Pré-tratamento de materiais lignocelulósicos (cont.)

Sumário e objetivo da aula (2 aulas)

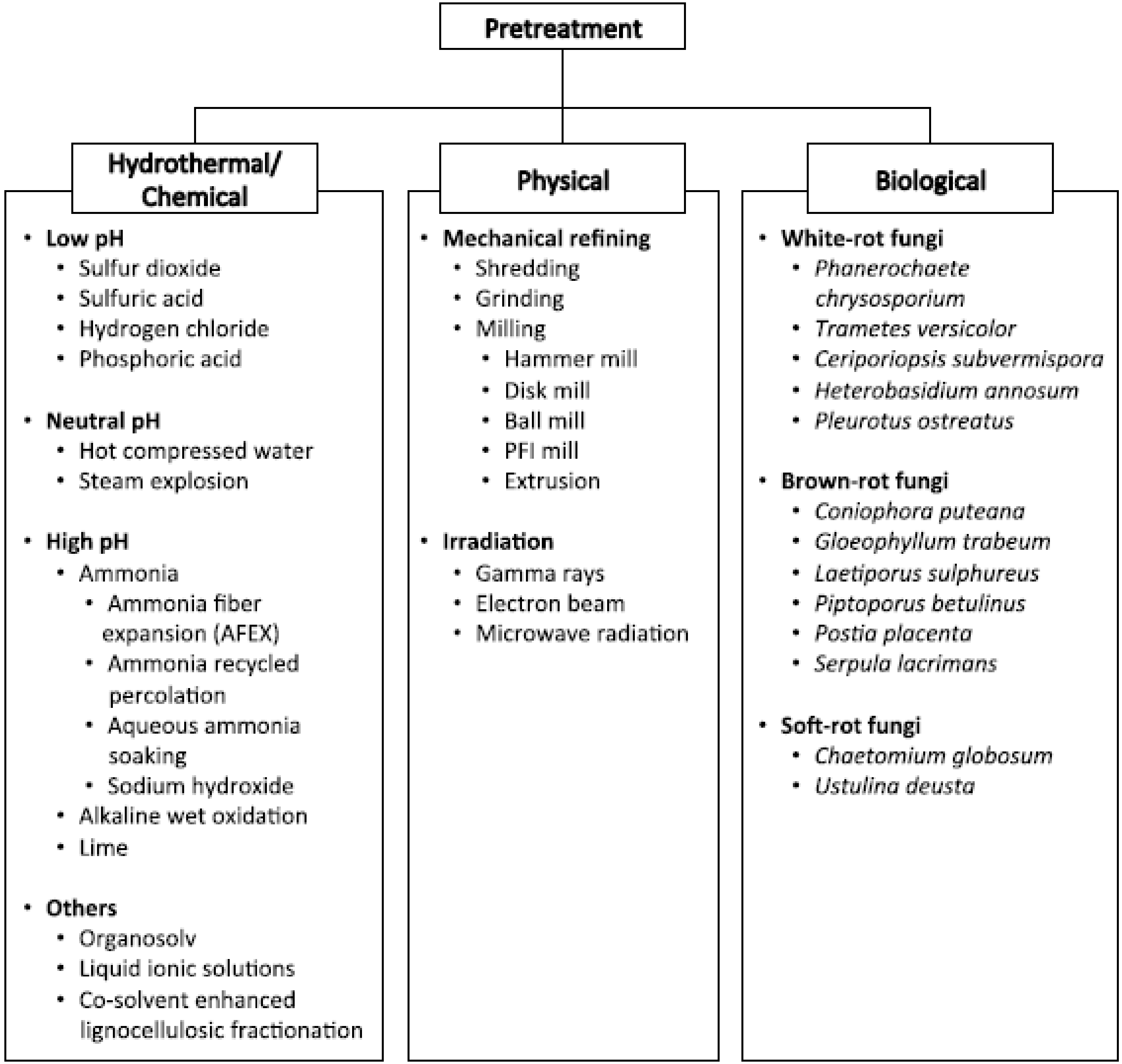
1. Qual a finalidade do prétratamento?

- Porque enzimas apresentam ação limitada na biomassa in natura?

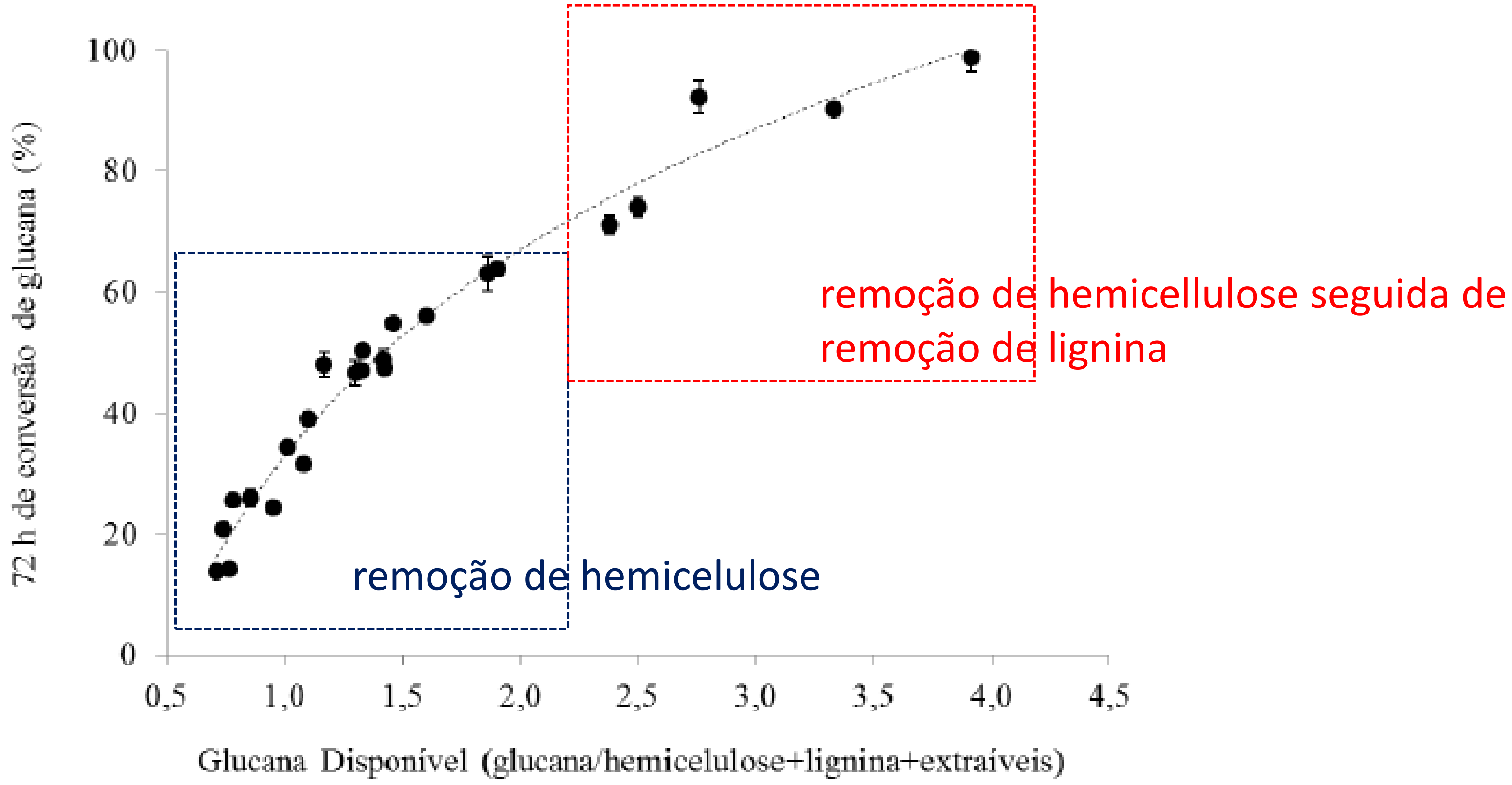
2. Fundamentos e tipos de pré-tratamento

