

# Pretreatment of Wood to Promote Enzymatic Hydrolysis

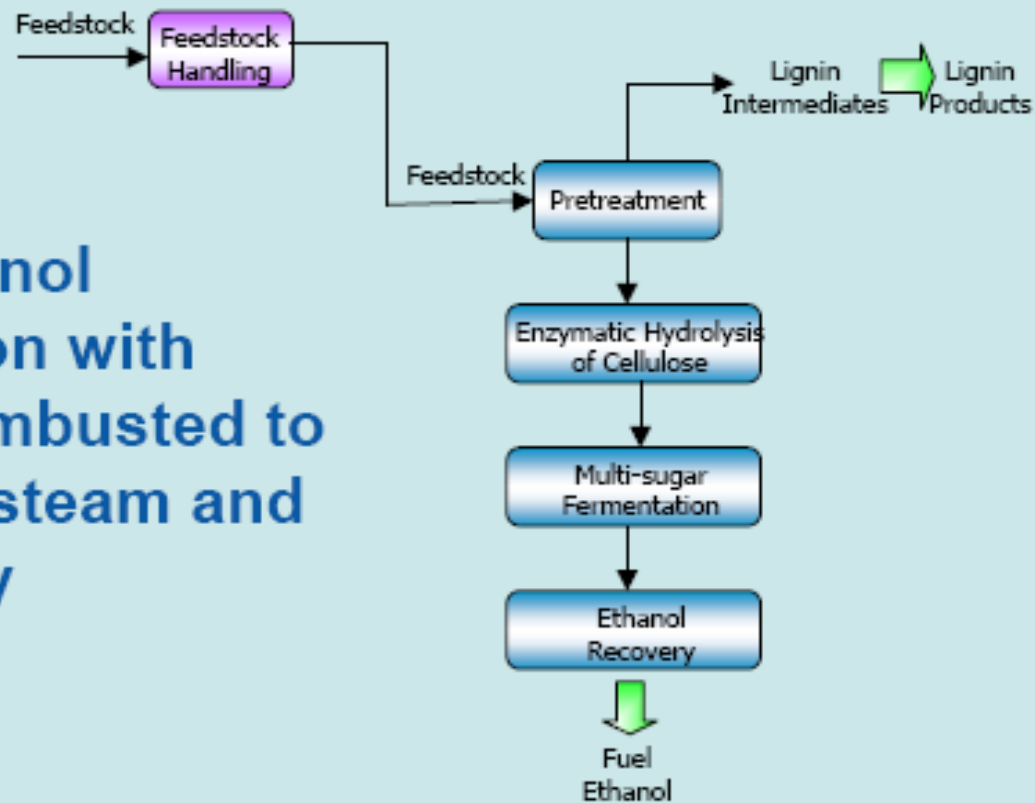
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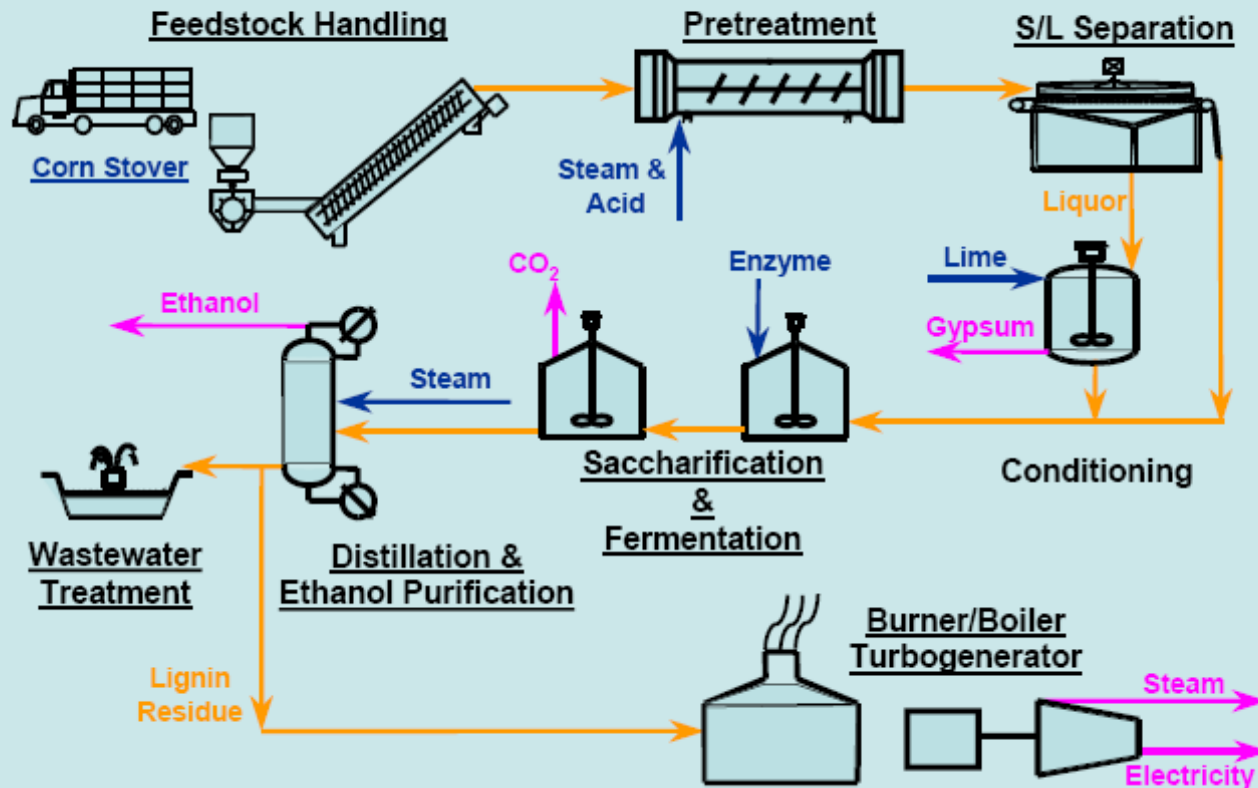
Georgia Institute of Technology

