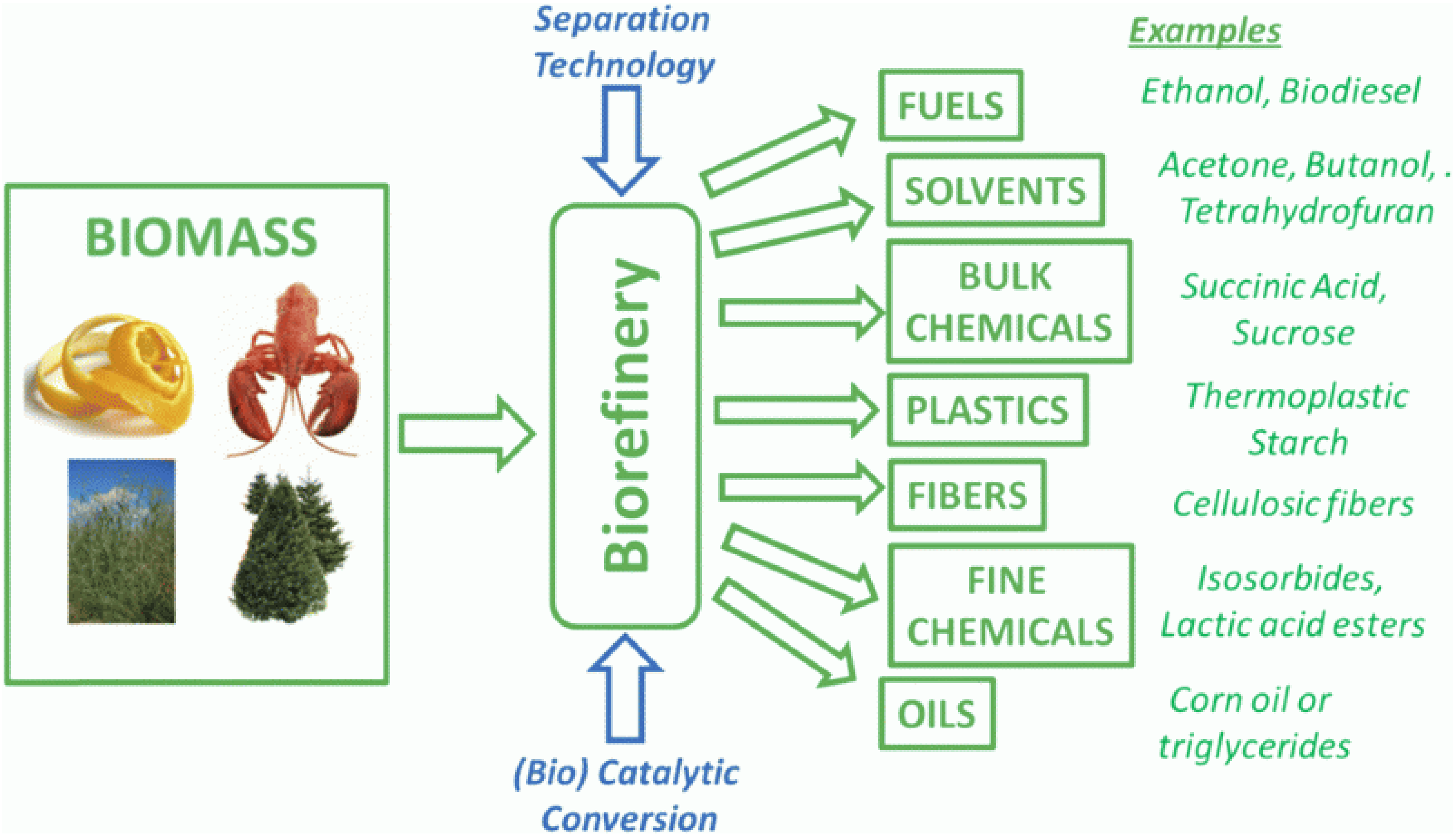
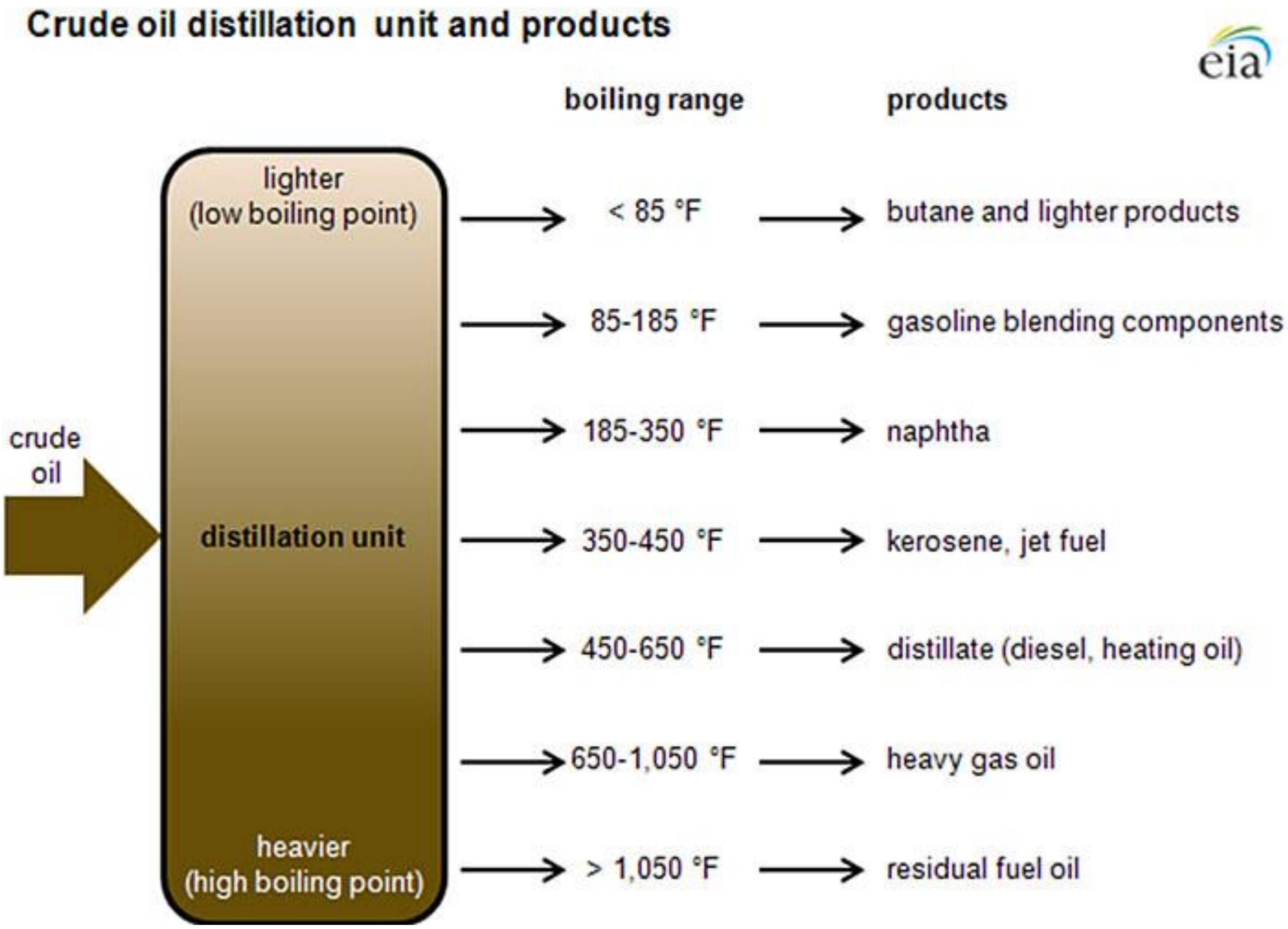
Biorefinarias
(conceitos de uso integrado da biomassa vegetal)

