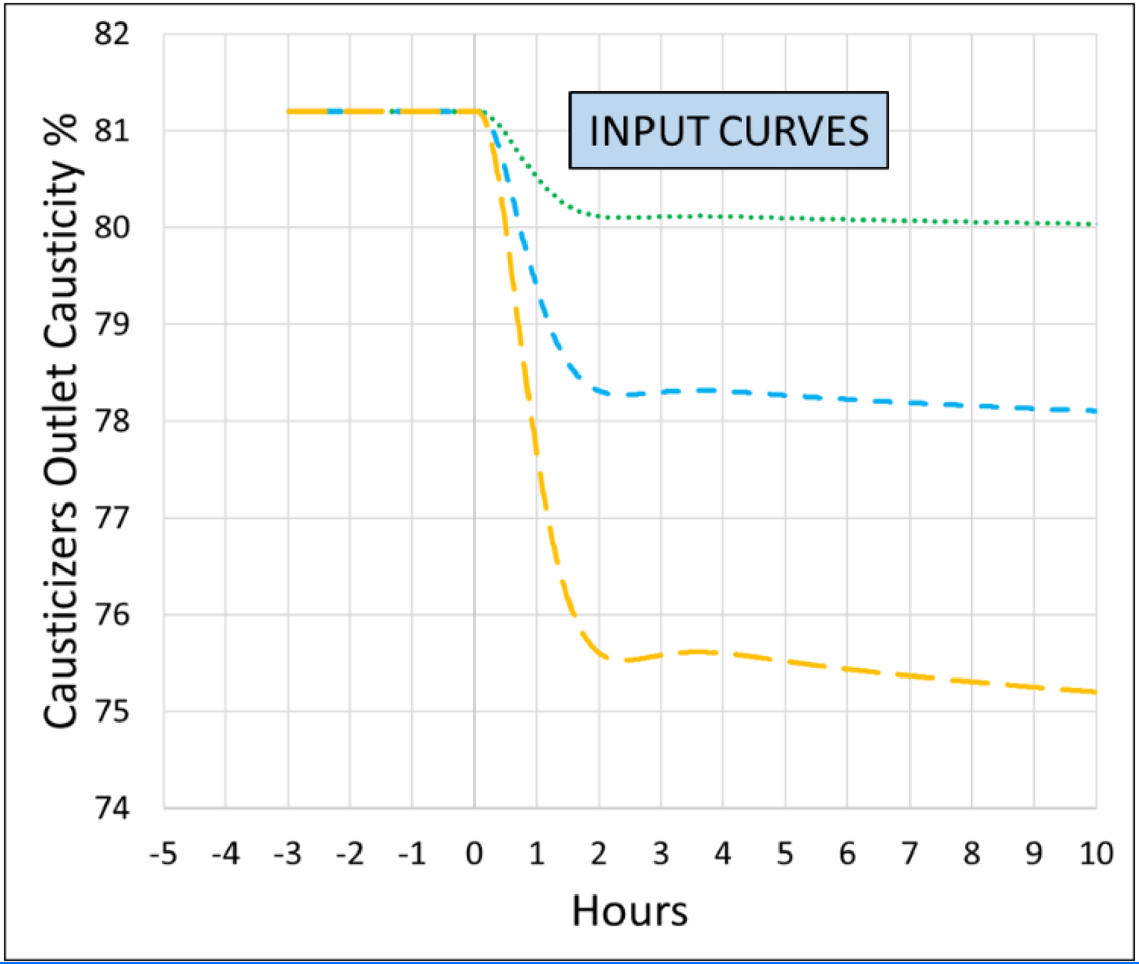


# Lag - Ex. Step Change in Causticity

**<u>Example</u>**

- ☞**Drop in causticity by change in lime addition**

- ☞**Time zero represents change in lime addition rate**

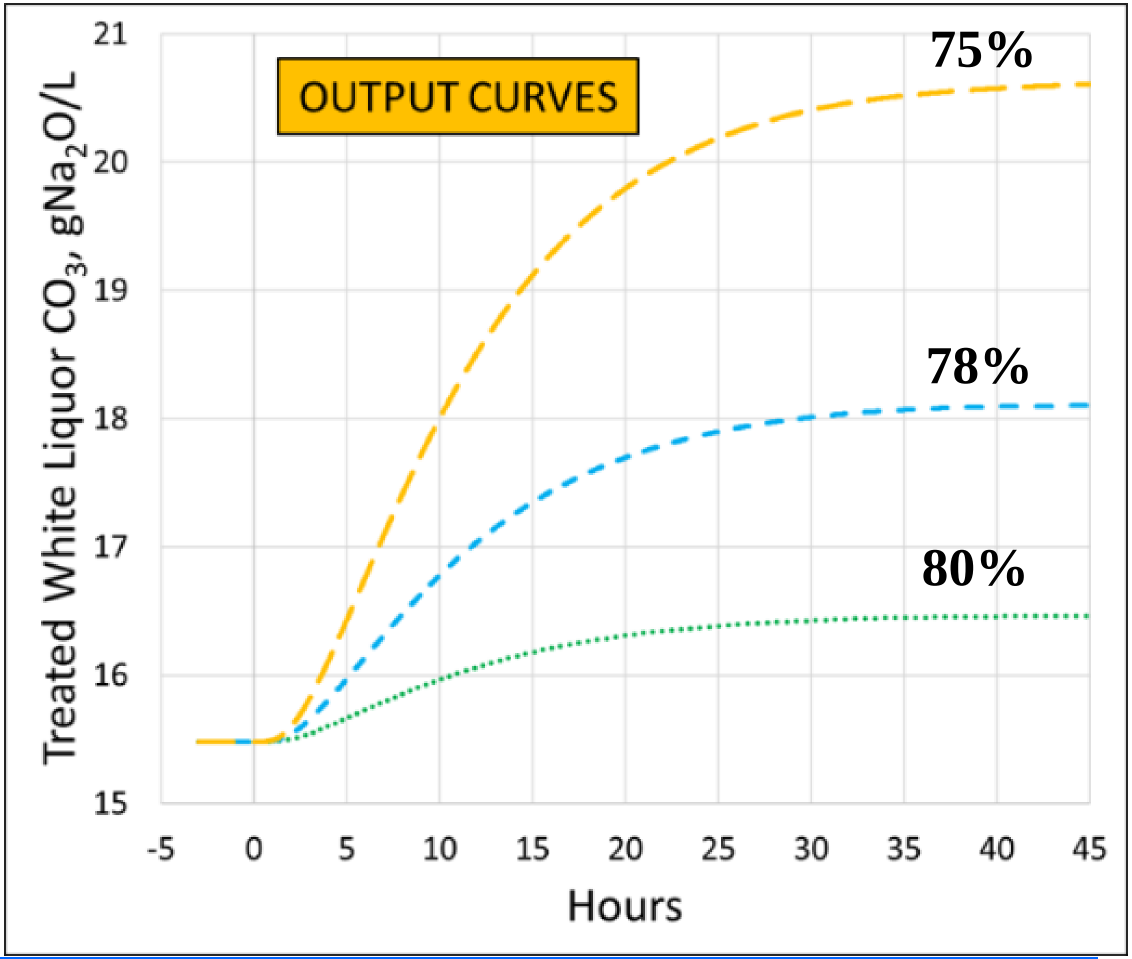


# Change in $CO_3^{2-}$ in WL to Digester

~2.5h before change in WL to digester seen

☞25-35h to reach ~ new steady state

☞WL to digester ↑ so inorganics to recovery boiler ↑

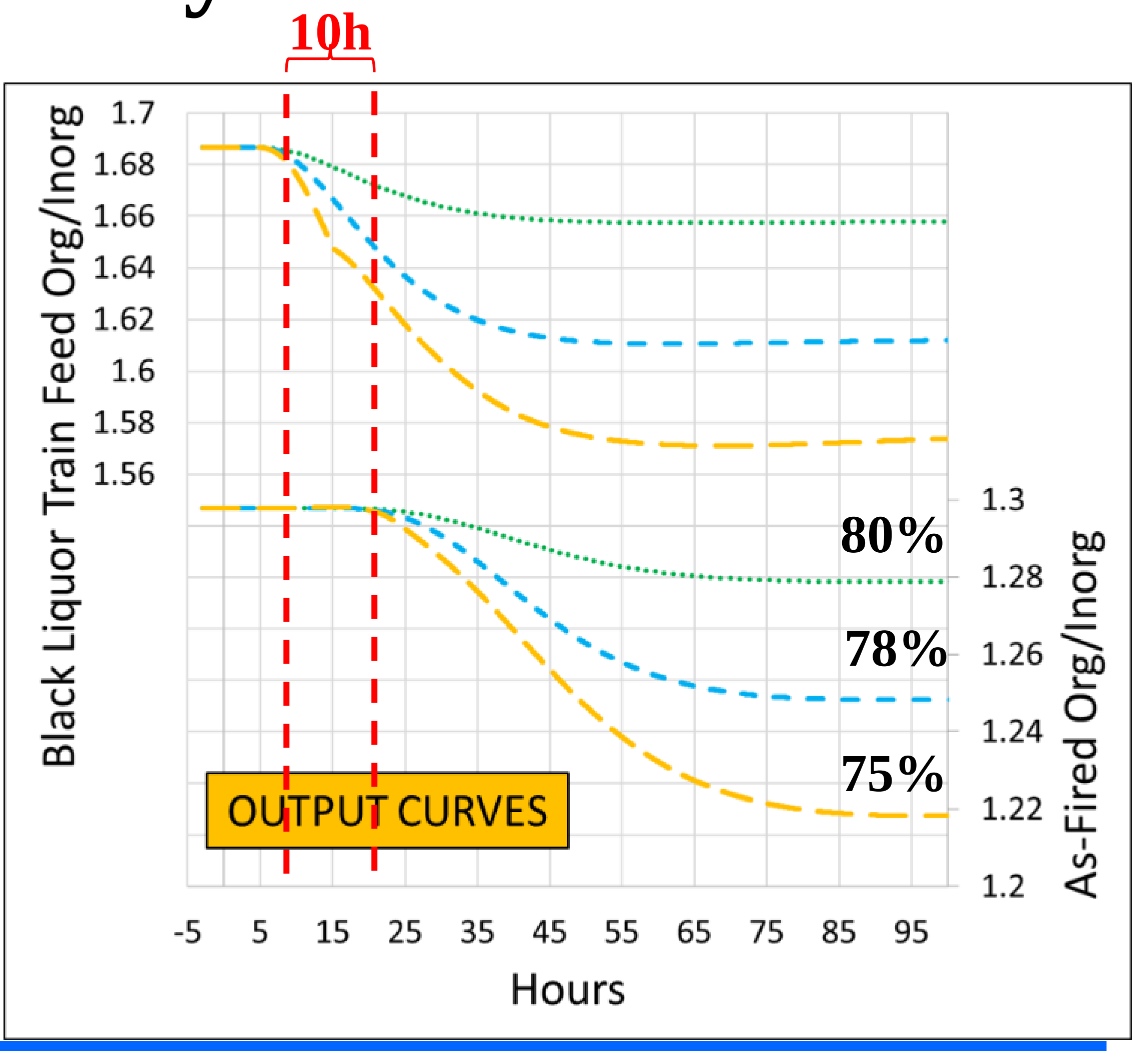


# Effect of Causticity – BL to RB

☞Change in Org/Inorg ratio first seen in BL in ~7.5h