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## Fuel ethanol production with lignin combusted to produce steam and electricity



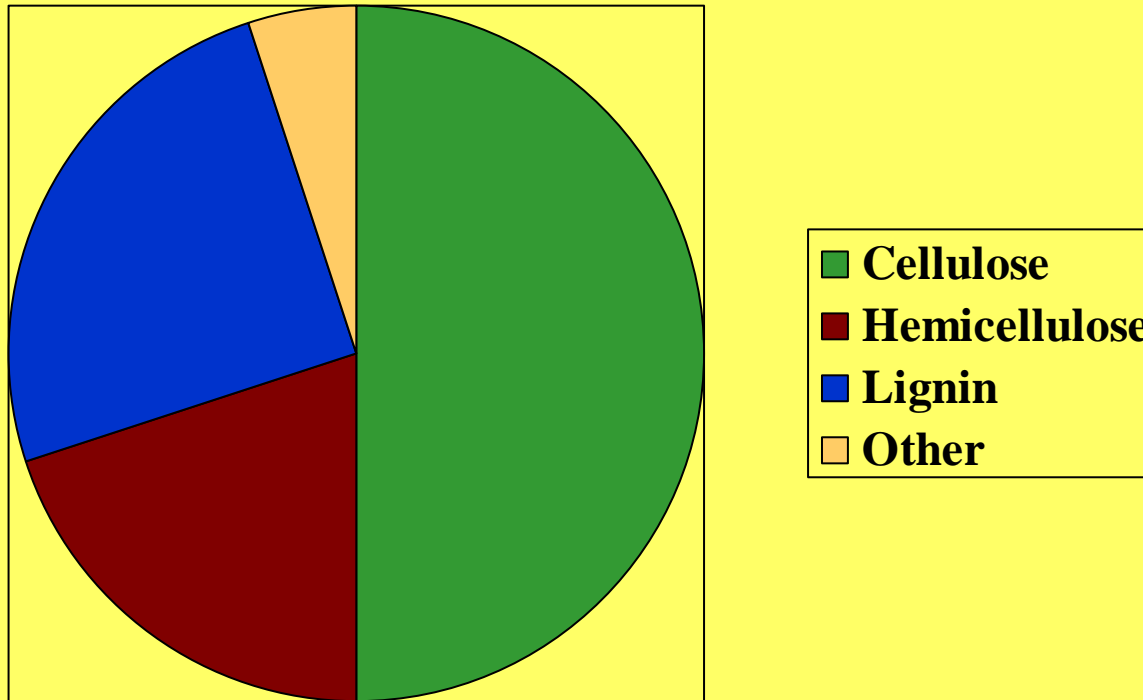
# Dilute Acid Prehydrolysis with Enzymatic Hydrolysis and Co-Fermentation Process Design



# Why is Pretreatment Necessary?

- Low rate of hydrolysis
- Low Yield
- Typically milled wood exhibits:
  - $< 20\%$  conversion in one day
  - $< 50\%$  conversion in three days

# Wood Composition



# Three Enzymes are needed for Effective Hydrolysis

1. Endoglucanase → Amorphous cellulose
  2. Exoglucanase → Non-reducing ends  
→ Cellobiose
  3.  $\beta$ -Glucosidase → Cellobiose → Glucose
- Also need hemicellulose hydrolysis
    - Particularly xylanase activity



# Pretreatment Requirements

- Inexpensive
  - Low capital, fast, cheap chemicals
- Rapid hydrolysis and/or rapid delignification
- High yield of carbohydrates
  - Minimize degradation reactions
- High sugar concentration
- Low enzyme make-up
- Valuable pretreatment byproducts

# Why Pretreat?

- Pretreatment enhances enzymatic hydrolysis by improving enzyme accessibility
- Accessibility is enhanced by
  - Delignification
  - Defibrillation
  - Swelling
  - Decrystallization
  - Depolymerization

**TABLE 1**

**Methods Used for the Pretreatment of Lignocellulosics.**

Physical		Physicochemical		Biological
Ball-milling		Steam explosion		Fungi
Two-roll milling		Ammonia Fiber Explosion		
Hammer milling				
Colloid milling				
High pressure steaming				
High energy radiation				
Pyrolysis				
<u>Chemical</u>				
Alkali	Acid	Gas	Oxidizing Agents	
Sodium Hydroxide	Sulfuric Acid	Chlorine Dioxide	Hydrogen Peroxide	
Calcium Hydroxide	Hydrochloric Acid	Nitrogen Dioxide	Ozone	
Ammonia	Hydrofluoric Acid			
Cellulose solvents		Solvent extraction		
		Ethanol-water extraction		
		Benzene-ethanol extraction		