3. Eficiência de hidrólise após o pré-tratamento

4. Correlações entre remoção de componentes no pré-tratamentoe eficiência de hidrólise


Pretreatment
Hydrothermal/ Chemical
Low pH
Sulfur dioxide
Sulfuric acid
Hydrogen chloride
Phosphoric acid
Neutral pH
Hot compressed water
Steam explosion
High pH
Ammonia
Ammonia fiber expansion (AFEX)
Ammonia recycled percolation
Aqueous ammonia soaking
Sodium hydroxide
Alkaline wet oxidation
Lime
Others
Organosolv
Liquid ionic solutions
Co-solvent enhanced lignocellulosic fractionation
Physical
Mechanical refining
Shredding
Grinding
Milling
Hammer mill
Disk mill
Ball mill
PFI mill
Extrusion
Irradiation
Gamma rays
Electron beam
Microwave radiation
Biological
White-rot fungi
Phanerochaete chrysosporium
Trametes versicolor
Ceriporiopsis subvermispora
Heterobasidium annosum
Pleurotus ostreatus
Brown-rot fungi
Coniophora puteana
Gloeophyllum trabeum
Laetiporus sulphureus
Piptoporus betulinus
Postia placenta
Serpula lacrimans
Soft-rot fungi
Chaetomium globosum
Ustulina deusta

Efeito combinado da remoção de componentes

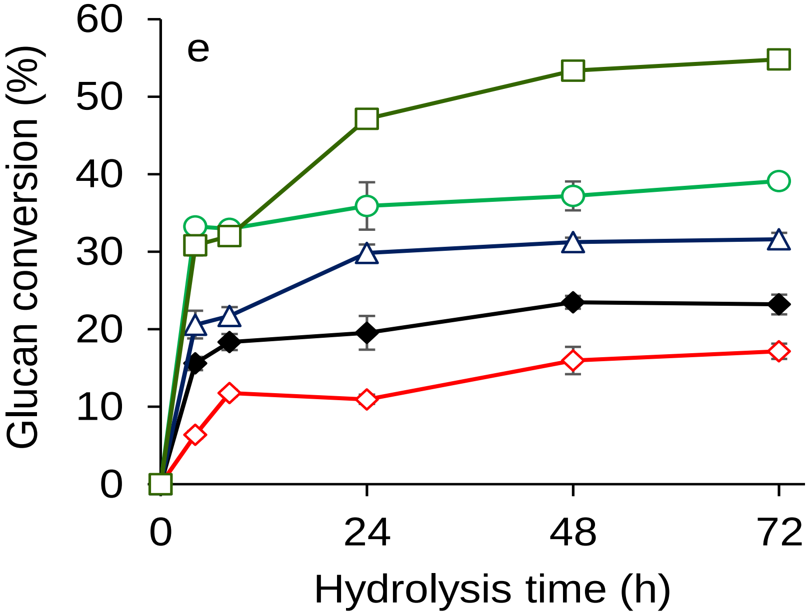


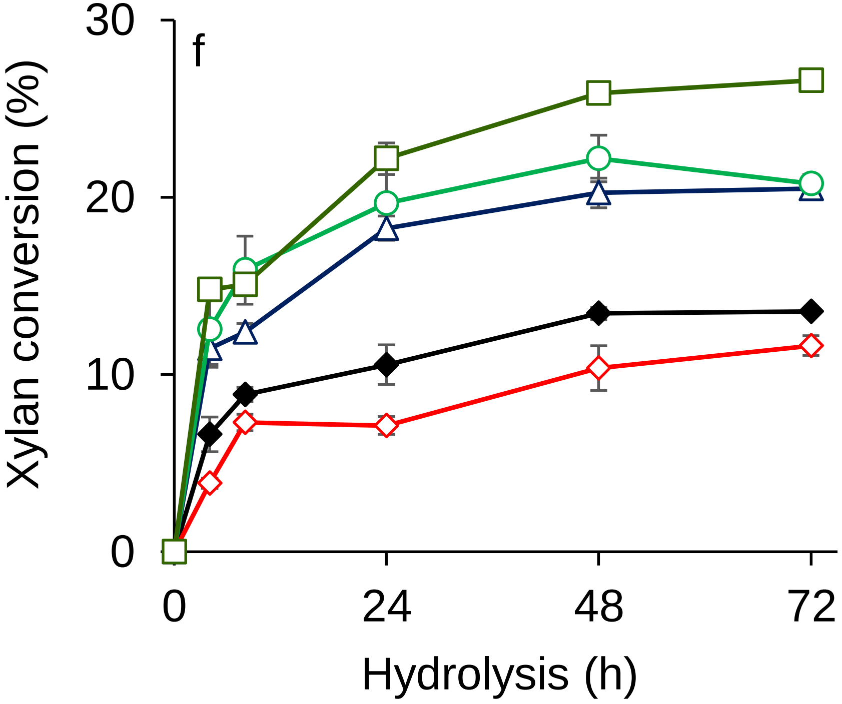
Exemplo sobre o balanço de massas dentro do processo de pré-tratamento

Table 1. Chemical composition and mass balance of sugarcane bagasse components after biotreatment with wood-decay fungi.

Bagasse samples	Bagasse components (g/100 g bagasse)						Yield of residual solids (%)	Mass balance for bagasse components after biotreatment (g/100 g untreated bagasse)					
	Glucan	Hemicellulose			Lignin	Ethanol soluble fraction		Glucan	Hemicellulose			Lignin	Ethanol soluble fraction
		Xylan	Arabinosyl	Acetyl					Xylan	Arabinosyl	Acetyl		
Untreated	40.5 ±0.4	21.9 ±0.2	1.7 ±0.1	3.1 ±0.4	20.7 ±0.8	3.4 ±0.1	100	40.5	21.9	1.7	3.1	20.7	3.4
Biotreated by *L. sulfureus*													
7 days	42.7 ± 0.2	22.4 ±0.1	1.7 ±0.1	3.7 ±0.1	20.9 ± 0.6	1.6 ±0.1	94.8 ± 2.6	40.5	21.2	1.6	3.5	19.9	1.5
14 days	42.8 ± 0.2	22.6 ±0.1	1.5 ±0.1	3.5 ±0.4	20.6 ± 0.5	2.5 ±0.1	94.9 ± 0.6	40.7	21.4	1.5	3.3	19.6	2.4
30 days	40.4 ±1.0	21.2 ±0.6	1.6 ±0.1	3.1 ±0.2	22.1 ± 0.6	3.9 ±0.1	90.4 ± 1.9	36.6	19.2	1.5	2.8	20.0	3.6
60 days	41.4 ± 0.5	21.3 ±0.3	1.3 ±0.1	3.1 ±0.3	22.1 ± 0.7	2.2 ±0.1	88.9 ± 1.5	36.8	18.9	1.2	2.8	19.7	2.0
Biotreated by *P. ostreatus*													
7 days	42.1 ± 0.6	23.1 ±0.3	2.0 ±0.1	3.2 ±0.2	21.0 ± 0.7	3.0 ±0.1	93.1 ± 1.0	39.2	21.5	1.9	3.0	19.6	2.8
14 days	42.7 ± 0.9	23.4 ±0.5	2.1 ±0.1	3.5 ±0.3	20.4 ± 1.2	4.1 ±0.1	90.5 ± 2.3	38.6	21.2	1.9	3.2	18.5	3.7
30 days	43.3 ± 0.6	22.2 ±0.1	1.9 ±0.1	3.4±0.1	20.5 ± 1.1	4.0 ±0.1	89.0 ± 0.2	38.5	19.8	1.7	3.0	18.3	3.5
60 days	42.2 ±1.8	20.8 ±0.6	1.5 ±0.1	3.2 ±0.1	20.9 ± 0.4	1.8 ±0.3	87.9 ± 0.5	37.1	18.3	1.3	2.9	18.4	1.6
Biotreated by*C. subversmipora*													
7 days	40.6 ± 0.6	22.2 ±0.5	1.5 ±0.1	3.1 ±0.2	21.8 ± 0.1	3.8 ±0.2	90.3 ± 1.6	36.6	20.0	1.4	2.8	19.7	3.5
14 days	42.9 ± 0.2	21.1 ±0.3	1.5 ±0.2	3.0 ±0.2	20.9 ± 0.3	4.5 ±0.3	77.6 ± 1.2	33.4	16.4	1.1	2.4	16.2	3.5
30 days	46.5 ± 0.6	19.4 ±0.2	1.1 ±0.1	2.7 ±0.1	18.5 ± 0.6	3.4 ±0.2	72.1 ± 1.1	33.5	14.0	0.8	1.9	13.4	2.5
60 days	51.5 ± 0.4	17.4 ±0.2	1.0 ±0.1	2.4 ±0.1	15.9 ± 0.4	3.5 ±0.1	67.9 ± 0.6	35.0	11.8	0.7	1.7	10.8	2.4

