



# Enhanced Biomass Hydrolysis with Hot Wash Separation

**Melvin P. Tucker, Nick J. Nagle, Edward W. Jennings,  
John Jechura, and Richard T. Elander**

**National Renewable Energy Laboratory  
National Bioenergy Center  
Golden, CO**

2003 AIChE Annual Meeting  
Separation of Processing Streams Derived from  
Renewable Feedstocks (Session 162)

San Francisco, CA  
November 20, 2003



# Outline

- Background
- Reactors and filter
- Integrated pretreatment and “hot-washing” of yellow poplar sawdust and corn stover
- Digestibility of residual cellulose
- Conclusions

# Background

- Lignin affects the enzymatic hydrolysis of pretreated biomass.
- Small amount of lignin is solubilized by dilute acid and steam pretreatments.
- Lignin may re-precipitate upon pretreated solids when cooled.
- Bench scale experiments show solubilized lignin can be removed by a flowing liquid medium at elevated temperatures.
- Enhanced enzymatic hydrolysis of residual cellulose to glucose.

# Background

- Present pretreatment process is a dilute - acid prehydrolysis step followed by enzymatic hydrolysis of the residual cellulose to glucose.
- One possible improvement to this process is the inclusion of a "hot wash" step following the dilute-acid prehydrolysis.
- "Hot wash" concept developed at NREL (U.S. Pat. No. 6,228,177).

# Background

## Related Work

- Univ. Hawaii (*Antal et al.*)
  - Liquid hot water/steam in an immersion/percolation reactor
    - Batch steam and LHW immersion
    - LHW with intermittent addition and removal
  - Enhanced xylan solubilization, xylose recovery (oligomers), lignin solubilization, and enzymatic digestibility, especially at higher L:S ratios (>10:1)

# Background

## Related Work

- Dartmouth College—CAFI (Wyman *et al.*)
  - Liquid hot water and dilute to very dilute sulfuric acid
  - Batch, flowthrough, and start-stop flow regimes
  - Relates xylan removal, xylose recovery, monomer:oligomer ratio, lignin removal to flow regime
    - Function of flow rate, flow velocity, L:S, acid conc., *etc.*

# Background

## This work

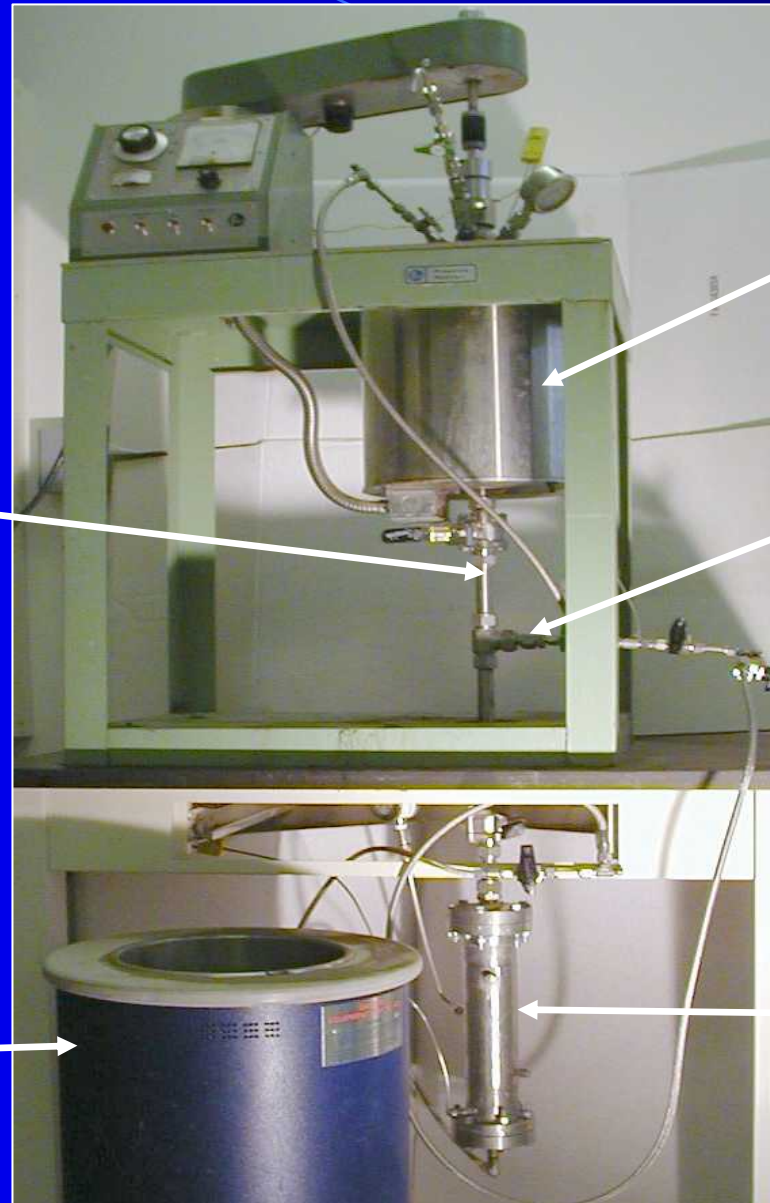
- Outgrowth of flowthrough percolation "wonderwood" process
  - Greater xylan and lignin removal, higher xylose yields, resulting in enhanced enzymatic digestibility
- Technoeconomic analysis identified that high L:S ratio is a "show stopper"
  - Dilution effects
  - Steam demands to heat up required liquid volumes in pretreatment

# This Work

- Decouple the pretreatment and separation/washing
  - High solids pretreatment (>25% solids)
  - "Hot" separation and washing
    - $Temp_{\text{pretreat}} > Temp_{\text{s/w}} > Temp_{\text{lignin phase trans.}}$
  - Validated in bench-scale device
  - Scaled to a pilot-scale system



# Bench-Scale "Hot Wash" Test System



Stirred Parr Reactor  
(1 L)--inside  
heating mantle

Preheated Wash  
Liquor Addition

Pneumapress  
Filter Test Unit--  
inserted in  
heated sand bath  
during operation