ilustração típica do conceito de biorrefinaria



Refinaria de petróleo

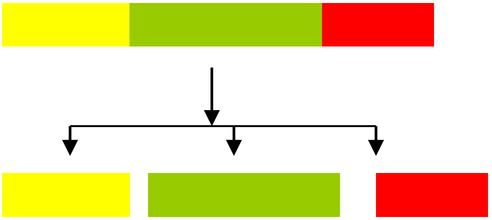
ilustração típica de uma refinaria de petróleo



Biorefinarias
(conceitos de uso integrado da biomassa vegetal)

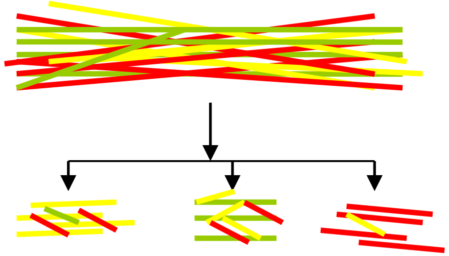
O problema

HemCel:Cel:Lig



Seria relativamente fácil e simples

HemCel:Cel:Lig



Mais difícil e não há plena separação dos componentes

A solução:????

Há uma infinidade de processos (planejados, algumas vezes testados e poucas vezes demonstrados em escala ampliada) que propõem vias de fracionamento

Definição do NREL para biorrefinarias
http://www.nrel.gov/biomass/biorefinery.html

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry.

By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but **high-volume liquid transportation fuel**, while generating electricity and process heat for its own use and perhaps enough for sale of electricity. The high-value products enhance profitability, the high-volume fuel helps meet national energy needs, and the power production reduces costs and avoids greenhouse-gas emissions.

Soluções usadas em escala industrial ou escala ampliada

Polpação kraft

(produz celulose/hemicelulose polimérica na forma de fibras, além de vapor/eletricidade para uso próprio e excedente)

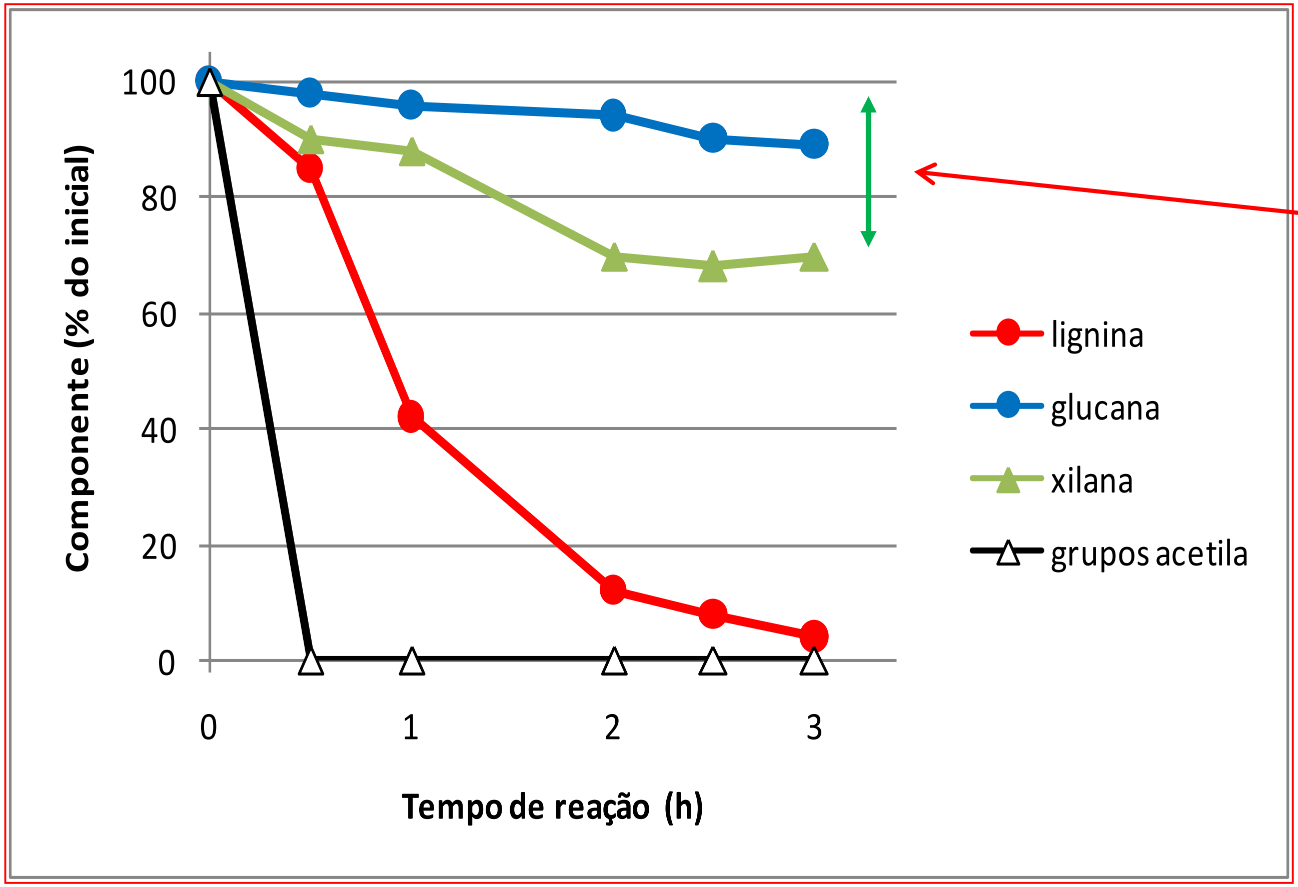
- A fração de celulose é recuperada com rendimento elevado;