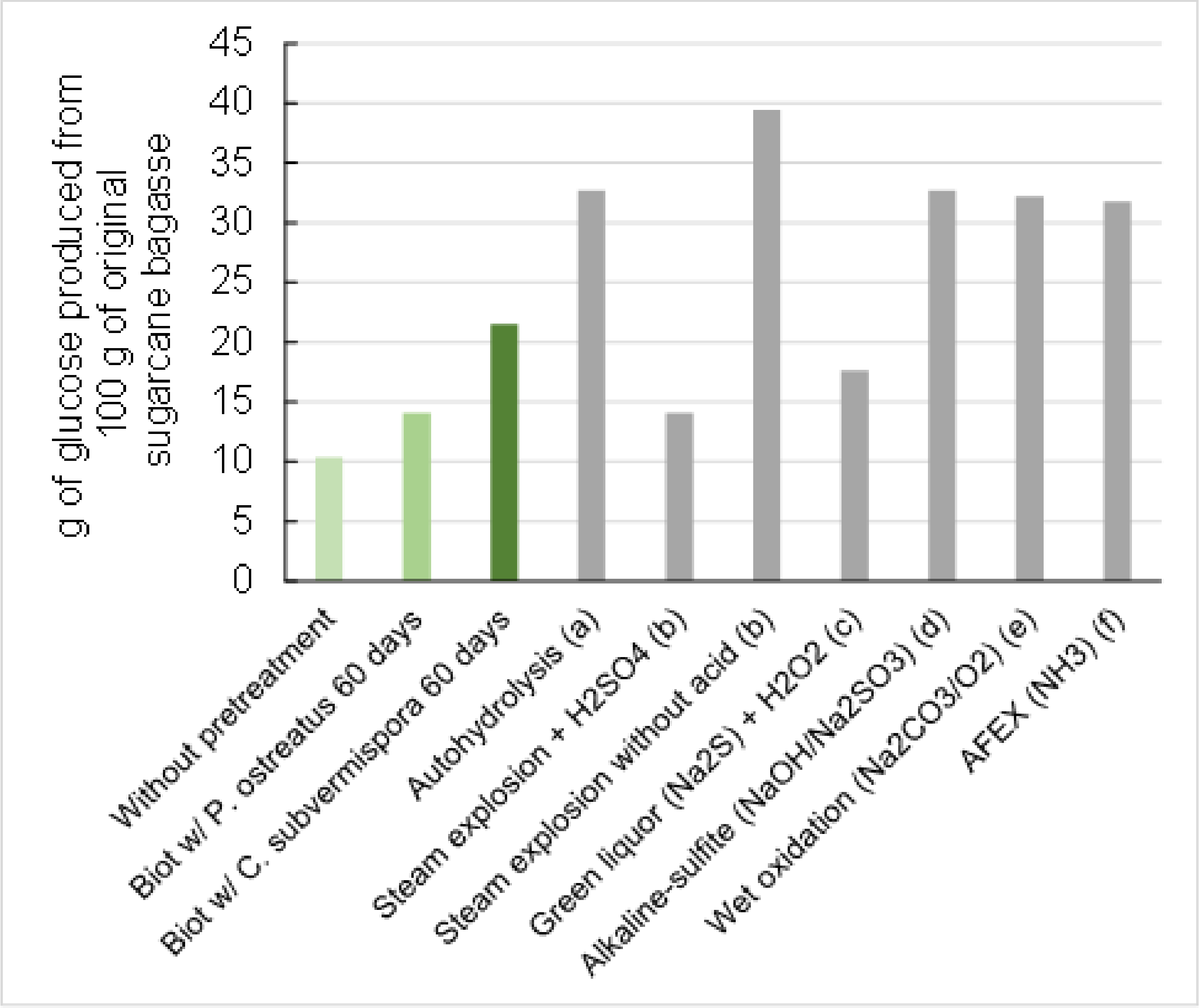
Conversão enzimática de polissacarídeos expressa com base na massa de componente presente no material pré-tratado





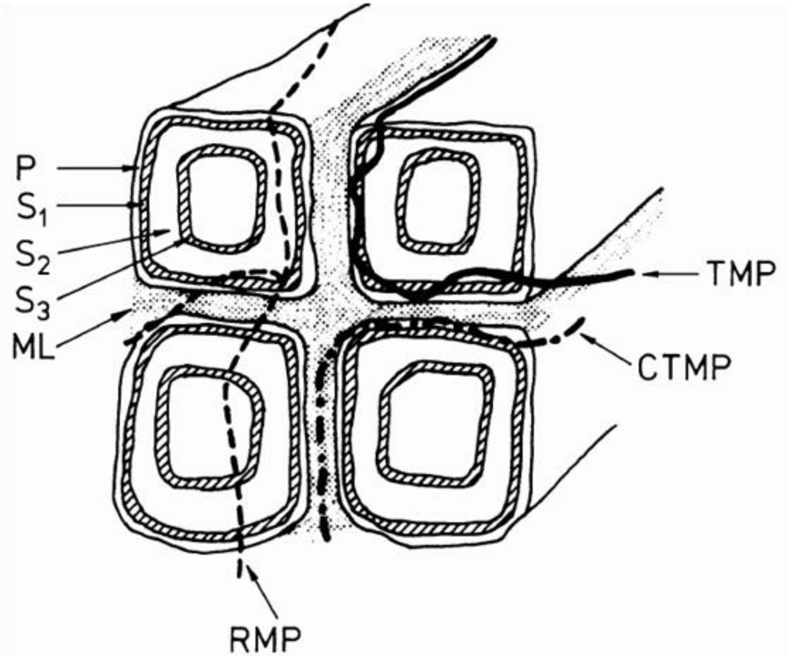
Conversão enzimática de polissacarídeos expressa com base no balanço de massas de componentes

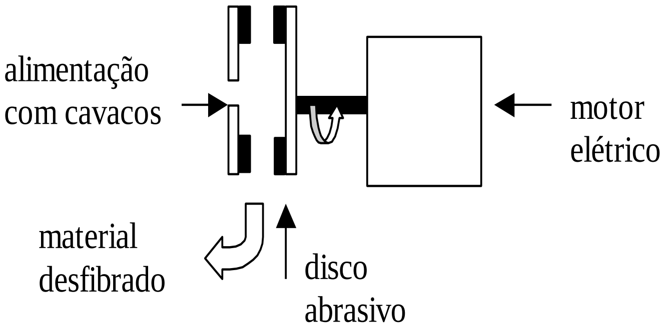
(expressos com base na massa inicial de biomassa)



The concept of mild-high-yield pretreatment

>>> CTMP pulping





CTMP pulping: available industrial facilities and technology

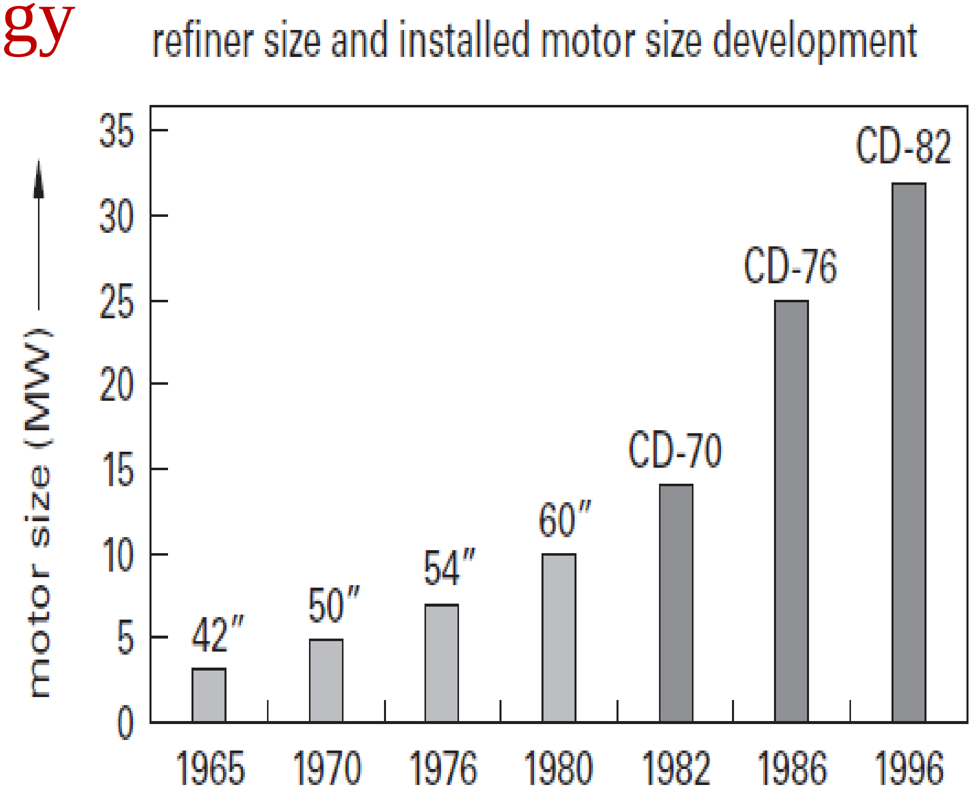


Figure 4.23. The size and capacity of commercial refiners has increased dramatically over the last 20 years. CD = Conical disc.