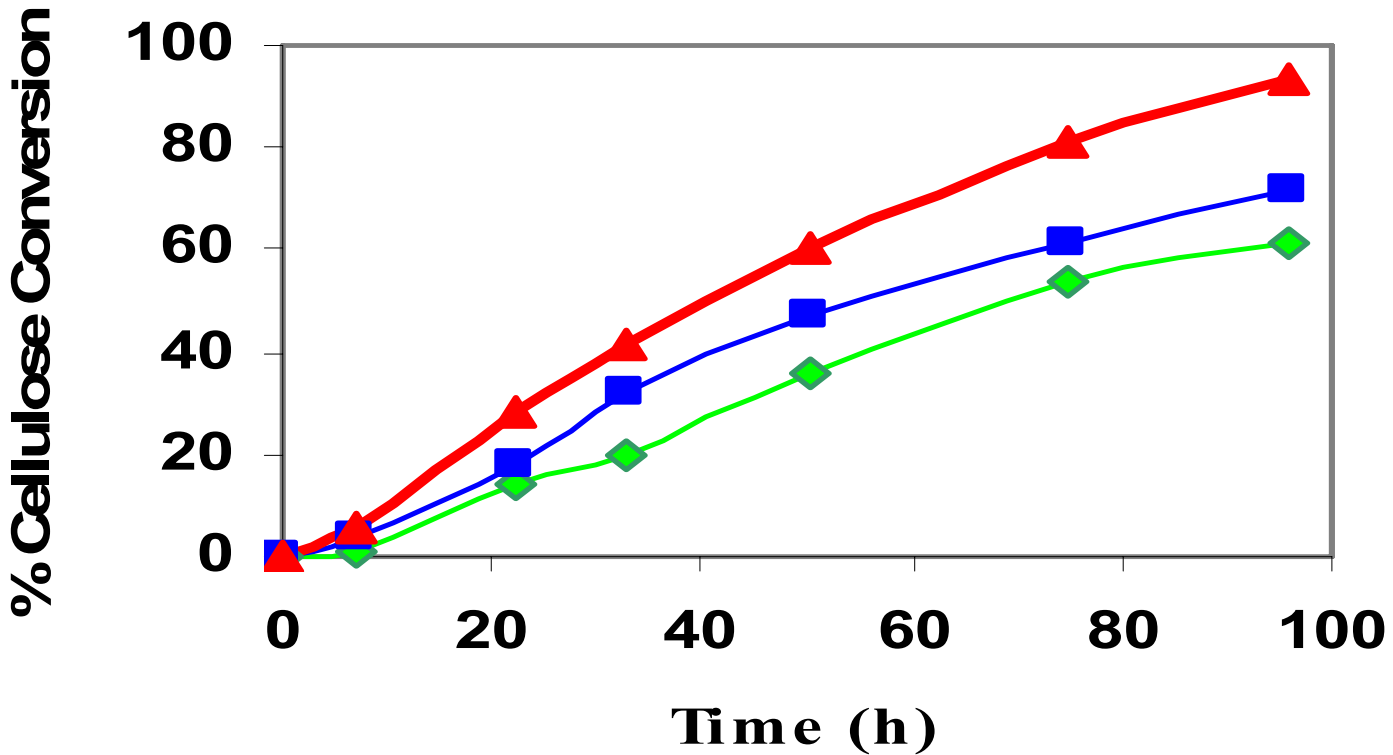
Piping and Valve  
for Elevated  
Temperature  
Transfer from  
Parr Reactor to  
Pneumapress  
Filter Test Unit

Heated Sand  
Bath

# Hot Wash Process Configuration

- Separation/washing can occur at lower temperature than pretreatment reaction
  - ~160-200°C for pretreatment reaction
  - ~130-140°C for separation/washing

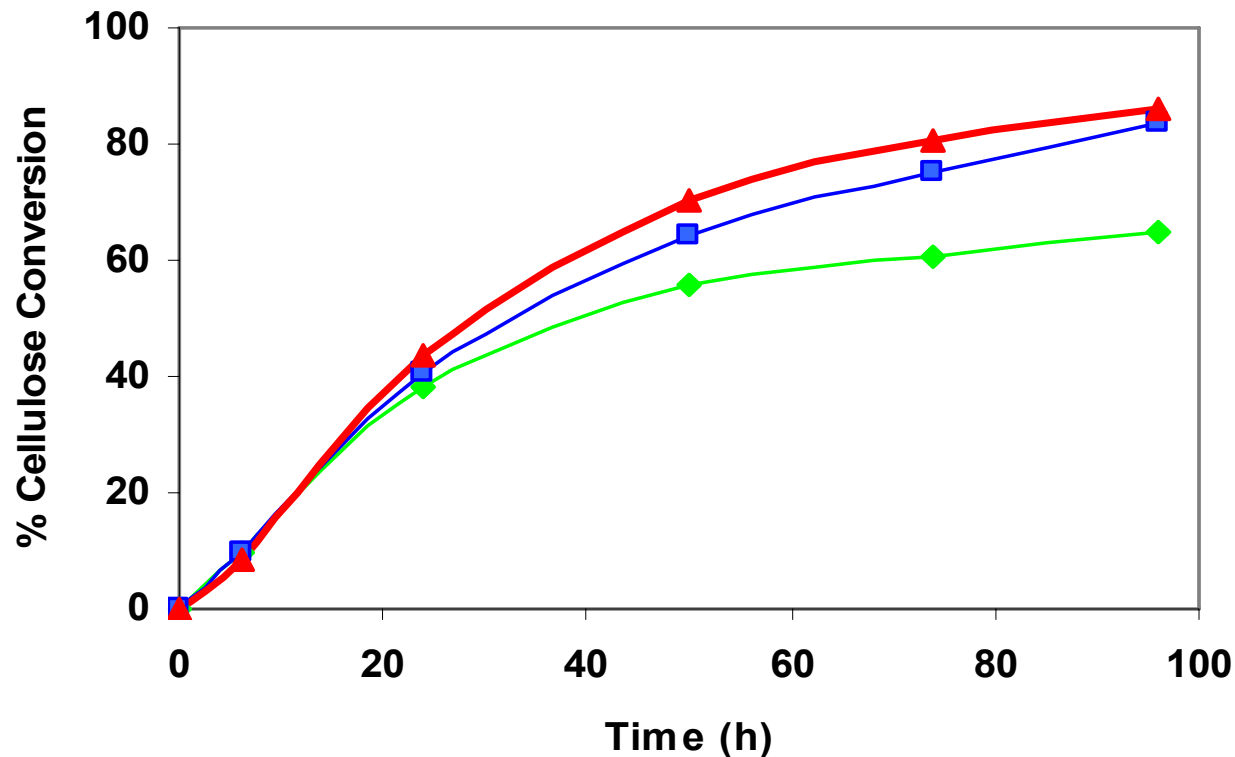
# Enzymatic Digestibility of Hot Washed Pretreated Biomass from Bench Scale Equipment Hardwood (Yellow Poplar)



- ◆— No Separation or Washing
- Hot Separation Only
- ▲— Hot Separation and Washing -- 10:1 L:S Ratio