- Há perda significativa das polioses na forma polimérica;

- A lignina é recuperada na forma quebrada e dissolvida. Para ser usada na geração de calor, demanda concentração até cerca de 60-70% de sólidos

Biorefinaria associada com o processo kraft

Pense >> como maximizar a utilização dos componentes??



Parte importante da hemicelulose é perdida no processo

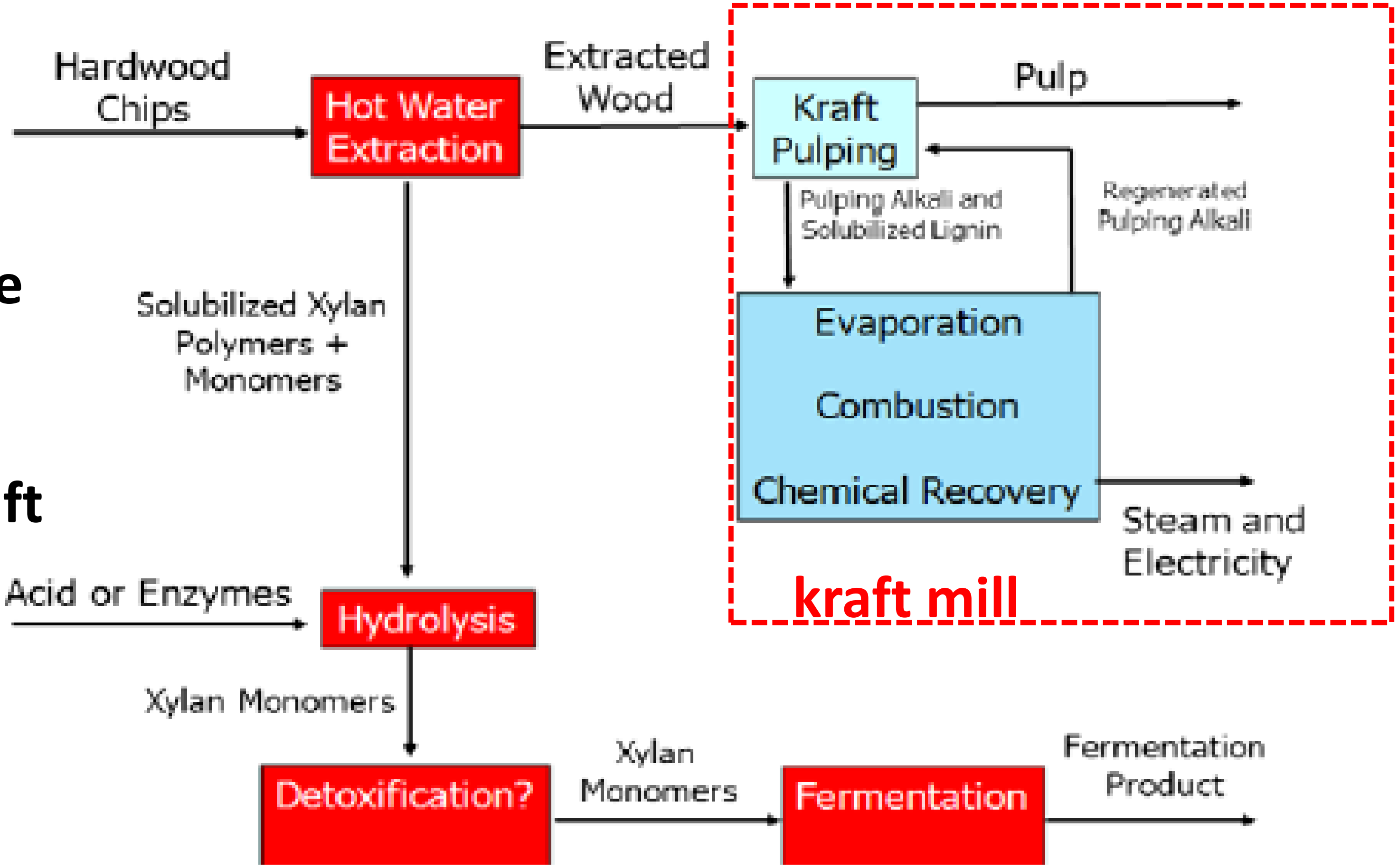
Dissolução dos principais componenmtes durante um processo de polpação kraft (Gomide e Almeida, Proc. BSCLWC 2001)