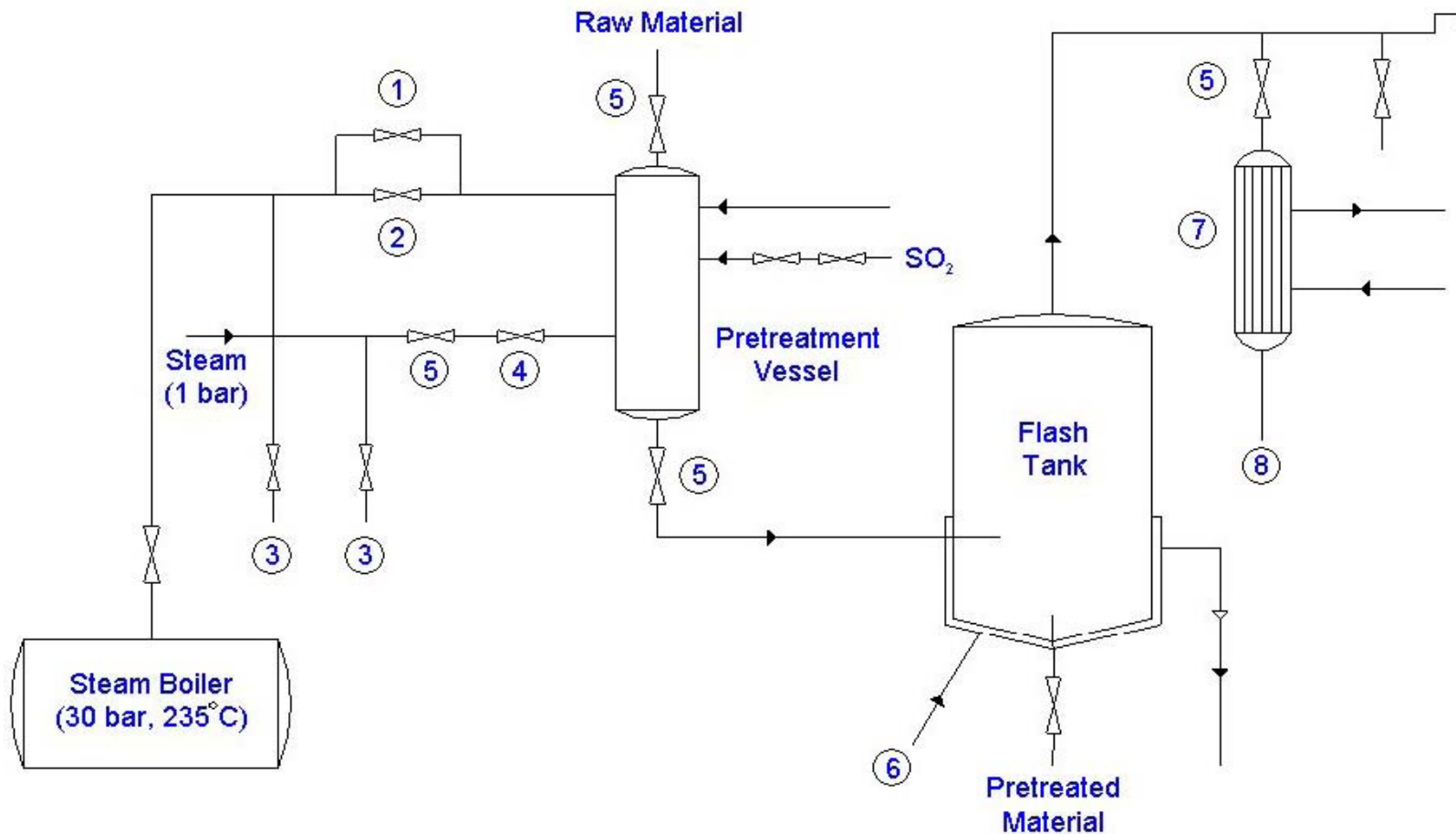
# Pretreatment Examples

- Steam explosion
- Steam explosion modifications
- Many more exist!

# Steam Explosion

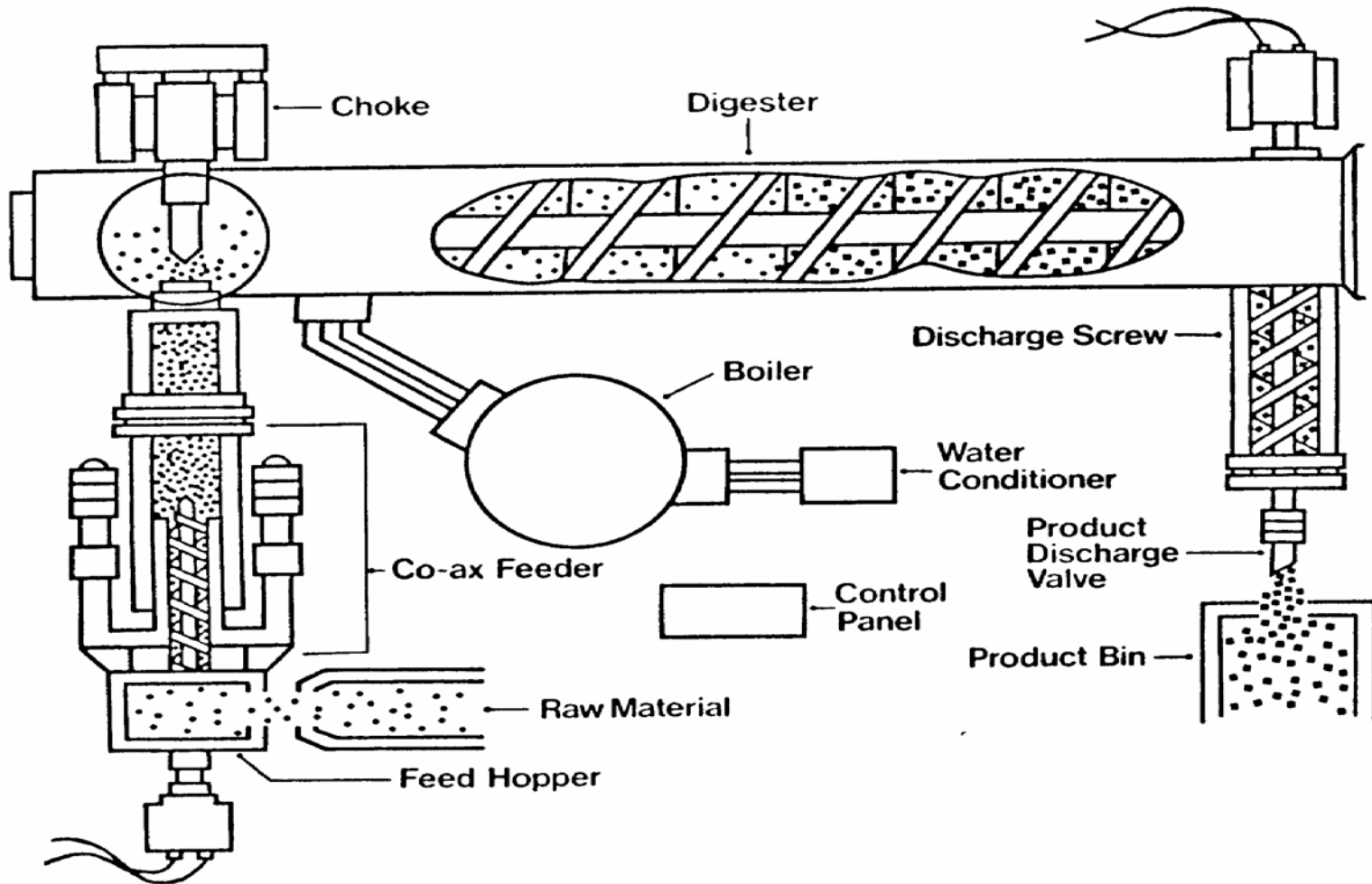
1. Expose to high pressure steam
  - 200 to 260 °C
  - 1 to 10 minutes
2. Explosively discharge
  - Processes:
    - Batch
    - Continuous