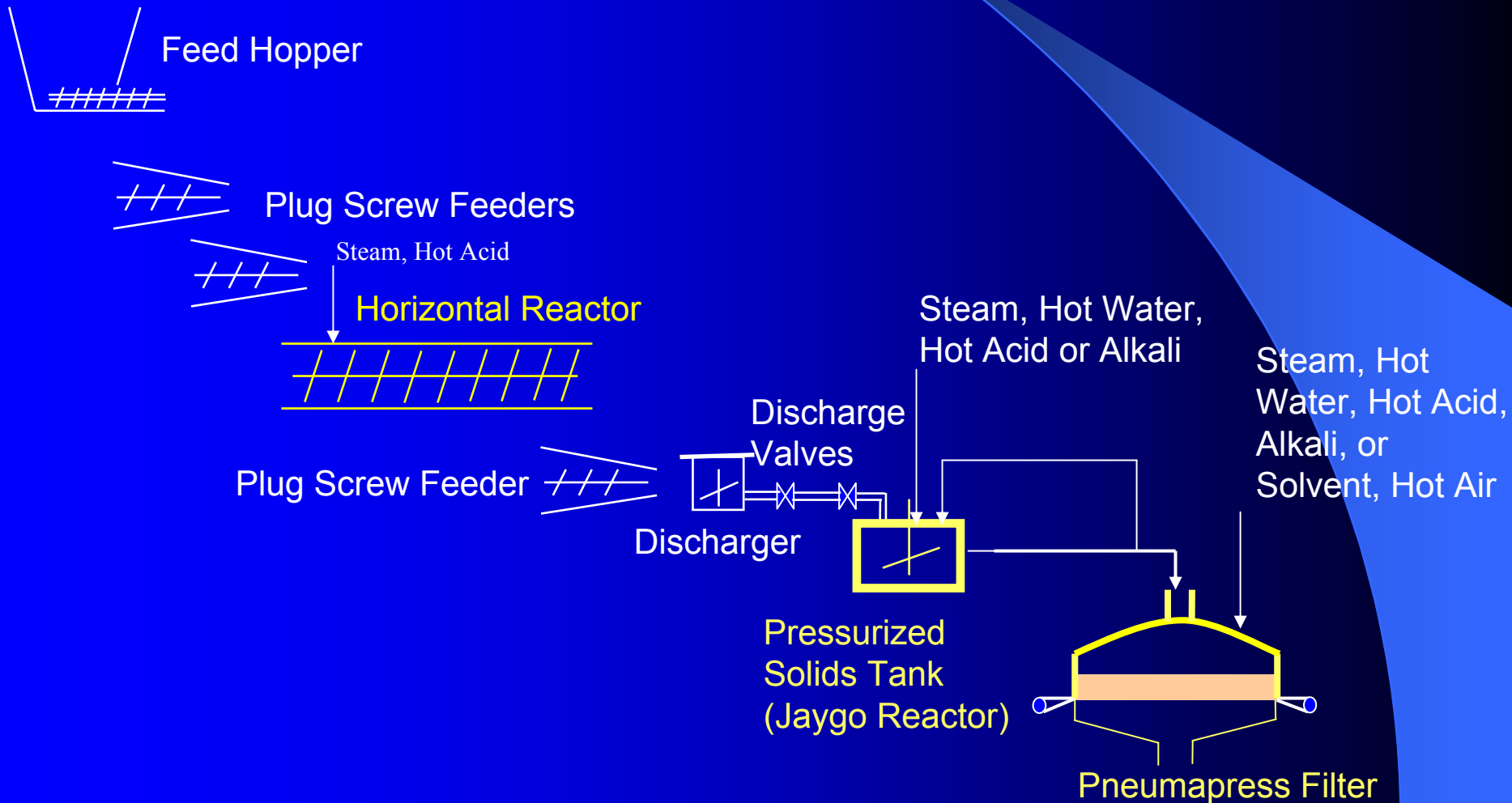
# Enzymatic Digestibility of Hot Washed Pretreated Biomass from Bench Scale System

## Corn Stover



- ◆ No Separation or Washing
- Hot Separation Only
- ▲ Hot Separation and Washing--12.5:1 L:S Ratio

# Pilot Scale "Hot Wash" System



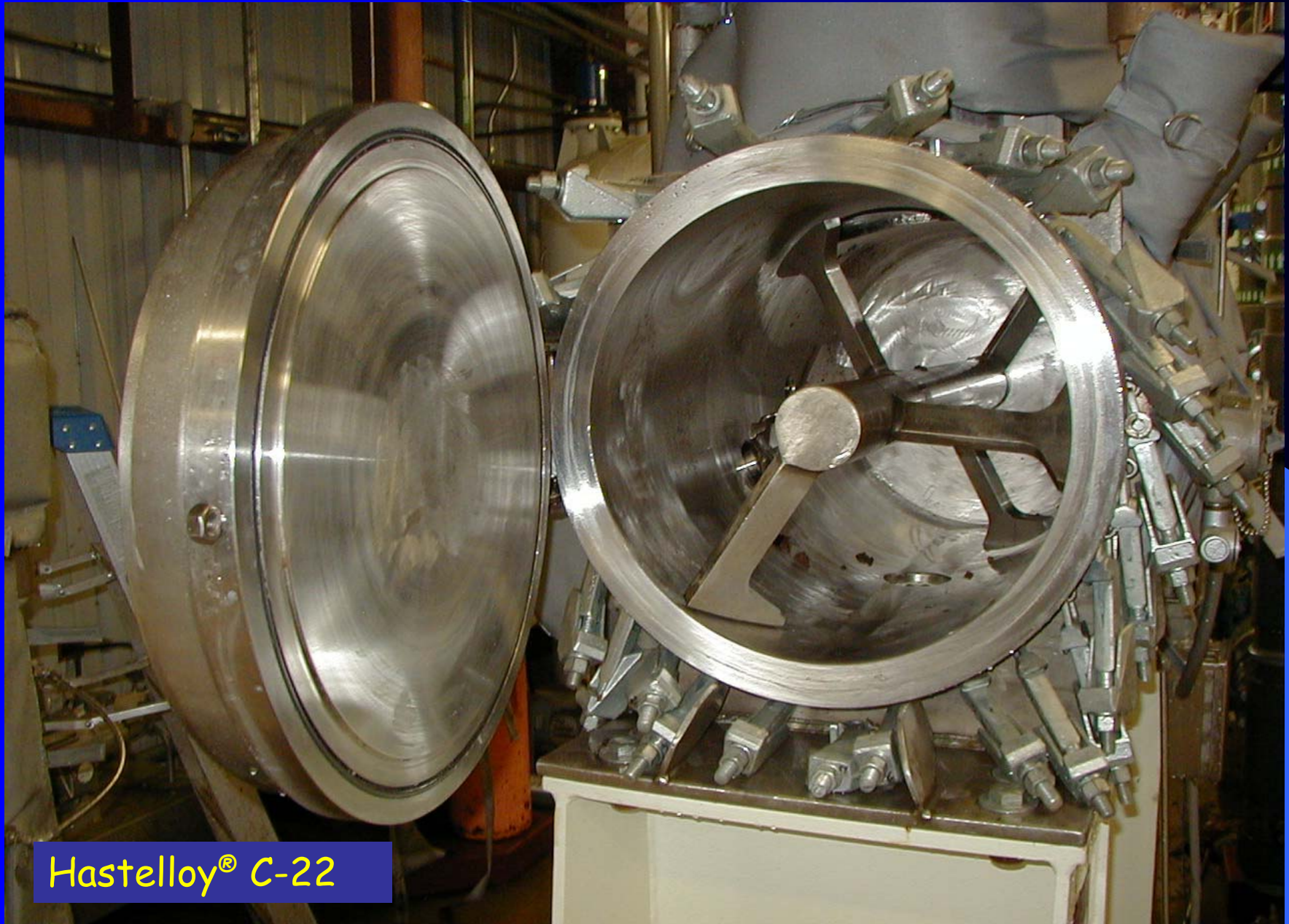
# Sunds Horizontal Screw Reactor



Hastelloy® C-2000 allows pretreatment with other catalysts including hot dilute acid, hot dilute alkali, hot dilute solvents, *etc.*