Alternativa para recuperar hemicelulose perdida

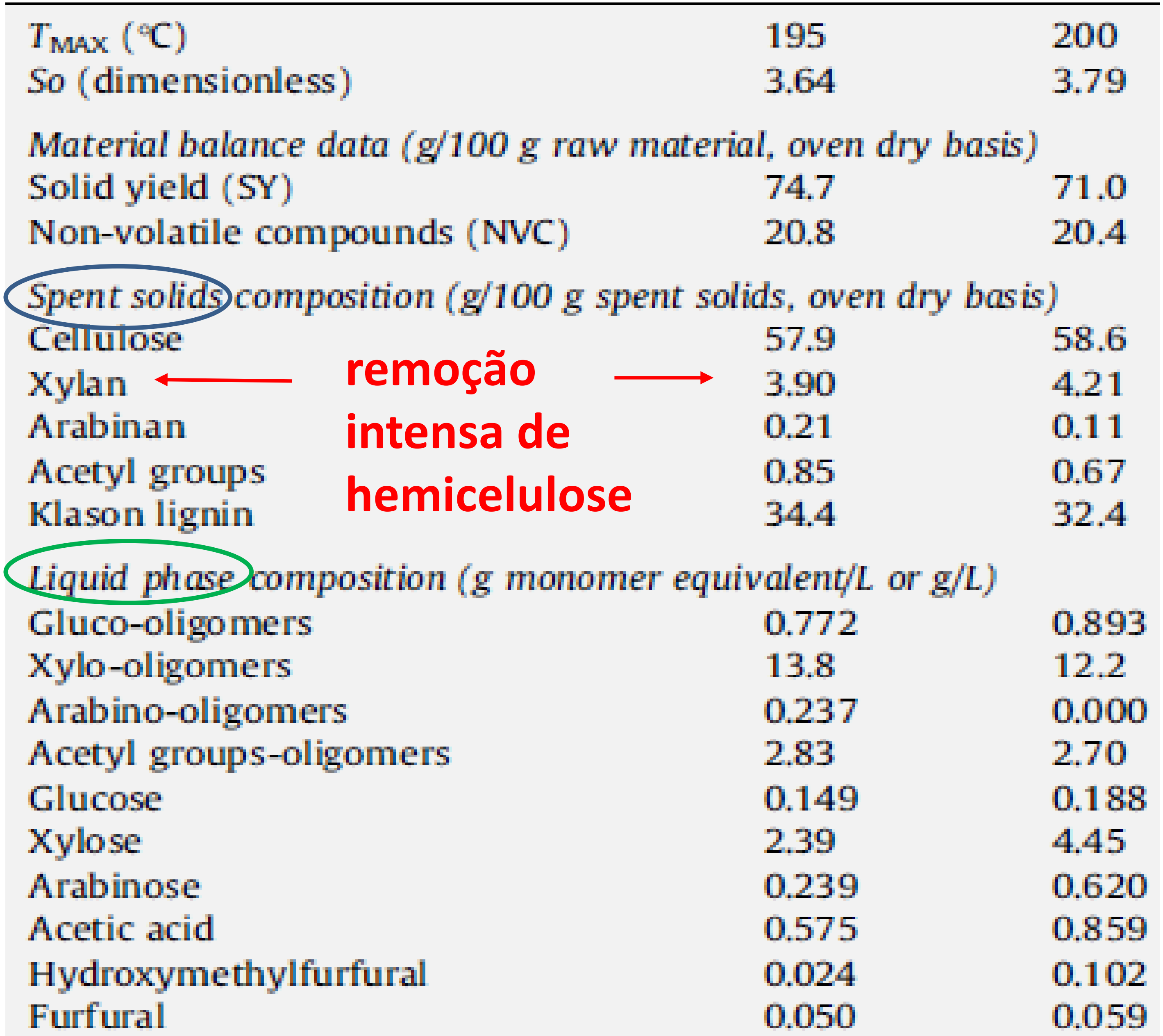
Remover a parte lábil por hidrólise ácida branda ou dissolução em meio alcalino, antes de iniciar o processo de polpação kraft.