# Batch Steam Explosion with SO<sub>2</sub> Option



1. On/off valve.
2. Control valve.
3. Condensate removal.
4. Check valve.
5. Ball valve.
6. Cooling water.
7. Condenser.
8. Condensate of flashed vapor.

# Stake Continuous Digester



# Steam Exposure Enhances Hydrolysis

% Conversion of Cellulose to Glucose from Bagasse

Hydrolysis time, days	Milled	200 °C, 10 minutes
1	18	40
2	21	63
3	23	75

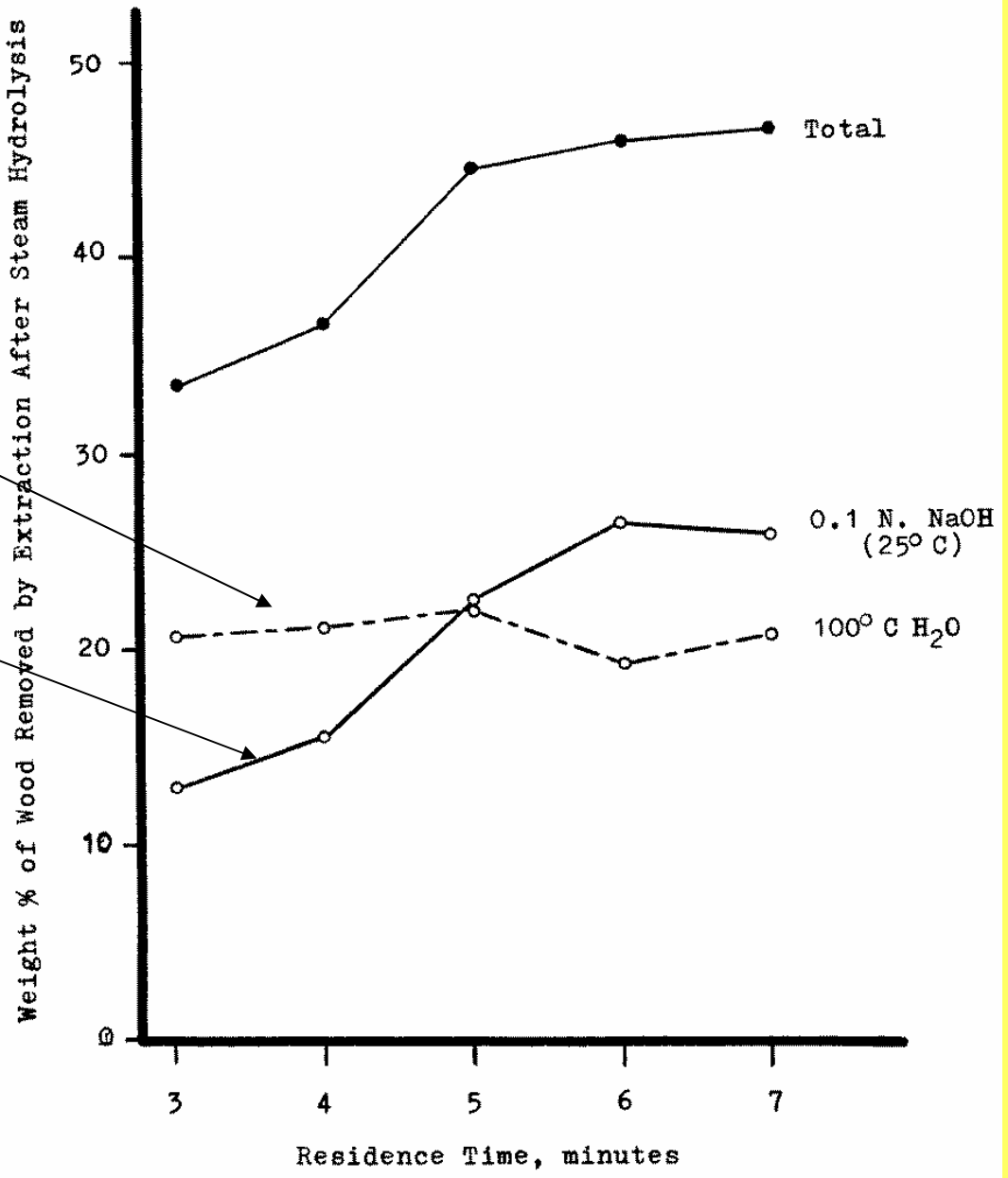
- 10 % dry substrate, 20 FPU *T. reesei* C-30
- ph 5, 50 °C
- Dekker and Wallis, 1983