# Jaygo paddle type batch reactor



Hastelloy® C-22

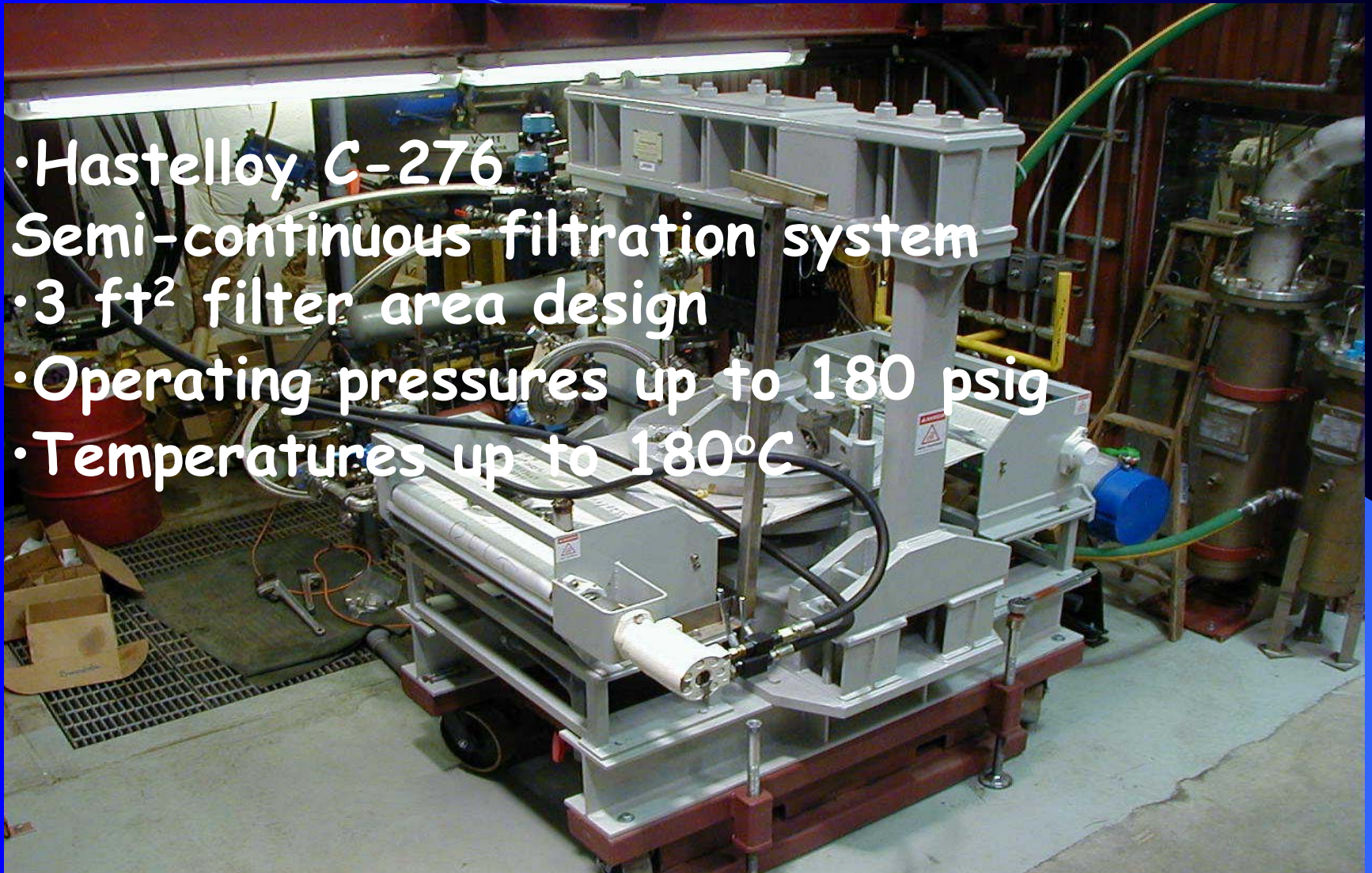


# Pneumapress<sup>®</sup> Automatic Pressure Belt Filter

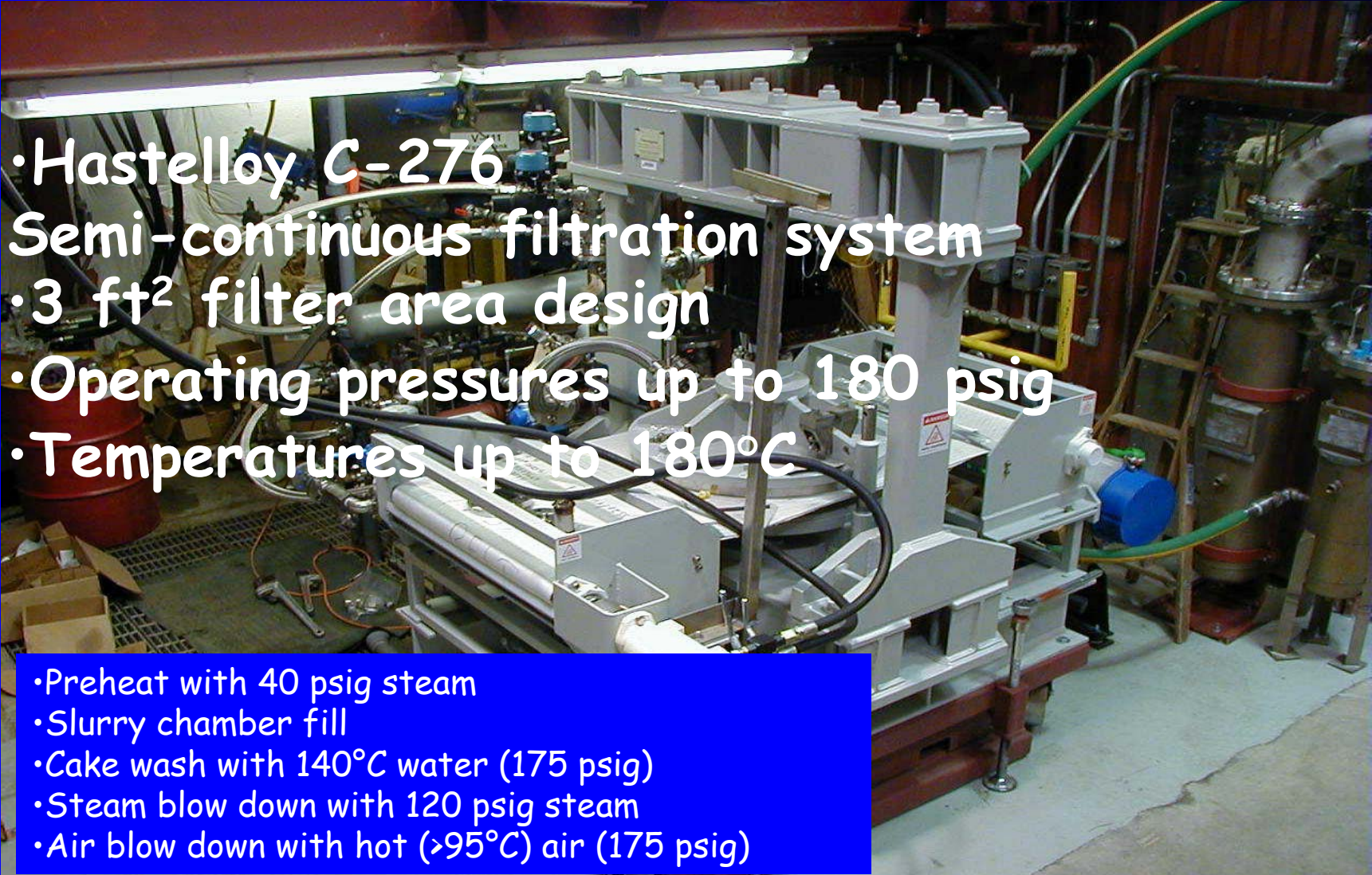




- Hastelloy C-276
- Semi-continuous filtration system
- 3 ft<sup>2</sup> filter area design
- Operating pressures up to 180 psig
- Temperatures up to 180°C