150 ton/day @
450 mL CSF

CTMP pulping at Lab scale

3 steps are necessary for wood chips

Cooking

Fibrillation

Refining

For sugar cane bagasse, fibrillation is not necessary

High-yield CTMP pulping >> low level of delignification

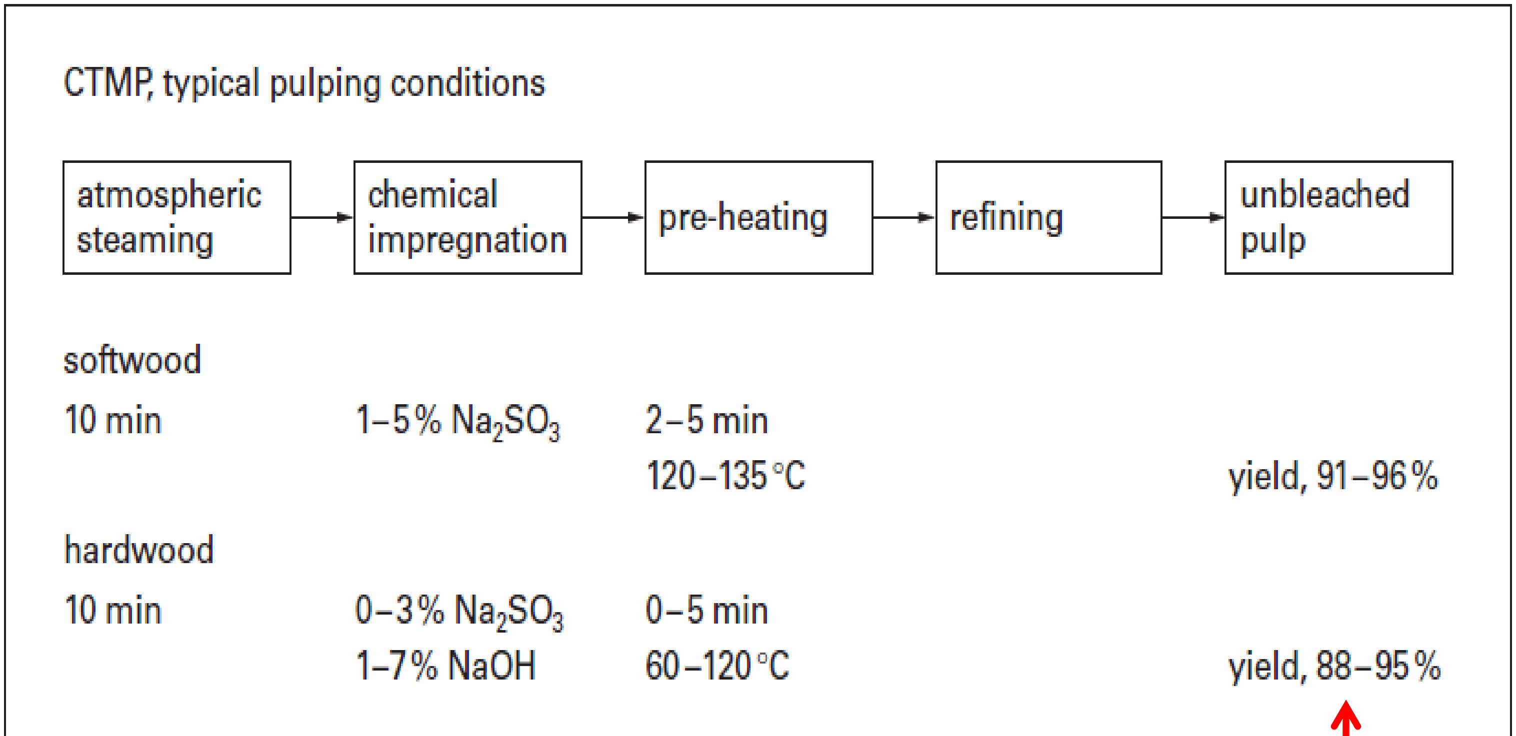
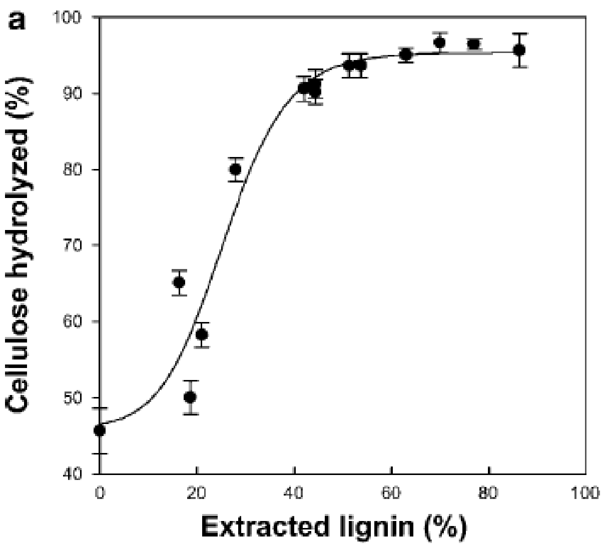


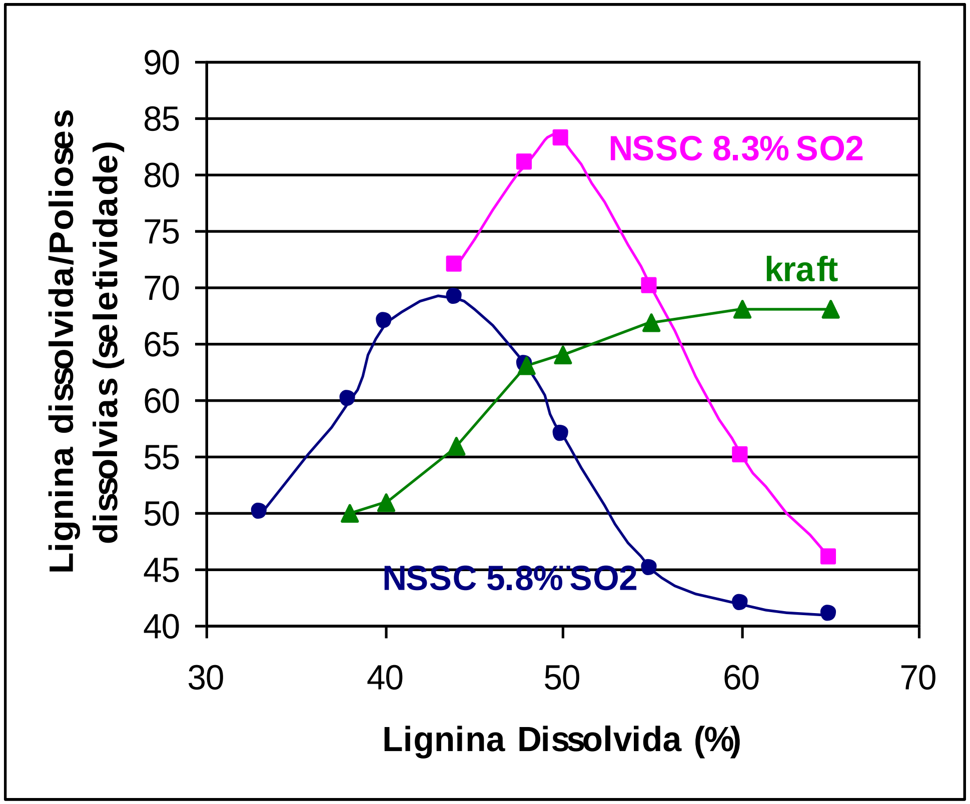
Figure 4.29. Unit operations in typical CTMP processes.