☞Change in BL to RB first seen in ~10h

☞New steady state in BL to recovery boiler ~85h



# Summary - Dynamic Modeling

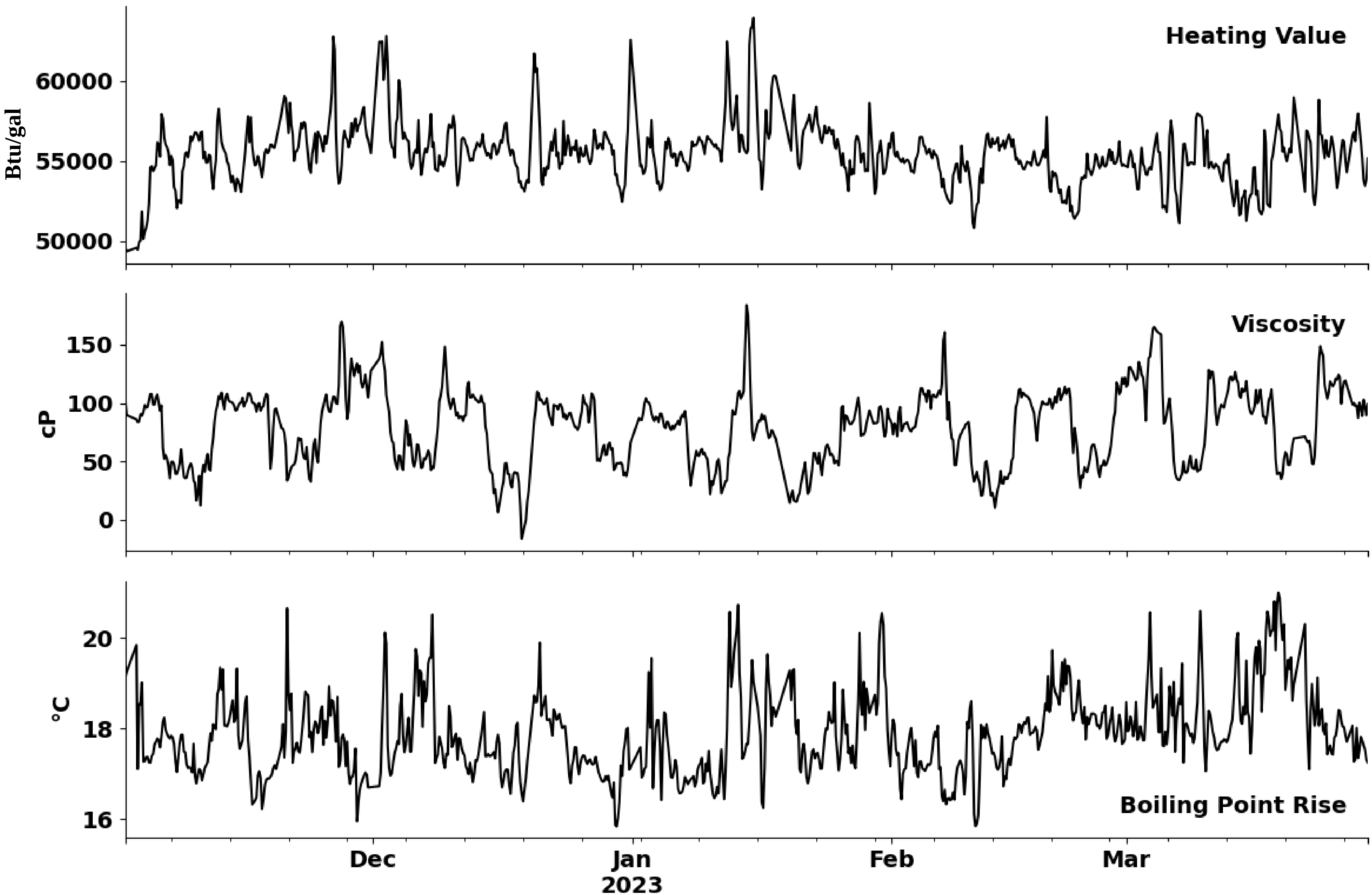
- Dynamic mass balance has potential as ”virtual analyzer” for BL
- Can provide new input for
  - steady operation
  - Machine Learning (or used in parallel with ML)
- Can inform
  - Urgency of addressing an issue
  - Recovery boiler control in the future?

# Prediction of As-Fired Liquor Properties

- Same mill
- 6 months of data (10-min frequency)
  - 21,456 rows x 87 columns
- Modeling Approaches
  - Classic time series modeling
    - Persistence model
    - Autoregressive Moving Average (ARMA)
  - Time series neural networks
    - N-BEATS
    - DeepAR

# Black Liquor Properties

- **HHV**
  - **$O_2$ consumption and solids firing rate.**
  - **Calorimeter measurements to inform mill's model**
  - **Our spot measurements confirmed**
- **Viscosity**
  - **Pump amps correlated to viscosity**
  - **Inline viscometer used to generate a correlation between pump amps and black liquor viscosity**
- **Boiling Point Rise**
  - **Temperature and pressure measurements from 1A evap**


Heating Value
Btu/gal
60000
55000
50000
Viscosity
cP
150
100
50
0
°C
20
18
16
Boiling Point Rise
Dec
Jan
2023
Feb
Mar

# Methodology

- **Models were trained to predict 1-8 h into the future (i.e., prediction horizon)**
  - **The linear filter models were trained only on the first month of data**
  - **Neural networks were trained on the first 3 months of data**

- **Model performances were evaluated with three metrics:**
  - **Coefficient of determination ($R^2$)**
  - **Mean absolute percentage error (MAPE)**
  - **Root mean squared error (RMSE)**