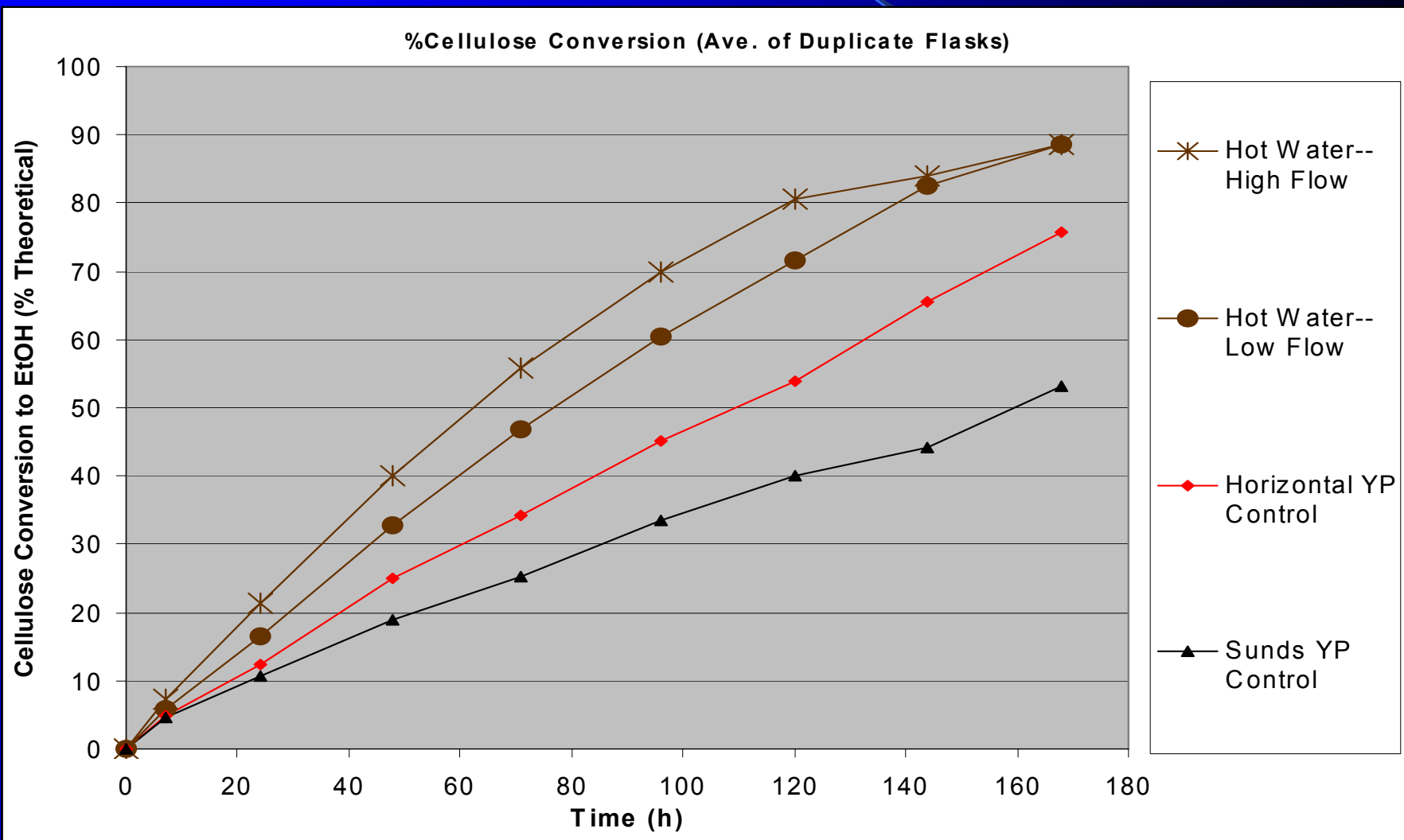


- 
- Hastelloy C-276
  - Semi-continuous filtration system
  - 3 ft<sup>2</sup> filter area design
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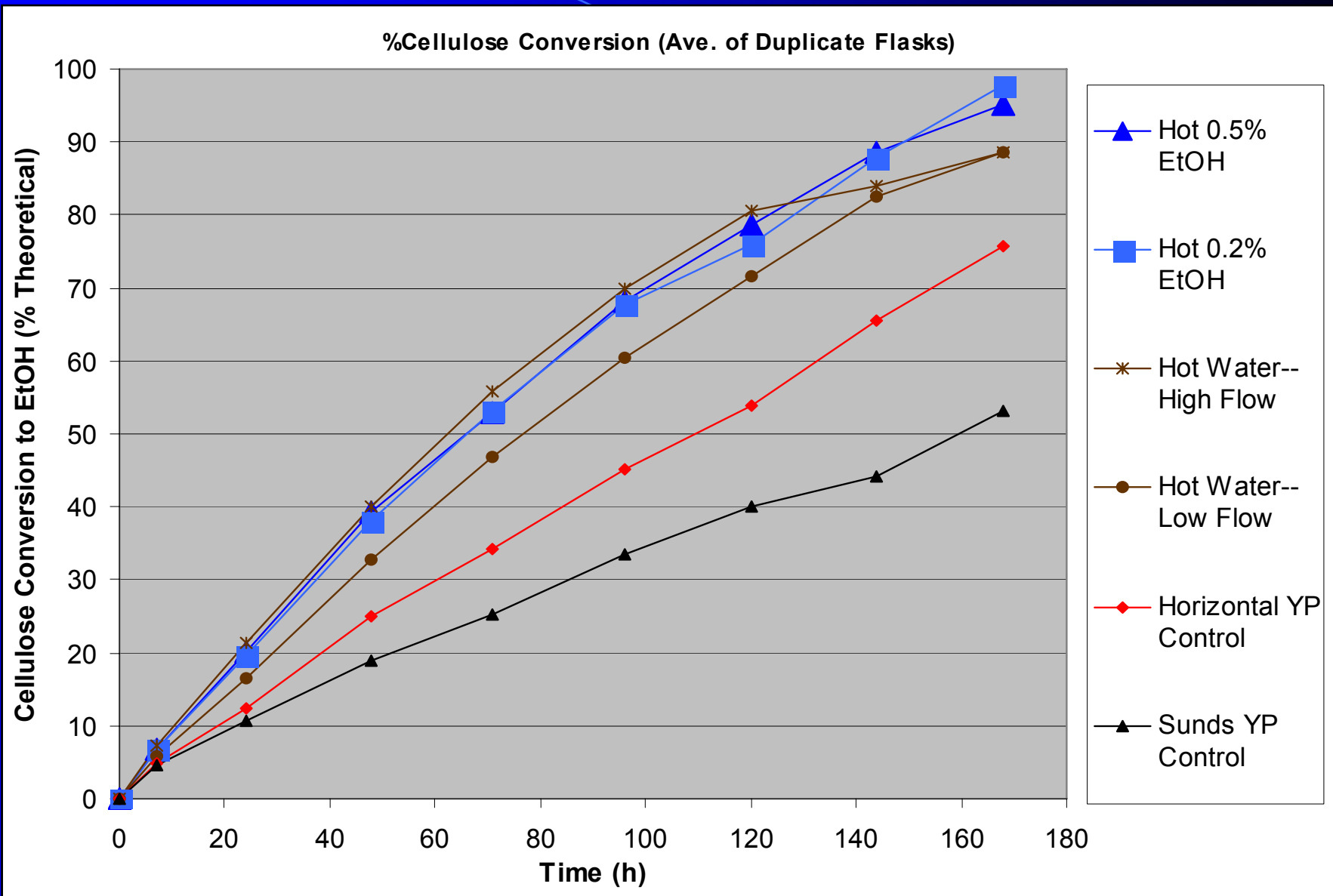
- Preheat with 40 psig steam
- Slurry chamber fill
- Cake wash with 140°C water (175 psig)
- Steam blow down with 120 psig steam
- Air blow down with hot (>95°C) air (175 psig)