High yield, but residual material also contains high lignin content

>> Plants with originally less lignin could take advantage of a mild-CTMP pretreatment

Sulfite based delignification is very selective up to 50% lignin removal – *useful for pretreatment*





↑

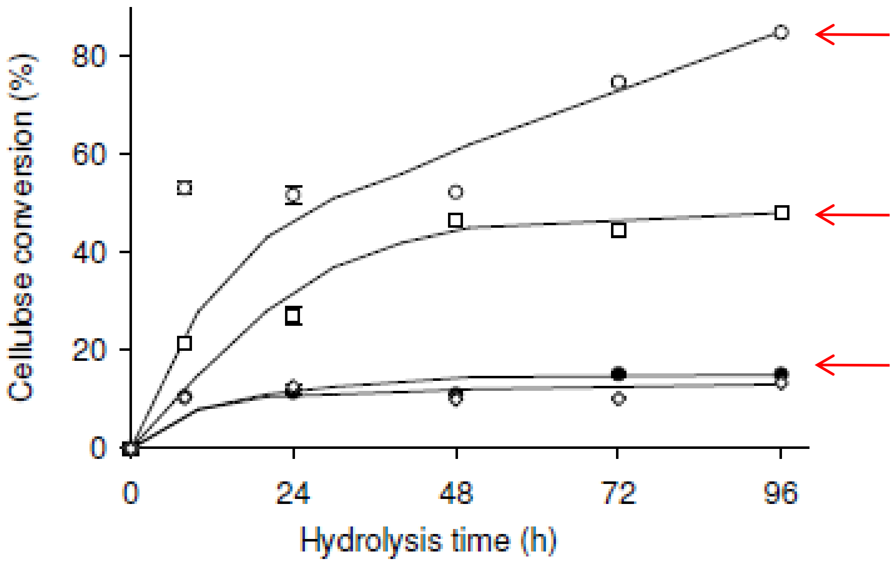
It is not necessary to remove more than 50% of the initial lignin to promote efficient hydrolysis

Alkaline sulfite CTMP pretreatment of sugar cane for enzymatic hydrolysis – samples with reduced initial lignin contents

Table 1. Process Variables, Yield, Fibrillation Level, and Chemical Composition of Sugarcane Bagasse Pretreated in Alkaline- and Alkaline/Sulfite-Chemithermomechanical Pretreatment

Bagasse Sample	NaOH (g/100 g of Bagasse)	Na_2SO_3 (g/100 g of Bagasse)	Yield of Treated Material (g/100 g of Bagasse)	CSF after 250 W h Refining (mL)	Bagasse Components (g/100 g of Original Bagasse)			Bagasse Components (% on Pulp Basis)		
					Lignin	Hemicellulose	Glucan	Lignin	Hemicellulose	Glucan
Mill-processed sugarcane bagasse										
Untreated	0	0	100	nd	24.4	27.4	43.7	24.4	27.4	43.7
Refined	0	0	94.0	670	20.4	27.2	41.2	21.7	28.9	43.8
Precooked with NaOH and refined	5	0	91.4	460	16.3	23.7	43.0	17.8	25.9	47
Precooked with NaOH/Na_2SO_3 and refined	5	10	74.9	180	11.4	19.5	40.5	15.3	26.9	54.5
Mill-processed sugarcane bagasse previously submitted to partial delignification										
Untreated	0	0	100	nd	14.2	30.8	42.5	14.2	30.8	42.5
Precooked with NaOH and refined	5	0	88.6	150	9.3	26.5	43.0	10.5	29.9	43.0
Experimental hybrid										
Untreated	0	0	100	nd	19.1	27.0	42.0	19.1	27.0	42.0
Precooked with NaOH and refined	5	0	78.6	340	12.8	22.6	37.3	16.3	28.8	47.5

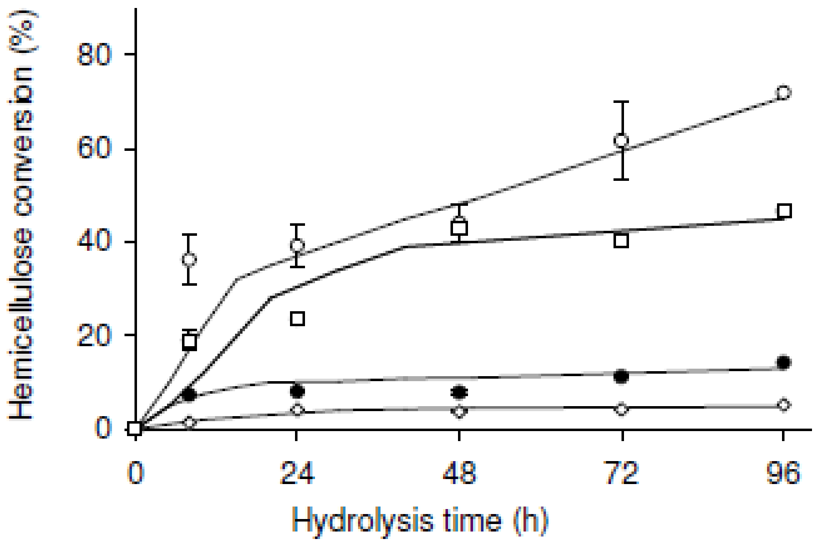
Mendes et al. , Biotechnol Progress, 2011

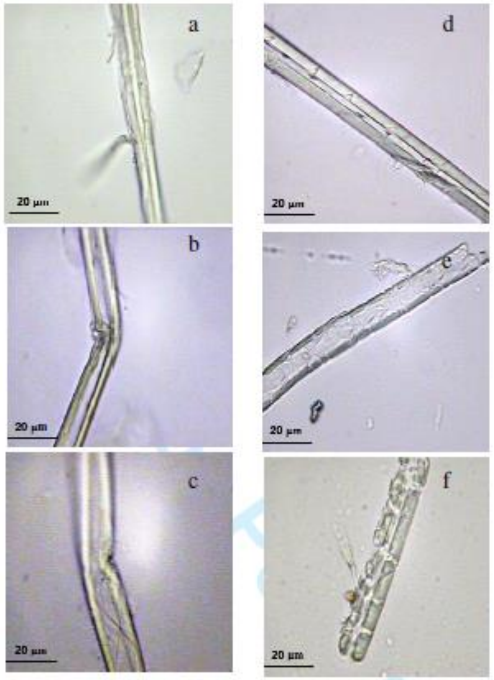


Alkaline-sulfite CTMP-treated mill sugar cane bagasse

Alkaline CTMP-treated mill sugar cane bagasse

Untreated and RMP-treated mill sugar cane bagasse





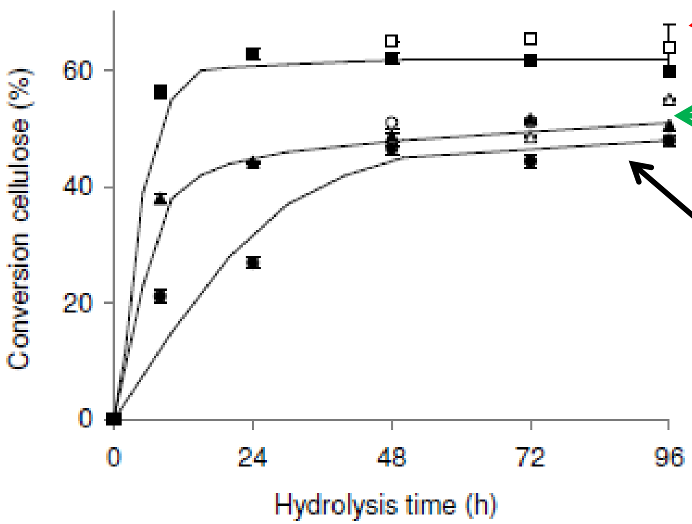
RMP

Alkaline-CTMP

Alkaline-sulfite CTMP

Before and after enzymatic treatment

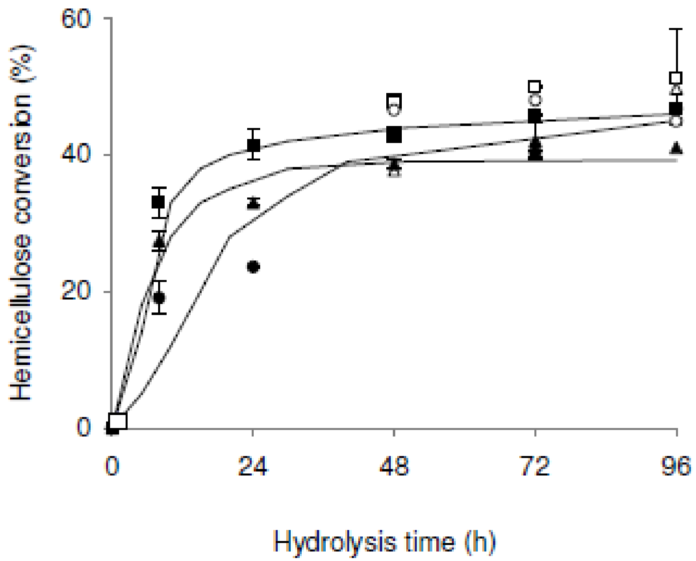
Enzymatic hydrolysis of Alkaline-CTMP pretreated
Samples with reduced initial lignin contents



Alkaline CTMP-treated sugar cane bagasse
pre-delignified sample

Alkaline CTMP-treated experimental hybrid with reduced initial lignin content

Alkaline CTMP-treated mill sugar cane bagasse



Why enzymatic hydrolysis stop after 48h?