# Physical-Chemical Consequences of Steam Explosion

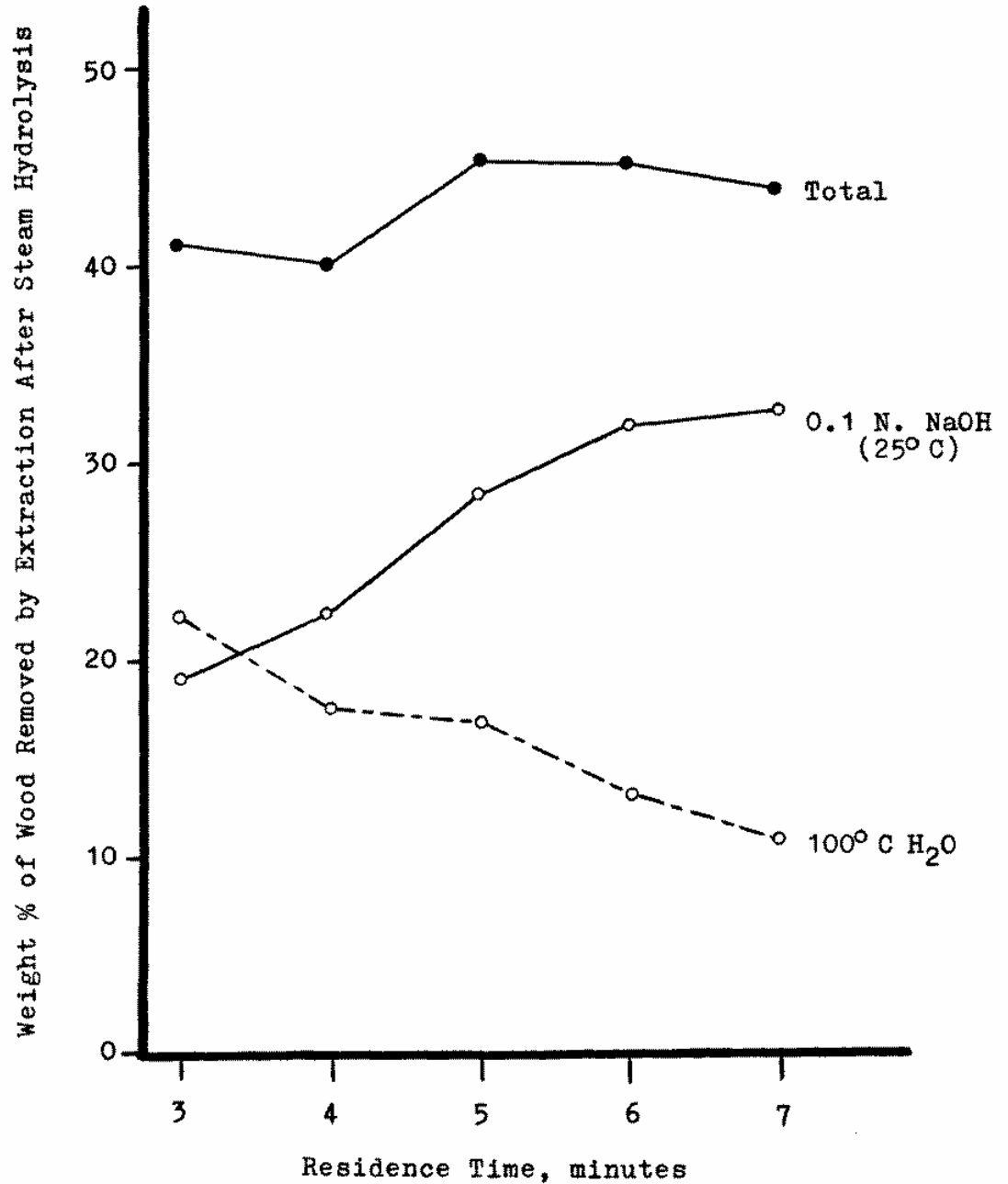
- Hemicelluloses degraded
  - Xylan content reduced
  - Acetic acid, furfural and methanol produced
- Lignin altered
  - Lignin disengaged
  - Lignin fraction increases
  - Lignin reactivity declines
- Cellulose DP decreases
- Wood defibrillated

# Tulip Poplar

- 1) Stake continuous digester at 300 psig
- 2) Hot water extraction
- 3) Dilute NaOH extraction