# Linear Filter Models

- **The persistence model:**

**White noise**

$$Y_t = Y_{t-1} + e_t = \frac{1}{1 - q^{-1}} e_t$$

**Shift operator**

- **Autoregressive Moving Average (ARMA) models, e.g.,**

**Previous Model Error**

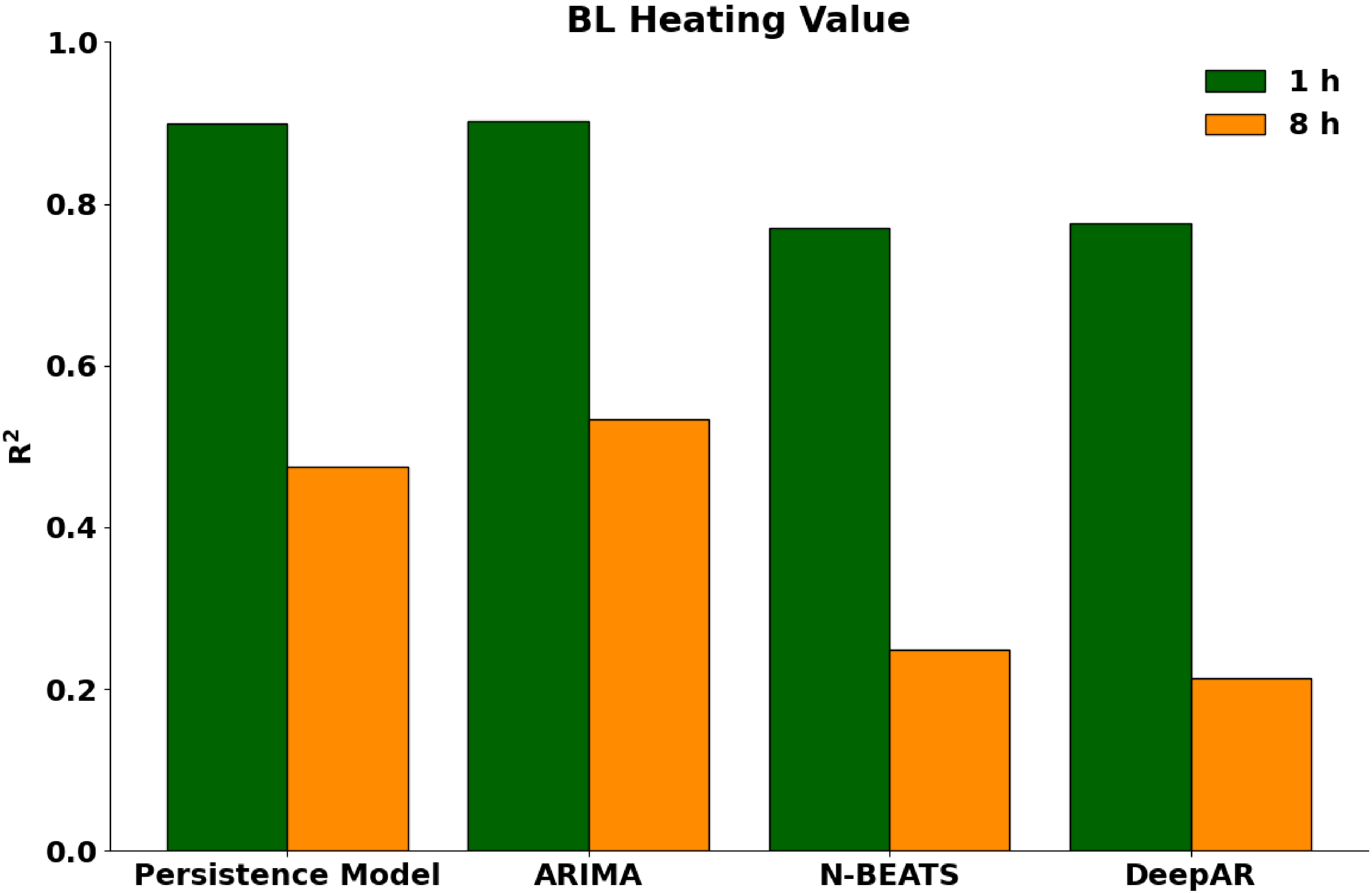
$$Y_t = \phi Y_{t-1} + e_t + \theta e_{t-1} = \frac{1 + \theta q^{-1}}{1 - \phi q^{-1}} e_t$$