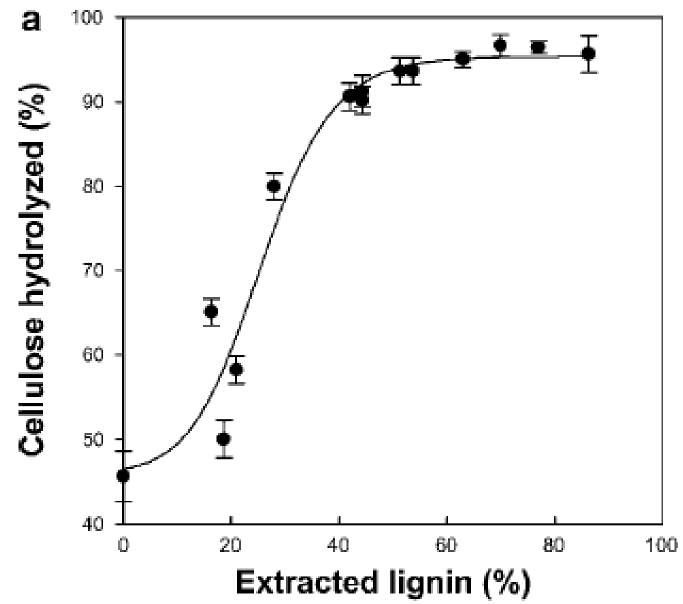
Unfilled symbols refer to a new load of enzymes in the reaction

>> Substrate seems to limit enzyme infiltration

The concept of mild-high-yield pretreatment/CTMP pulping

Partial delignification is enough, but wood chips are not disrupted at this delignification level

>> *However, for wood chips, a mechanical fibrillation is necessary*



Lee et al.., Biotechnol Bioeng, 2009
Selectively delignified Maple using ionic liquids

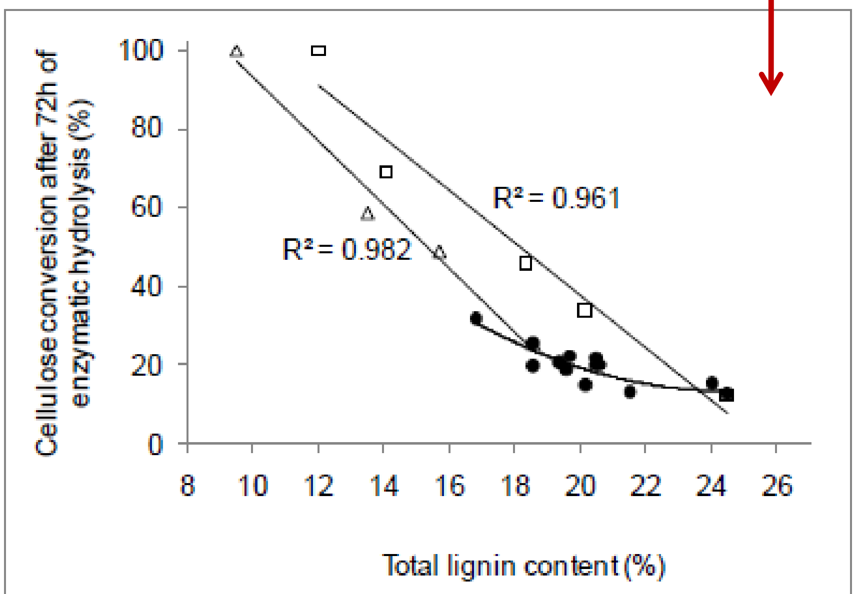


Figure 3 Cellulose conversion as a function of lignin.

Masarin et al.., Biotechnol Biofuels, 2011
Sugarcane hybrids with varied lignin contents

The use of sulfite pulping as pretreatment

Bioresource Technology 100 (2009) 2411–2418

Contents lists available at ScienceDirect

Bioresource Technology

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Sulfite pretreatment (SPORL) for robust enzymatic saccharification of spruce and red pine

J.Y. Zhu [a,b,*], X.J. Pan [b,*], G.S. Wang [c], R. Gleisner [a]

J.Y. Zhu et al. / Bioresource Technology 100 (2009) 2411–2418

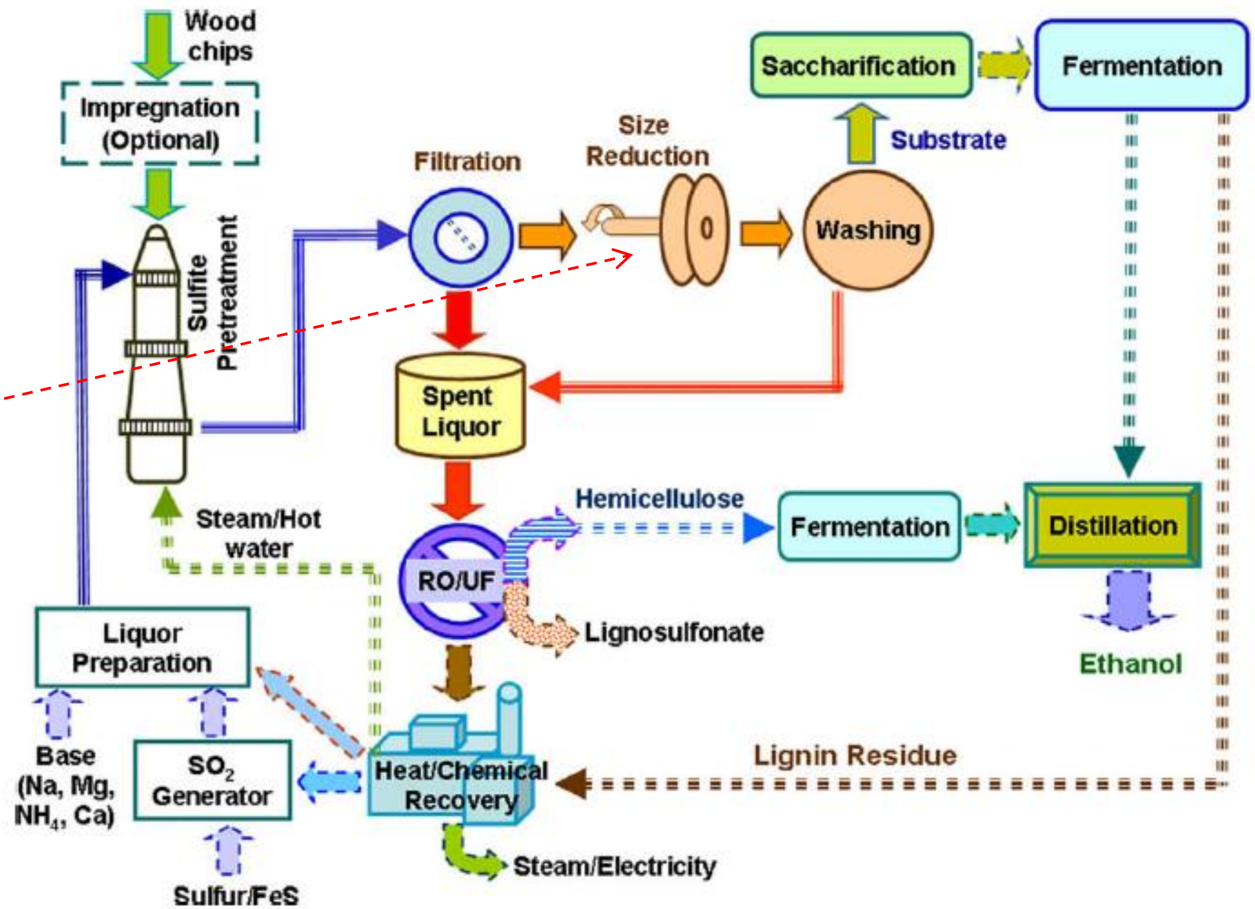

Fig. 1. Schematic process flow diagram of the SPORL.