O licor contendo as frações de hemicelulose dissolvida pode ser destinado a processos de bioconversão, por exemplo

Um modelo conceitual de biorrefinaria aplicado ao processo kraft



Exemplo com Eucalipto e autohidrólise

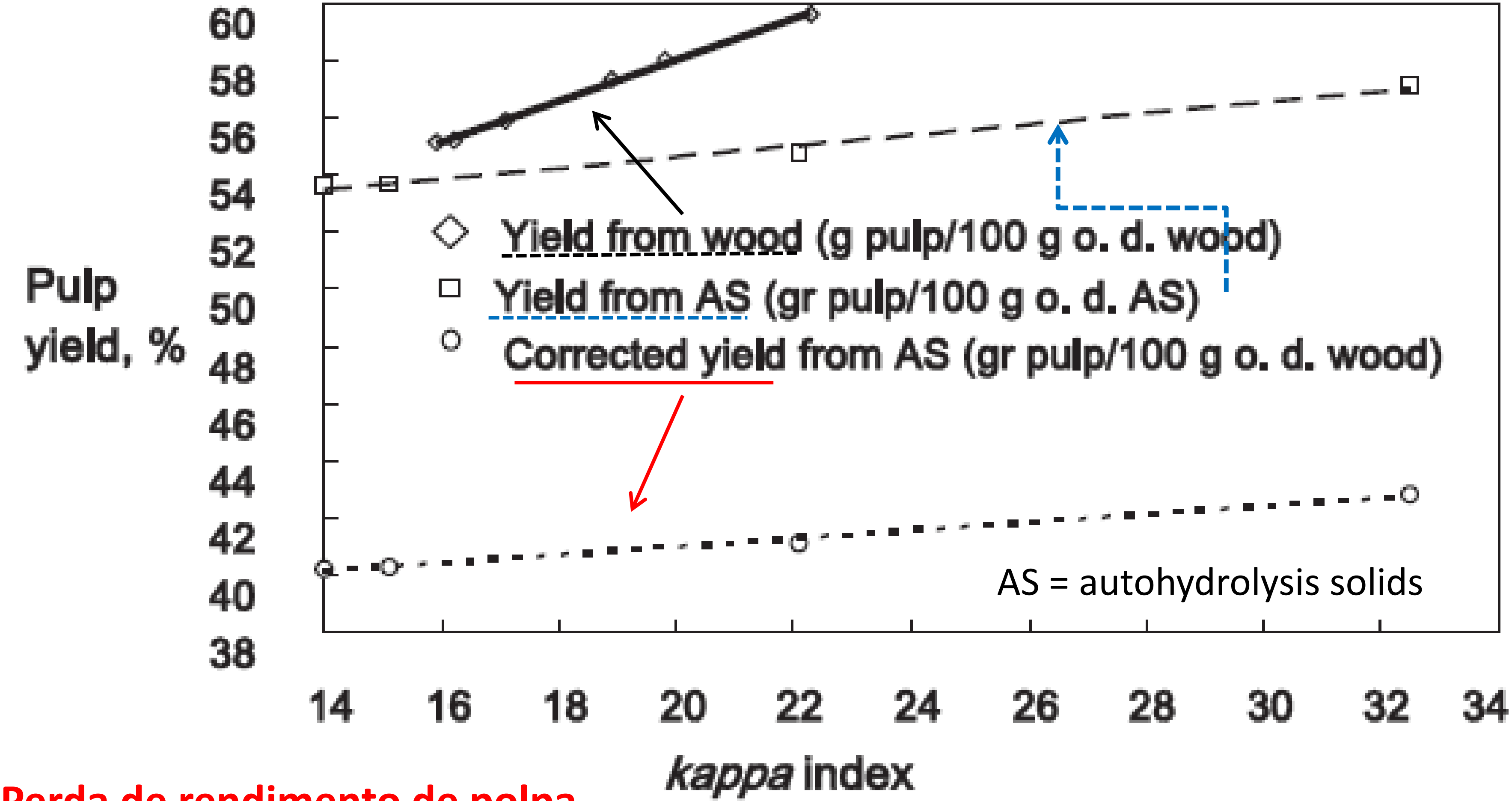


T_{MAX} (°C)	195	200
So (dimensionless)	3.64	3.79
Material balance data (g/100 g raw material, oven dry basis)		
Solid yield (SY)	74.7	71.0
Non-volatile compounds (NVC)	20.8	20.4
Spent solids composition (g/100 g spent solids, oven dry basis)		
Cellulose	57.9	58.6
Xylan	3.90	4.21
Arabinan	0.21	0.11
Acetyl groups	0.85	0.67
Klason lignin	34.4	32.4
Liquid phase composition (g monomer equivalent/L or g/L)		
Gluco-oligomers	0.772	0.893
Xylo-oligomers	13.8	12.2
Arabino-oligomers	0.237	0.000
Acetyl groups-oligomers	2.83	2.70
Glucose	0.149	0.188
Xylose	2.39	4.45