# Digestibility of "Hot Washed" Pretreated Yellow Poplar from Pilot Scale System

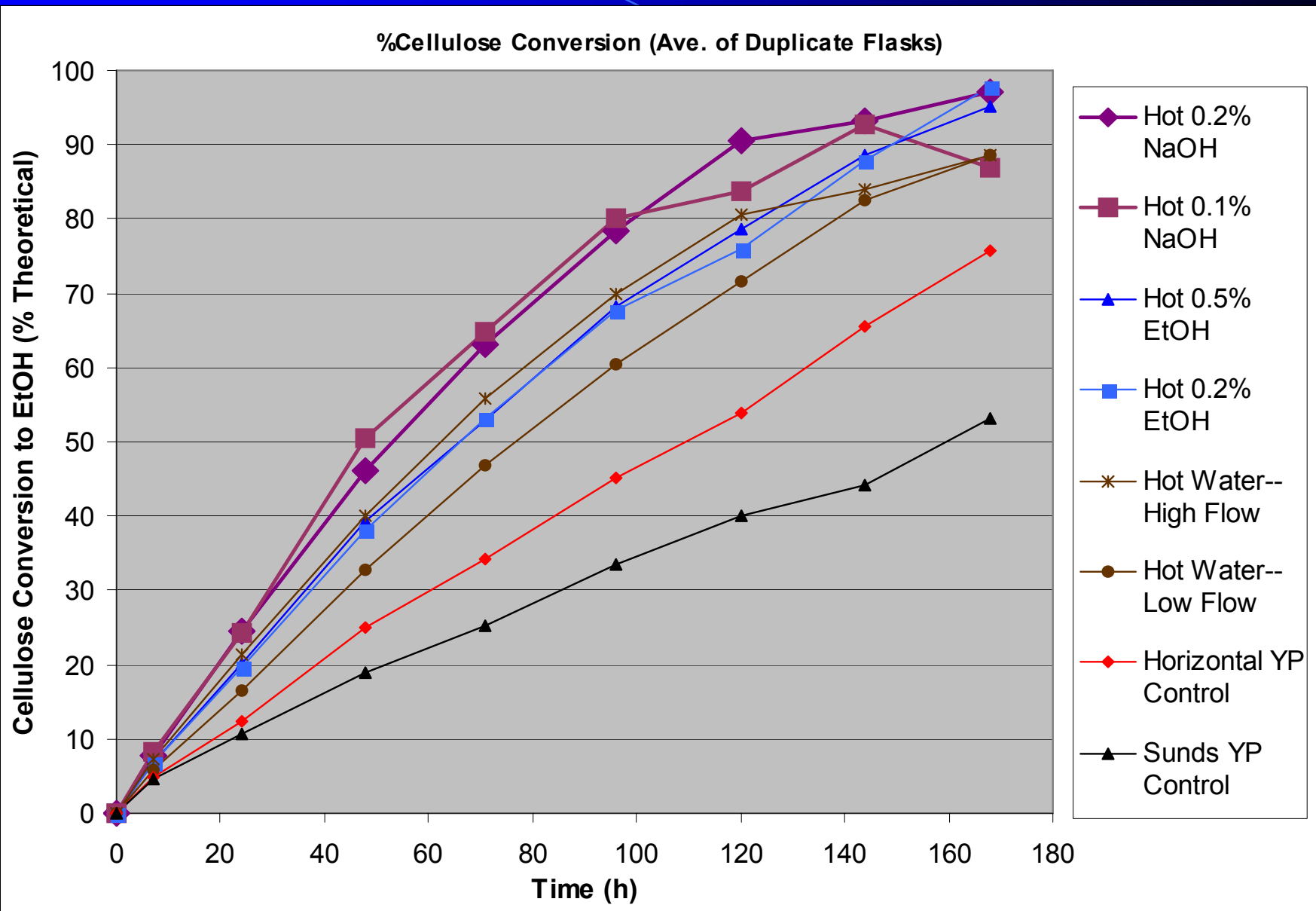
- SSF of Pretreated Yellow Poplar (175°C, 0.7% H<sub>2</sub>SO<sub>4</sub>, ~6 min)
- Cellulase loading: 20 mg protein/g cellulose (Genencor Spezyme CP) (~5 FPU/g cellulose)