# Neural Networks

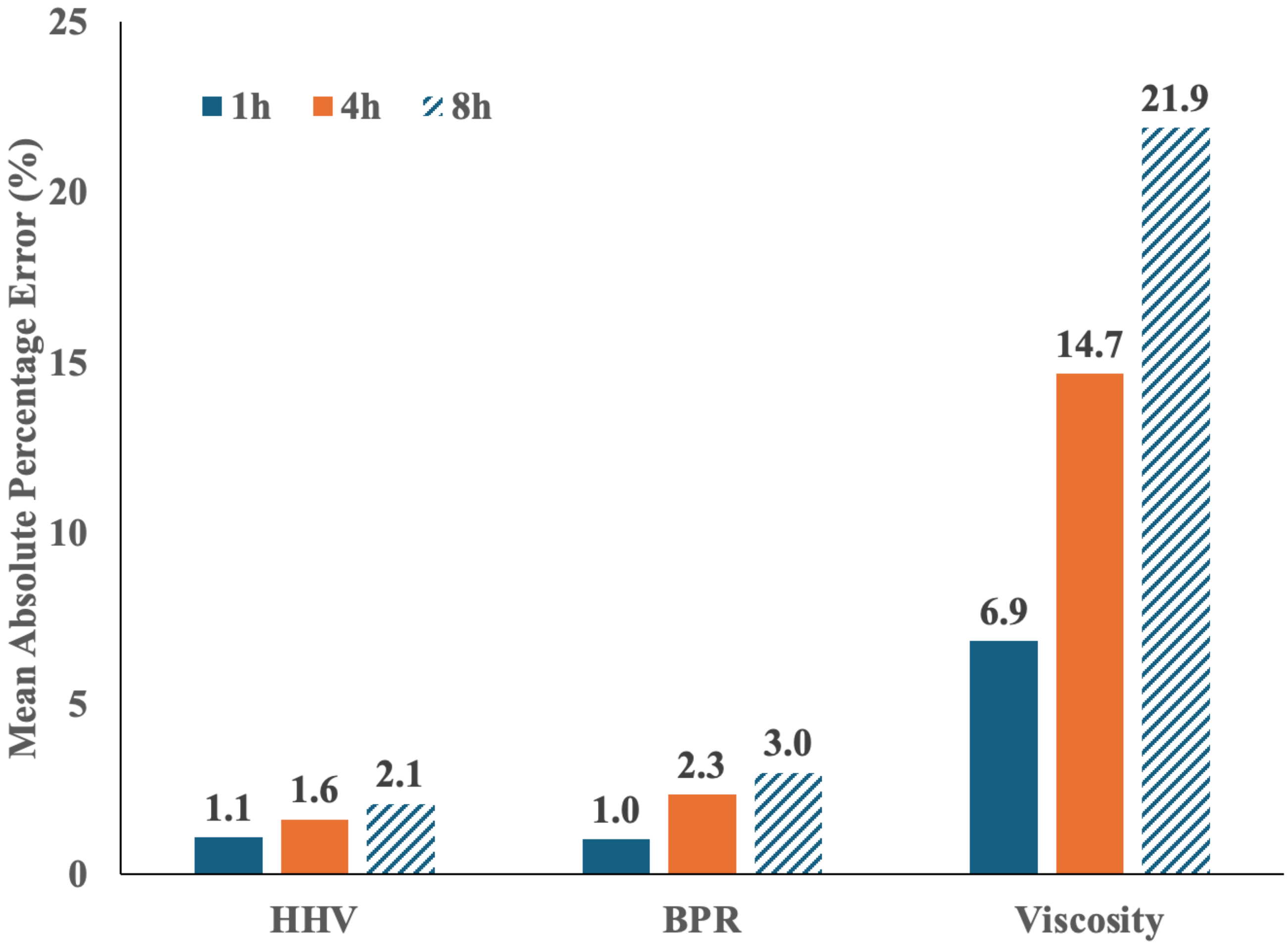
- Two state-of-the-art time series neural networks were considered

- N-BEATS (Oreshkin et al., 2020)
  - Univariate model: only considers past output measurements

- DeepAR (Salinas et al., 2020)
  - Multivariate model: considers past output measurements and external inputs
  - External inputs chosen based on process knowledge


BL Heating Value
1.0
0.8
0.6
0.4
0.2
0.0
$R^2$
1 h
8 h
Persistence Model
ARIMA
N-BEATS
DeepAR

# ARIMA - MAPE


25
20
15
10
5
0
Mean Absolute Percentage Error (%)
1h
4h
8h
1.1
1.6
2.1
1.0
2.3
3.0
6.9
14.7
21.9
HHV
BPR
Viscosity