J.Y. Zhu et al. / Bioresource Technology 100 (2009) 2411–2418

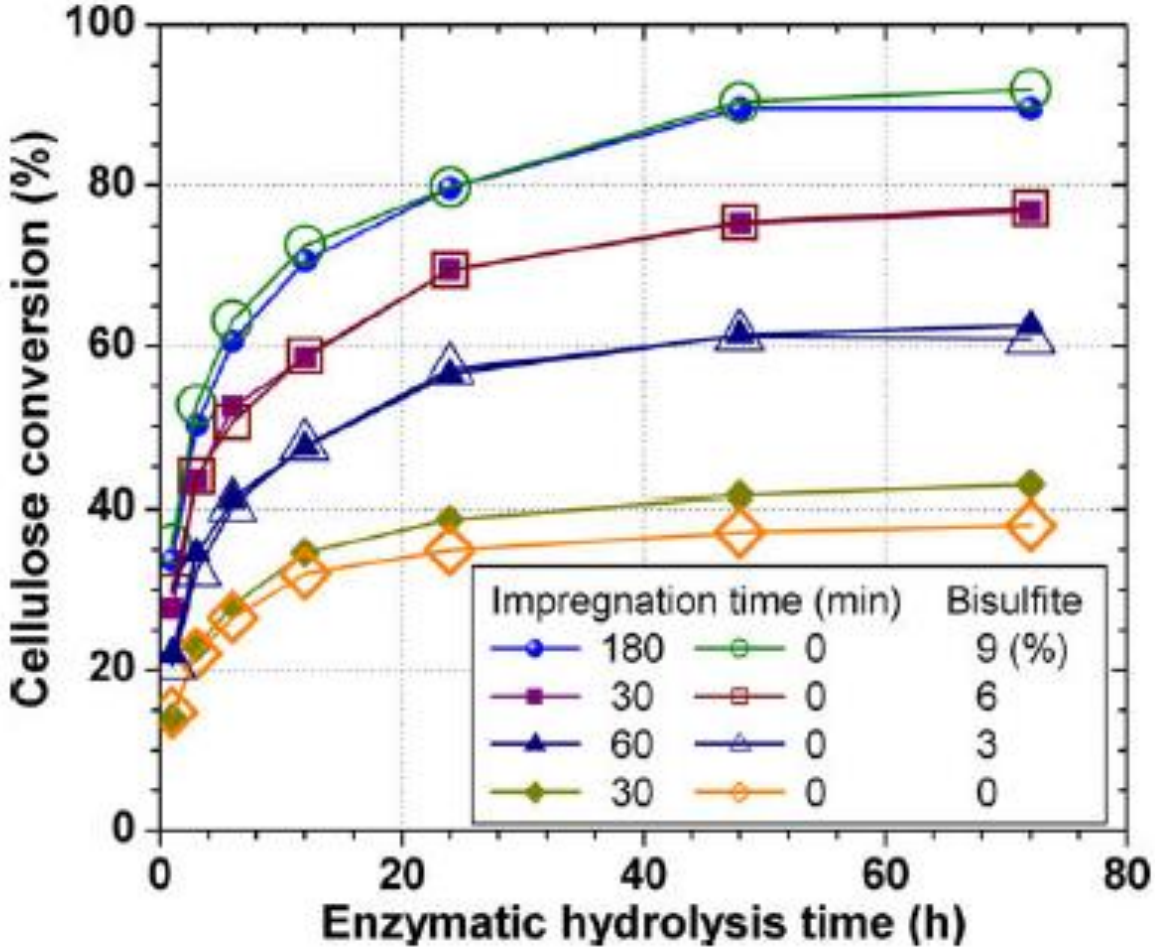

Fig. 2. Effect of wood chip impregnation time on time-dependent cellulose conversion of spruce at sulfuric acid charge of 1.84% on od wood.

Bioresource Technology 101 (2010) 2782–2792

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On energy consumption for size-reduction and yields from subsequent enzymatic saccharification of pretreated lodgepole pine ☆

W. Zhu [a], J.Y. Zhu [b,c,*], R. Gleisner [b], X.J. Pan [c]

Table 1

Effect of chemical pretreatment on size-reduction energy consumption and enzymatic hydrolysis glucose yield. Milling solids-loading at 20% with disk-plate gap of 0.76 mm.

Pretreatment @ 180 °C for 30 min[a]	Initial liquor pH	Pretreatment wood-chip yield (%)	Milling energy (Wh/kg od untreated wood)	Substrate yield from pretreatment (%)	ECSS[b] (%)	EHGY[c] (wt.% wood)
None		100.0	615.9	100	11.3	5.4
Hot-water	5.0	87.2	537.0	74.4	33.1	16.0
Acid	1.1	77.0	335.6	71.4	39.6	15.7
SPORL	4.2	86.1	499.3	68.9	84.1	43.1
SPORL	1.9	80.7	134.5	66.7	92.2	38.2

[a] Sodium bisulfite charge was 8% on od wood for the two SPORL runs. Sulfuric acid charge was 2.21% (wt./wt.) on od wood for the dilute-acid and low pH SPORL runs, and 0 for the hot-water and high pH SPORL runs.

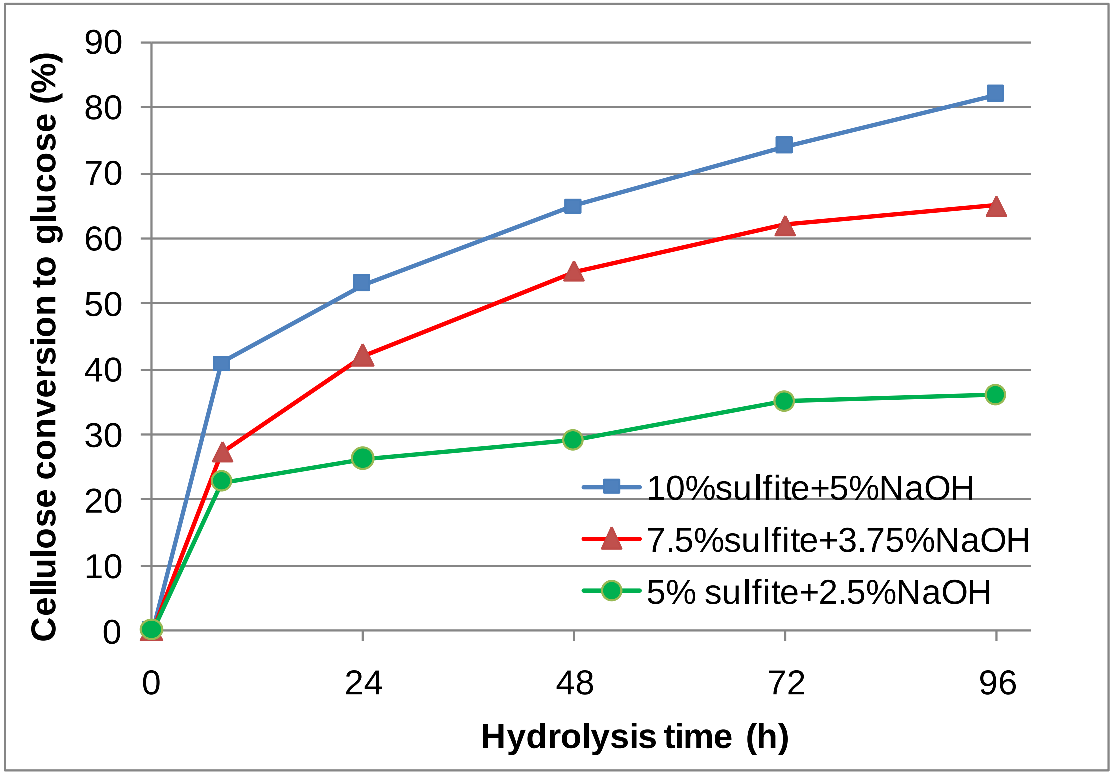
[b] wt.% of glucan in substrate converted to glucose after 48 h enzymatic hydrolysis.

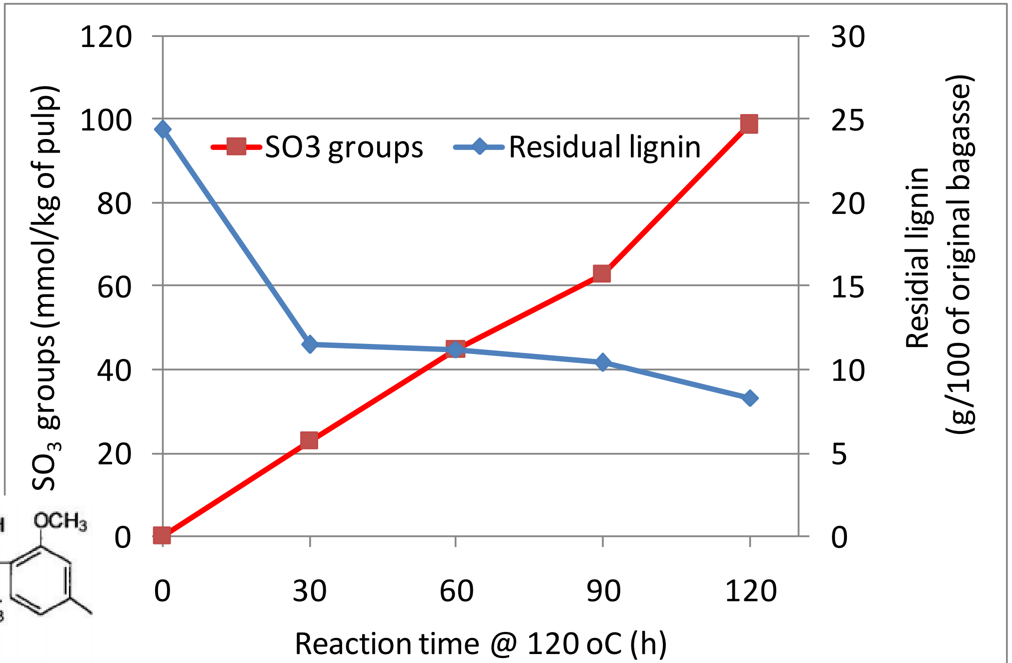
[c] Enzymatic hydrolysis glucose yield after 48 h, in wt.% od untreated wood.