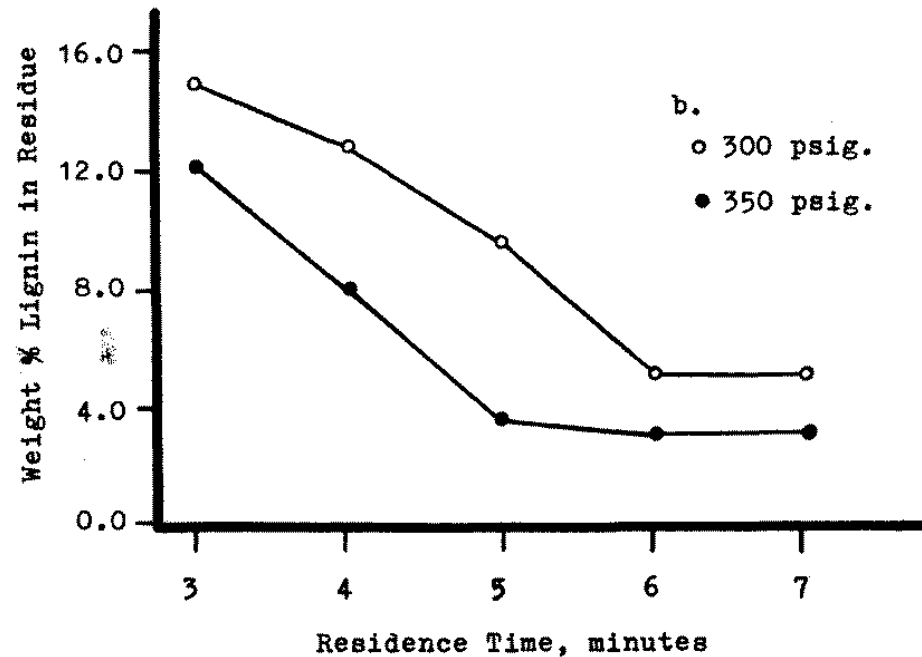
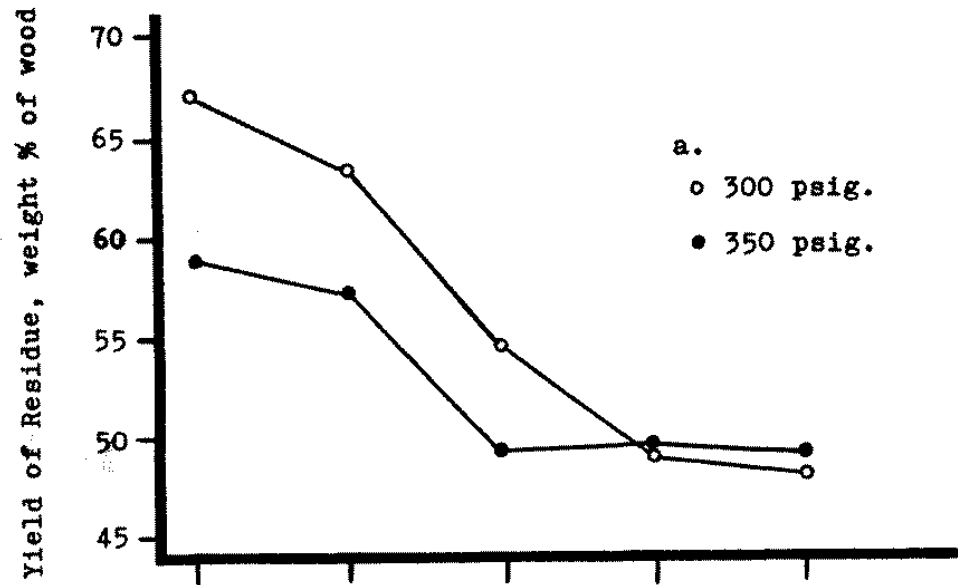
# Tulip Poplar Stake Digester 350 psig



# Tulip Poplar Stake Digester

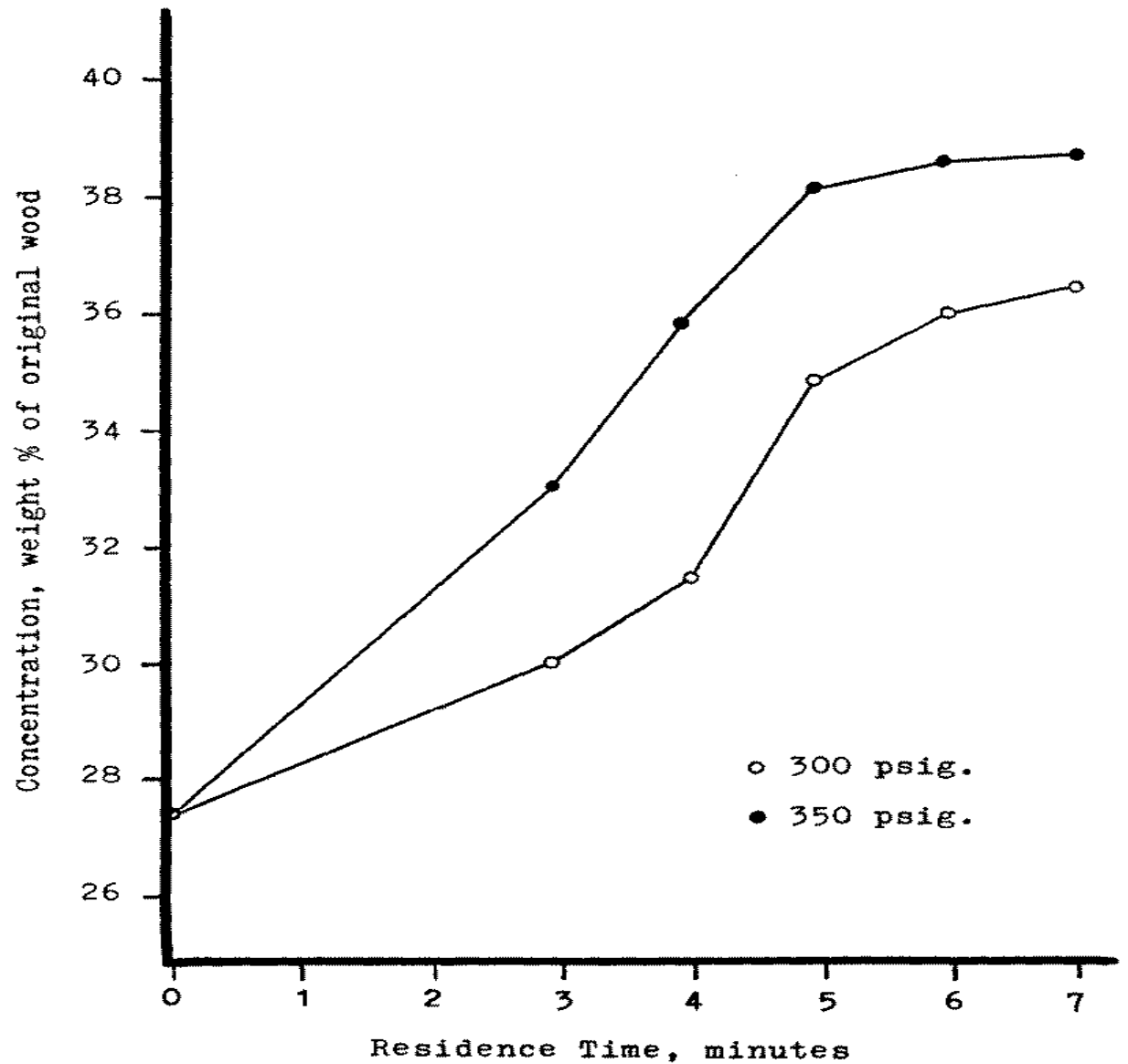
## Yield of Solids (High Cellulose)