# SSF Digestibility of "Hot dilute Ethanol Washed" Pretreated Yellow Poplar from Pilot Scale



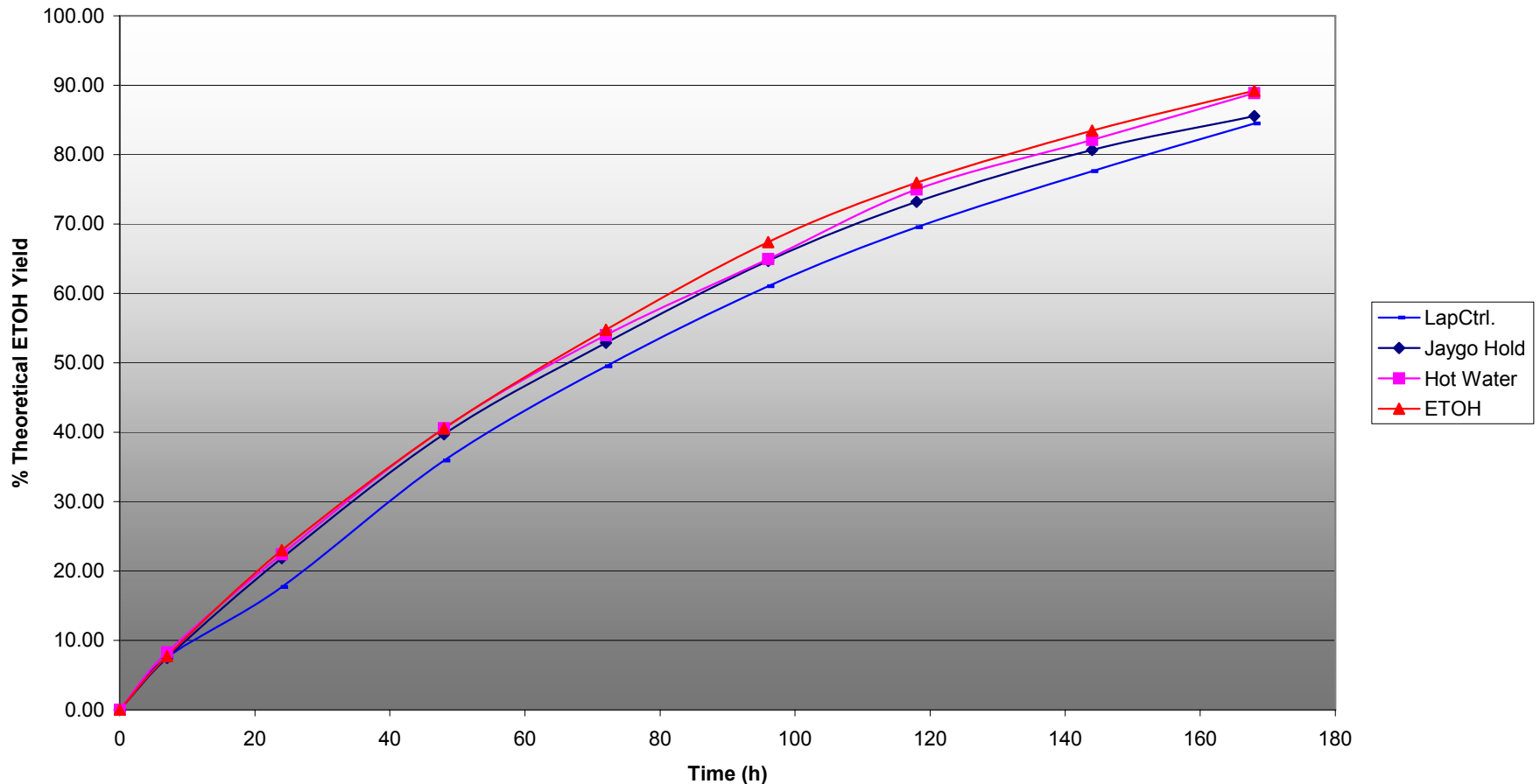
# SSF Digestibility of "Hot dilute Alkali Washed" Pretreated Yellow Poplar from Pilot Scale



# SSF Digestibility of Pilot-Scale "Hot Washed" Corn Stover from Pilot Scale System

- SSF of Corn Stover Pretreated in Jaygo Reactor(170°C, 0.5% H<sub>2</sub>SO<sub>4</sub>, 8 min)
- Hot washed at ~140°C
- Cellulase loading: 12 mg protein/g cellulose (Genencor Spezyme CP) (~3 FPU/g)

Corn Stover  
Cellulose Conversion





# Sunds Vertical Hydrolyzer



Zirconium highly resistant to strong acids (*i.e.*  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , acetic, formic, lactic, *etc.*) and strong bases

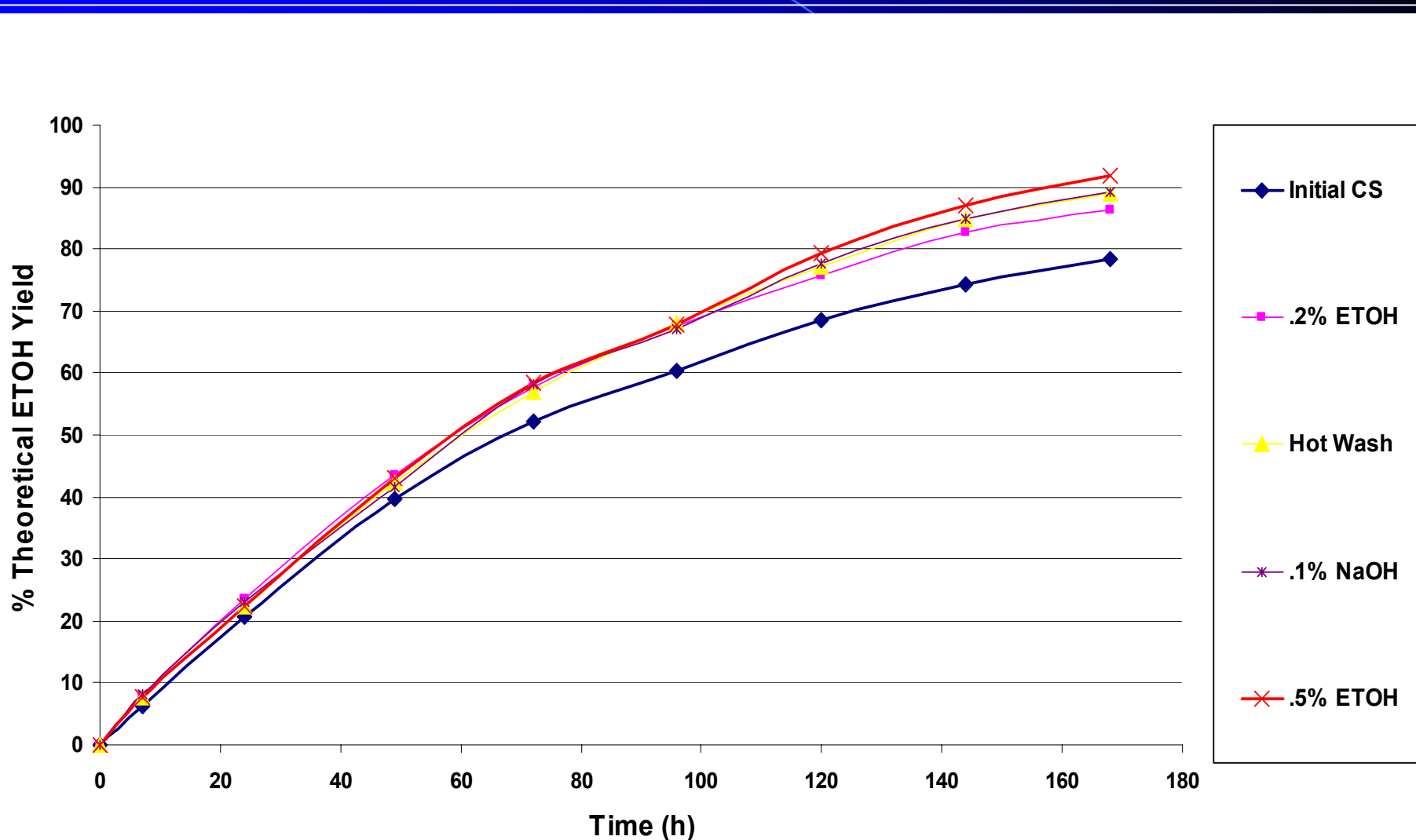
# SSF Digestibility of Pilot-Scale "Hot Washed" Corn Stover

SSF of Sunds Vertical Reactor Pretreated Corn Stover (165°C-190°C, 1% H<sub>2</sub>SO<sub>4</sub>, ~5-8 min)