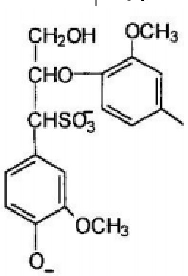
Efeito da carga de sulfito alcalino no teor de lignina residual

Tratamento	Tempo de cozimento	Lignina (%)	Grupos sulfônicos (mmol/kg)
5%NaOH e 10% sulfito	120 min	11.2	99 ± 3
3,75%NaOH e 7,5%sulfito	120 min	14.0	83 ± 1
2,5% NaOH e 5%sulfito	120 min	18.4	73 ± 3

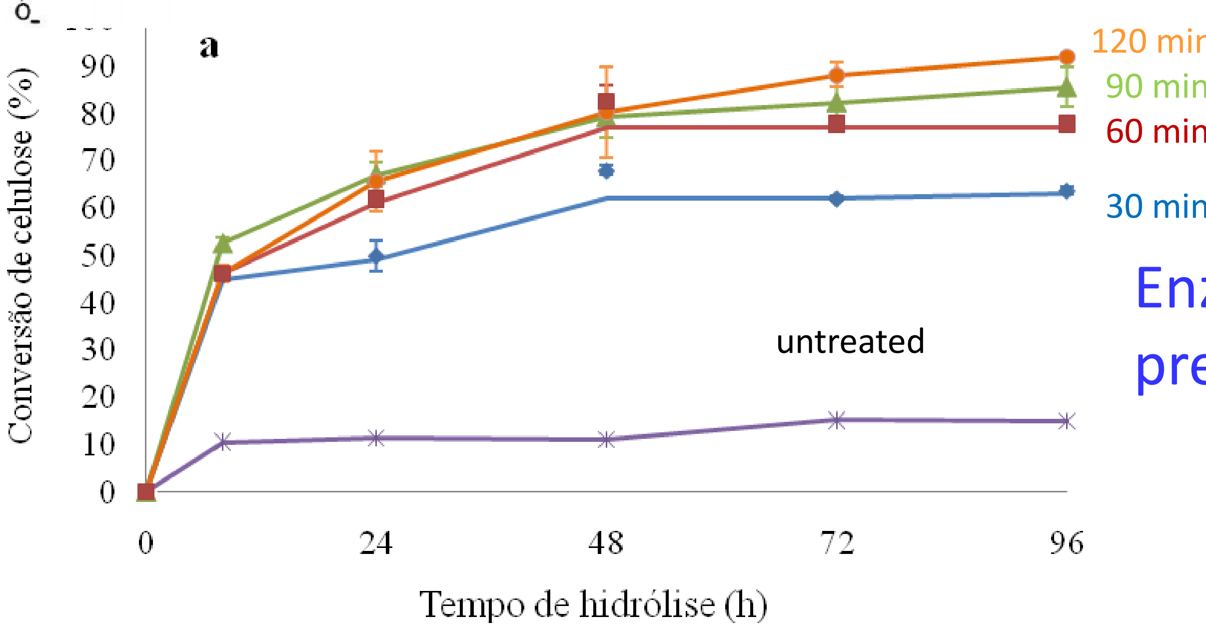
Hidrólise enzimática do material pré-tratado







Lignin removal and sulfonation of residual lignin during CTMP treatment of sugar cane bagasse (10% Na_2SO_3 and 5% NaOH



Enzymatic hydrolysis of pretreated samples

Tratamento mecânico associado ao pré-tratamento químico em meio ácido

>> remoção intensa de hemicellulose leva ao colapso da parede celular

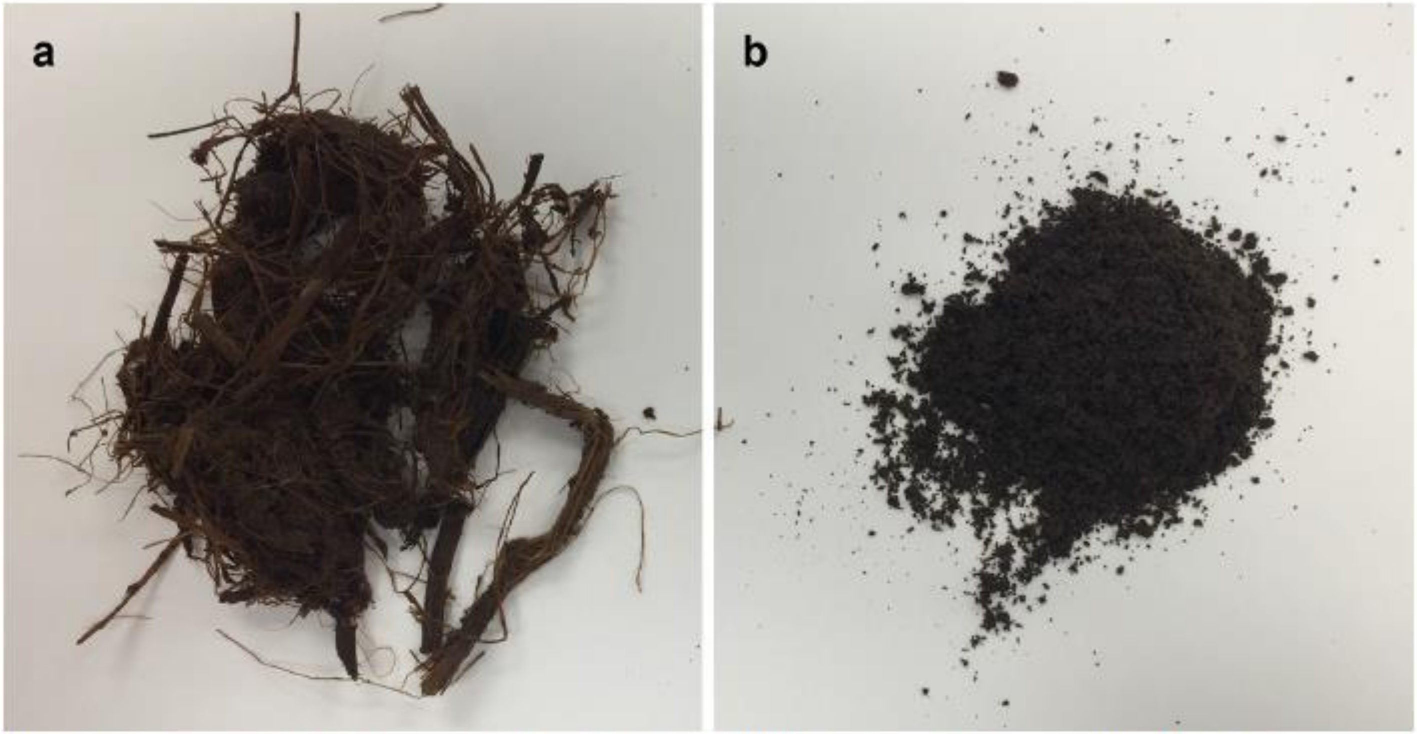


Fig. 6 Size reduction of dilute acid-pretreated corn stover by disk milling. **a** Dilute acid-pretreated sample; **b** dilute acid-pretreated and disk-milled sample

Tratamento mecânico associado ao pré-tratamento químico em meio ácido

>> corrosão dos discos feitos em aço comum é crítica (não ocorre em meio alcalino)

Table 3 Potential materials of construction for mills to grind dilute acid-pretreated samples. Corrosion rate tests were performed at the sulfuric acid boiling temperature [47]

Material	Condition, other factors and comments	Concentration (%)	Duration (h)	Corrosive rate (mm/year)
Irons and steels				
Altemp A-286	Solution treated	10	NR[a]	0.75
Stainless steels				
AL 29-4-2	Dilute[b]	10	NR	0.46
Altemp 625	Dilute[b]	10	NR	0.64
E-Brite	Dilute, nonactivated	5	48	0.356
Type 316 stainless steel	NR	0.25	24	0.0686