## Lignin in Solids



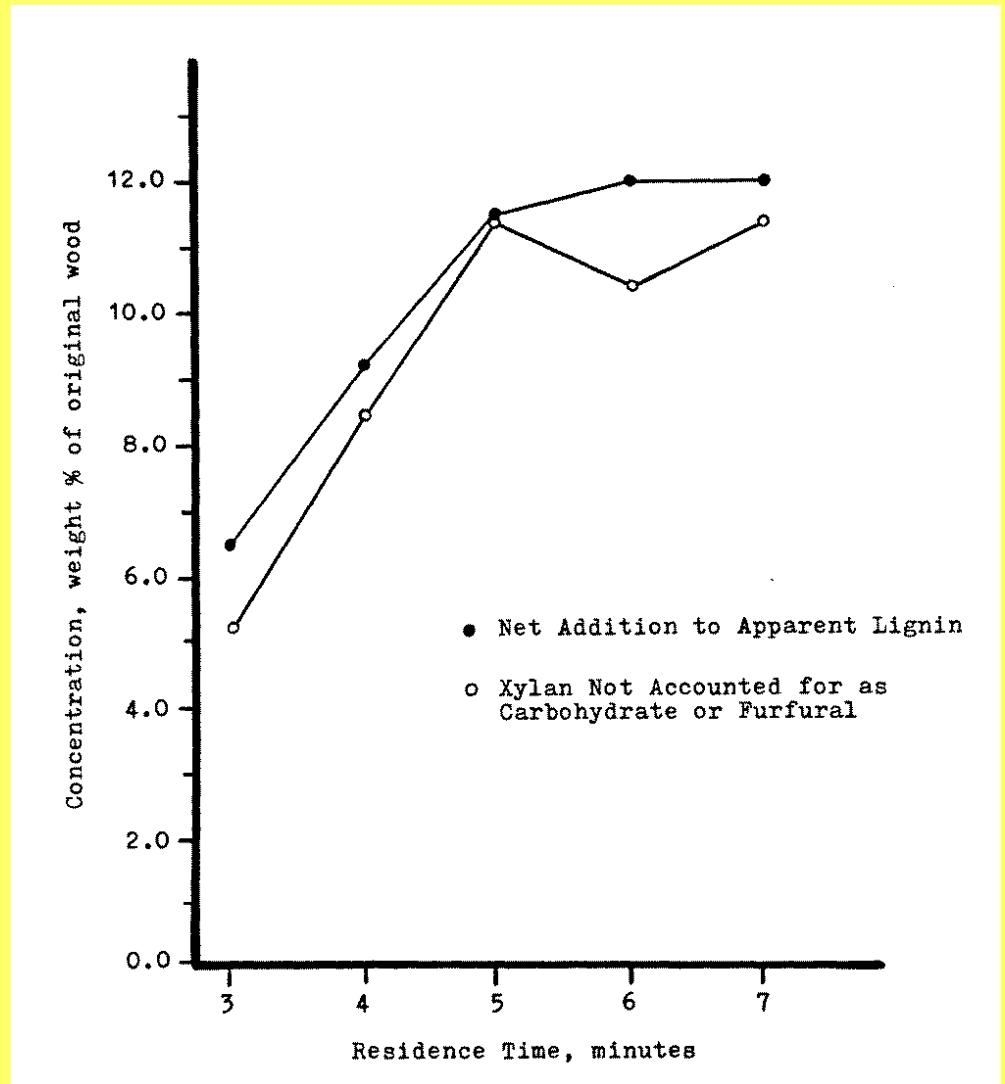
# Tulip Poplar Stake Digester

Increase in  
apparent  
lignin



# Tulip Poplar Stake Digester

Degraded Xylan  
reacts to increase  
apparent lignin



# Assessment of Steam Explosion

1. Inexpensive – yes (compared to conventional pulping)
2. Rapid hydrolysis – yes, for hardwoods
3. High yield – yes
4. High sugar concentration – yes
5. Low enzyme make-up – no
6. Valuable pretreatment byproducts - perhaps

# Additional Enhancements of Autohydrolysis

- Mild acid soaking before steam explosion
  - 2-3X glucose production in one day
- Intensive mixing
  - > 90 % conversion of SEW in 8 hours
- Two stages of steam explosion
  - Wash between stages to minimize sugar degradation
- Ethanol addition
  - More lignin extraction

# Organosolv Pretreatment must be supplemented to achieve effective enzymatic hydrolysis

- Organosolv pulping liquor:
  - Water
  - Organic solvent (ethanol, butanol)
  - Accelerator (acid, base, salt or buffer)
- Typical results
  - Partial delignification
  - Hemicellulose dissolution/degradation
  - Modest gains in enzymatic hydrolysis
  - Good quality pulp

# Secondary treatments following organosolv pulping increase substrate surface area

- Caustic swelling (Holtzapple, 1981)
- Wet milling (Ghose, Selvam, Ghosh, 1983)
- Attrition during hydrolysis (Neilson, Shafizadeh, Aziz, Sarkanen, 1983)
- Many more