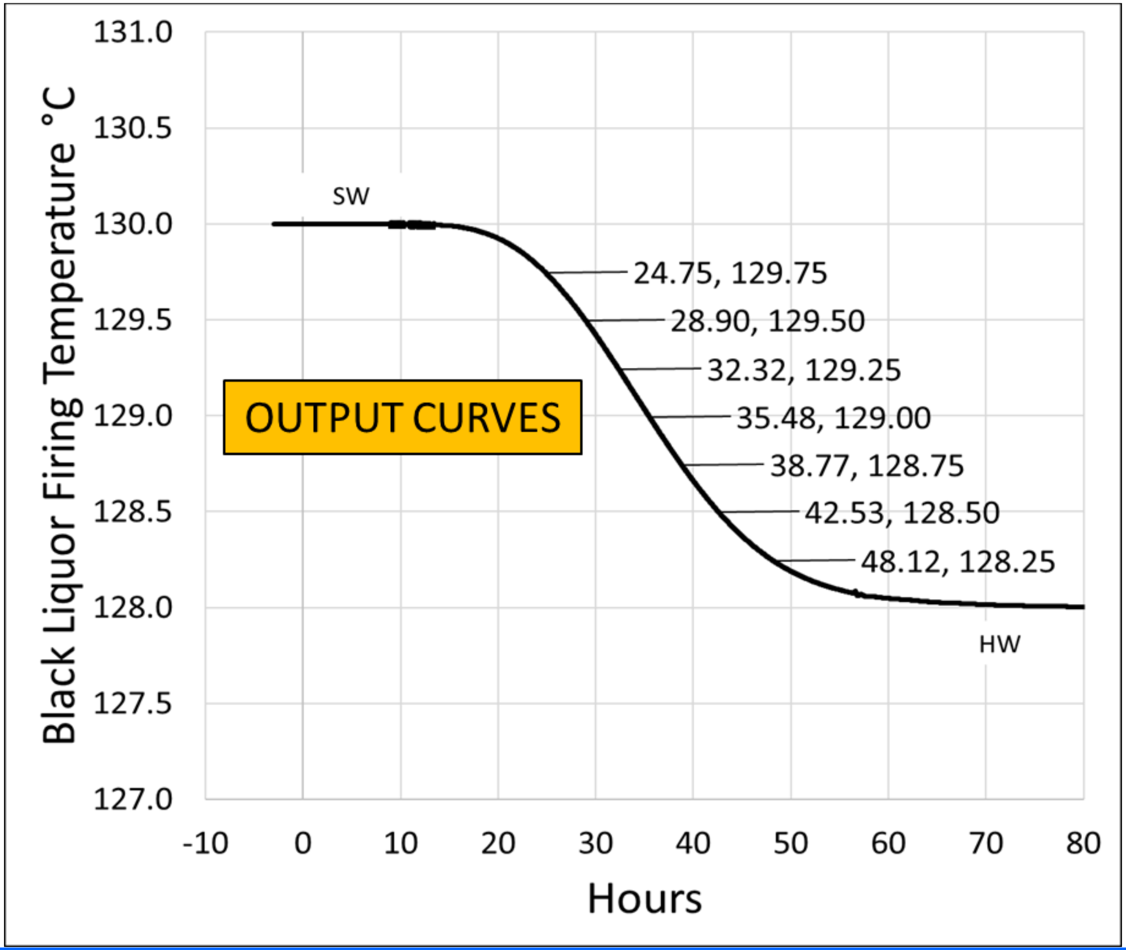
# Conclusions

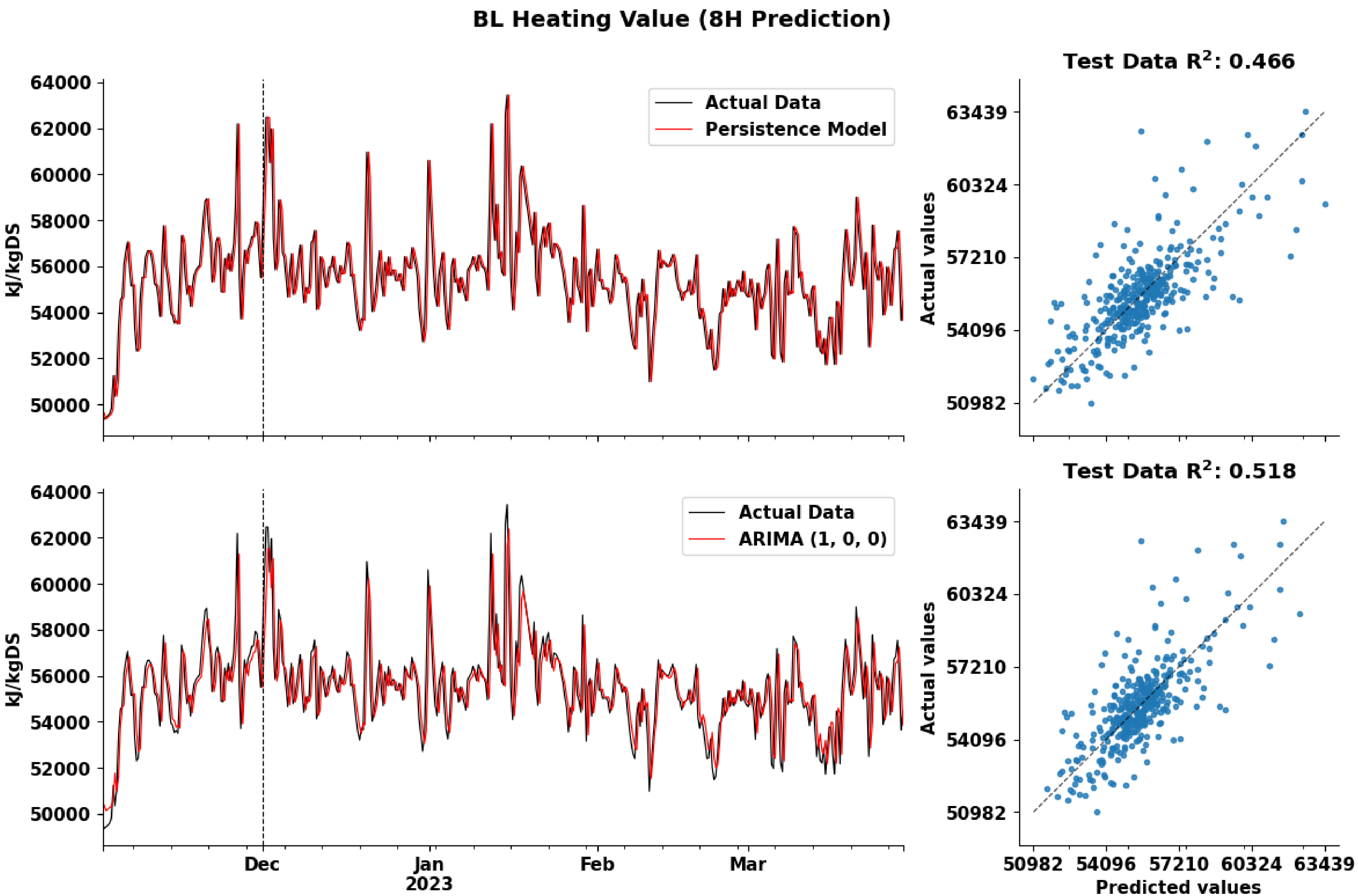
- **As-fired liquor properties can be accurately predicted with linear filter models**
  - **Auto-correlation such that external inputs do not improve prediction**
- **Combined use of phenomenological model & a linear filter model**
  - **Can provide dynamic understanding of BL as a fuel and lead to more stable operation**

# 2025 International Chemical Recovery Conference – Toronto!

- **September 24-26, 2025 (Wed – Fri)**
- **Location: University of Toronto's Chestnut Conference Centre, located at 89 Chestnut Street, Toronto,**
- **Information:**
  - **Website coming soon**
  - **Abstract/Paper deadlines to be announced soon**
  - **Mandeep.Rayat@utoronto.ca>**
  - **Nikolai.DeMartini@utoronto.ca**

# Firing Temp Adjusted to Species Change Example




BL Heating Value (8H Prediction)
Actual Data
Persistence Model
ARIMA (1, 0, 0)
kJ/kgDS
64000
62000
60000
58000
56000
54000
52000
50000
Dec
Jan
2023
Feb
Mar
Test Data $R^2$: 0.466
Test Data $R^2$: 0.518
Actual values
Predicted values
50982
54096
57210
60324
63439

| Unit | Residence Time ($\tau$) | Time between Measurements ($\Delta t$) | Correlation with Input ($1-\rho$) | Autocorrelation ($\rho$) |
|---|---|---|---|---|
| Digester | 12 h* | 1 h | 0.08 | 0.92 |
| Sextuple | 42 min* | 30 min | 0.42 | 0.58 |
| All units between digester feed and liquor guns | 49 h** | 8 h | 0.14 | 0.86 |

***Estimate from Rogerson (2022)**
****Estimate from Lag Estimation Presentation**

$$\rho = \frac{1}{1 + \frac{\Delta t}{\tau}}$$