Pretreated solids allowed to cool before hot washing

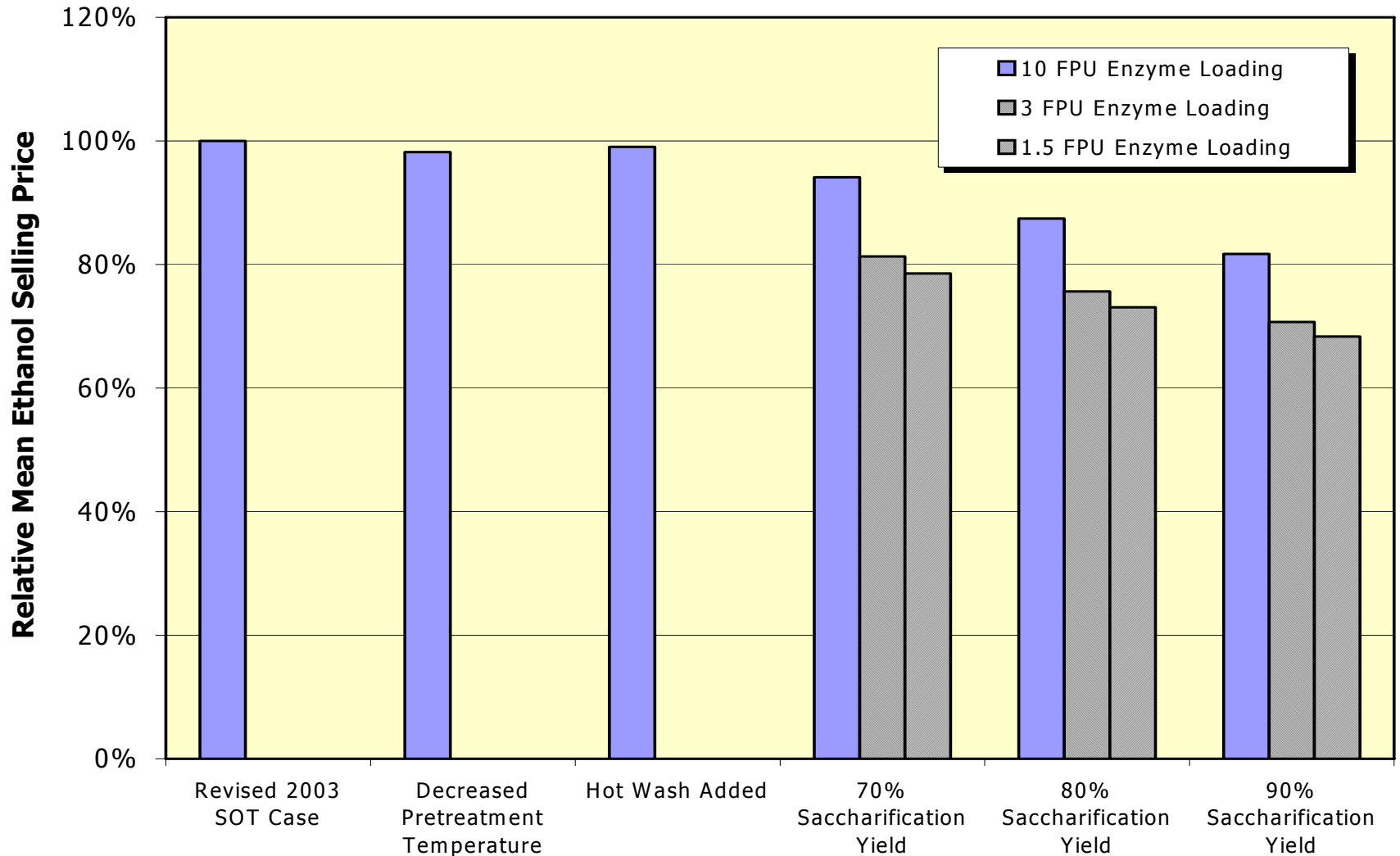
Hot washed at ~140°C

Cellulase loading: 12 mg protein/g cellulose (Genencor Spezyme) (~3 FPU/g)





# Economic Analysis of Hot Wash Process



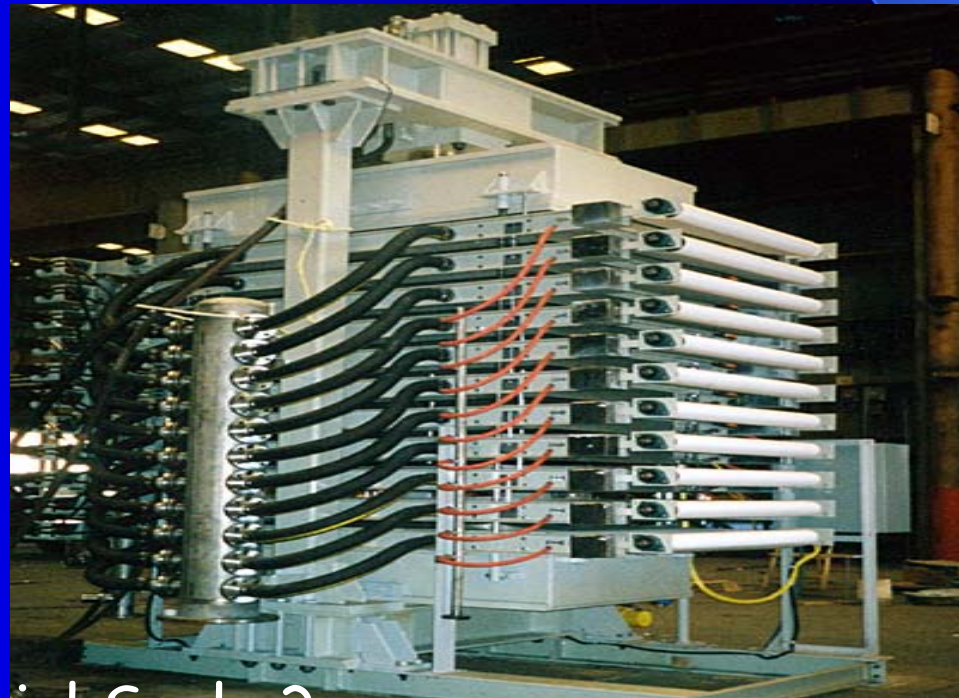
# Hot Wash Filters



Bench Scale



Pilot Scale



Commercial Scale ?

# Conclusions

- Integrated pilot-scale “hot washing” system installed at NREL.
- “Hot washing” pretreated YP increased digestibility from 74% to 97%
- Low enzyme loadings (5-FPU/g of cellulose).
- “Hot washing” pretreated CS increased digestibility of cellulose from 78% to 90%.
- Low enzyme loadings (3-FPU/g of cellulose).
- Lower severity dilute-acid pretreatments of YP and CS gave high enzymatic digestibility of “hot washed” residues.

# Conclusions

- “Hot washing” cooled pretreated corn stover significantly increased the digestibility of the residual cellulose.
- Selective washing processes can produce lignin-based co-products.
- Optimized conditions for Pneumapress solid/liquid separation could reduce time required for substrate bioconversion.
- Lower severity pretreatments may be achieved in less expensive pretreatment reactors
- High enzymatic digestion of the residual cellulose to glucose for fermentation to other bio-based products.

# Acknowledgements

U.S. Department of Energy  
Office of the Biomass Program



Steve Benesi, Patrick Costelloe, Tony Miller  
Pneumapress Filter Corp., Richmond, CA