# Wet milling can increase organosolv treated rice straw conversion to 100% in one day

<u>Substrate</u>	<u>One day glucose yield, %</u>
• Untreated	22
• Ethanol pulping	80
• Ethanol pulping and wet milling to 40 mesh	100
• Solka flock SW 40	30

# Assessment of Buffered Ethanol Water (Organosolv) Pretreatment

1. Inexpensive – no
2. Rapid hydrolysis – yes if supplemented
3. High yield – yes if supplemented
4. High sugar concentration – possible
5. Low enzyme make-up – possible
6. Valuable pretreatment byproducts - yes

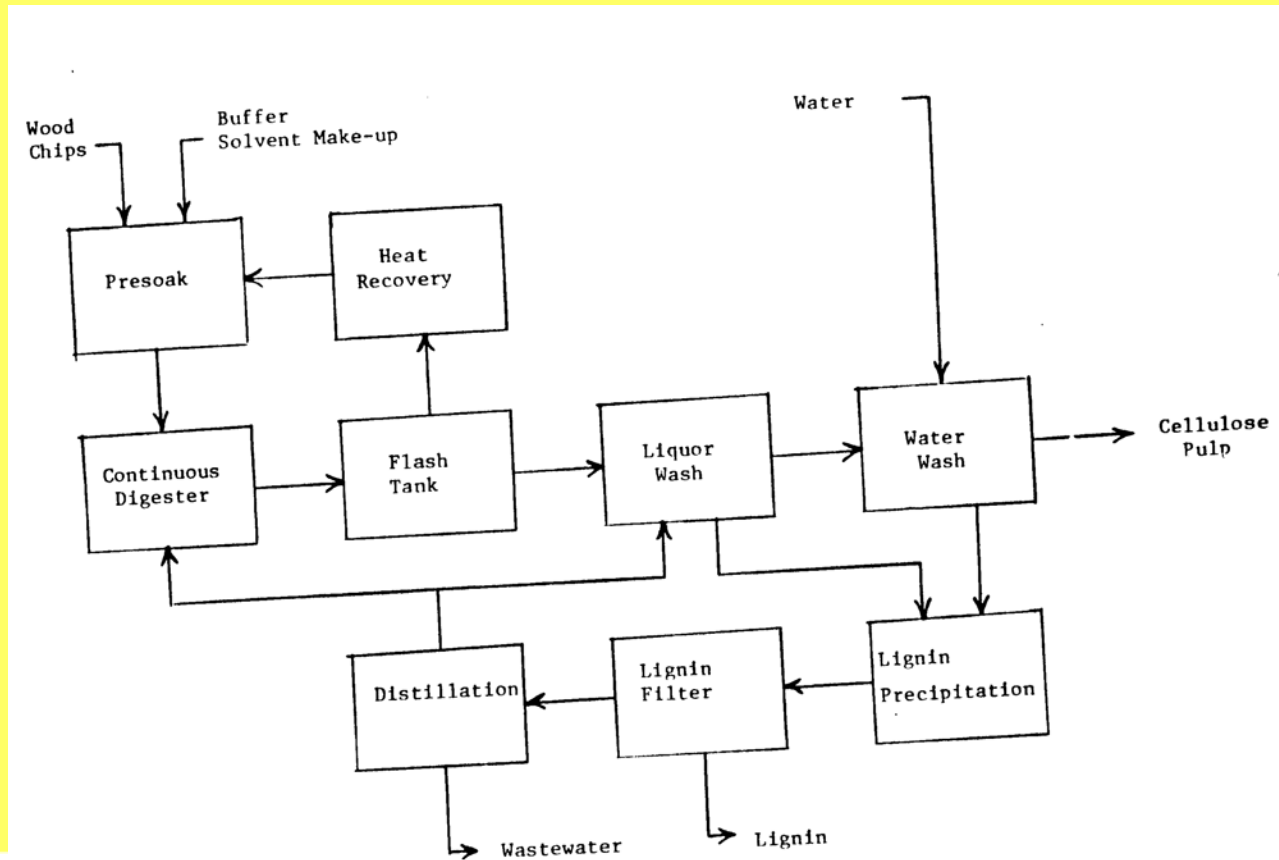
# Pretreatment by buffered ethanol-water delignification with explosive discharge

1. Inexpensive – yes
2. Rapid hydrolysis – yes
3. High yield – possible
4. High sugar concentration – possible
5. Low enzyme make-up – possible
6. Valuable pretreatment byproducts - yes

# Pretreatment costs by Steam explosion and Buffered Ethanol-Water explosion are similar

- Why?
  - Higher yield from buffered ethanol water
  - Ease of solvent recycle
  - Ease of lignin recovery
  - Both are rapid processes (high throughput)

# Buffered Ethanol-Water Pretreatment



Buffered Ethanol-Water Pretreatment Process

# Preliminary Enzymatic Hydrolysis

Sample	Relative Extent of Hydrolysis
1. Solka floc	1.0
2. Milled tulip poplar	0.4
3. Exploded, dried poplar	2.1
4. Exploded, wet poplar	2.3
5. Exploded, dried aspen	0.7
6. Exploded, wet aspen	1.3
7. # 6 bleached	2.0

# Potentially Valuable Lignin from Buffered Ethanol-Water Pulping

- A liquid at 70 to 80 °C
- > 65 % conversion to oil via base catalyzed hydrolysis
- Represents a potential credit of 5 cents/lb of pulp
  - Leading to a pulp value of 4 cents/lb (dry)

# Conclusions

- Pretreatment has a major influence on enzymatic hydrolysis
- Steam explosion is a well developed, effective pretreatment process
- Organosolv pretreatment is more expensive
  - But, may provide more valuable byproducts
- Organosolv delignification can be combined with explosive defibrillation to provide an effective pretreatment process.