Arabinose	0.239	0.620
Acetic acid	0.575	0.859
Hydroxymethylfurfural	0.024	0.102
Furfural	0.050	0.059

remoção intensa de hemicelulose

A. Romaní et al. / Bioresource Technology 101 (2010) 8706–8712

Exemplo com Eucalipto: autohidrólise seguida de polpação kraft



AS = autohydrolysis solids

Perda de rendimento de polpa
Qualidade da polpa indica produto útil para polpa de dissolução (preparação de derivados de celulose)

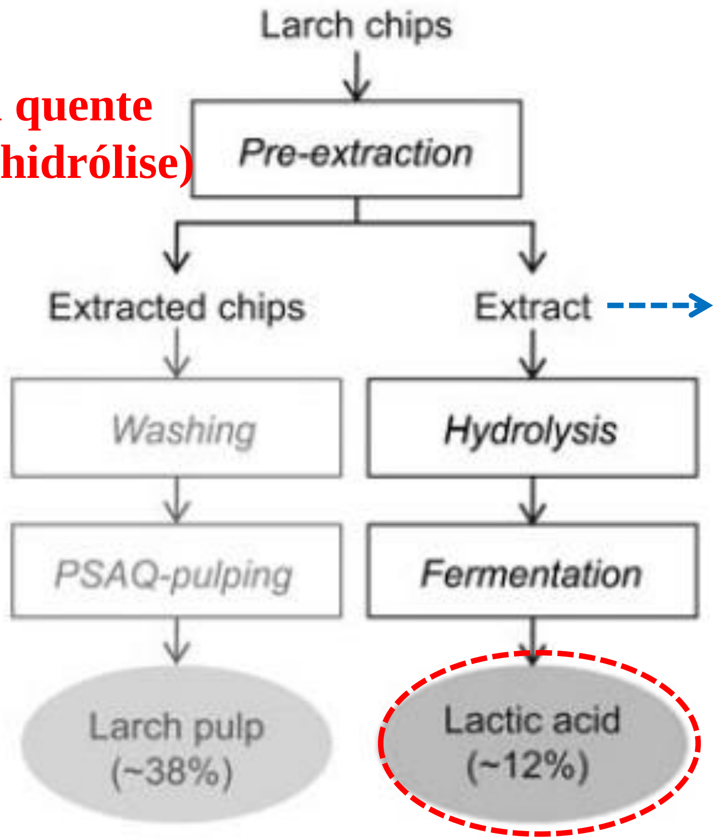
C. Vila et al. / Bioresource Technology 102 (2011) 5251–5254

A larch based biorefinery: pre-extraction and extract fermentation to lactic acid

Hanna Hörhammer[1,*], Sara Walton[2] and Adriaan van Heiningen[1,2]

Holzforschung, Vol. 65, pp. 491–496, 2011

Água quente (autohidrólise)


Larch chips

Pre-extraction

Extracted chips

Extract

Washing

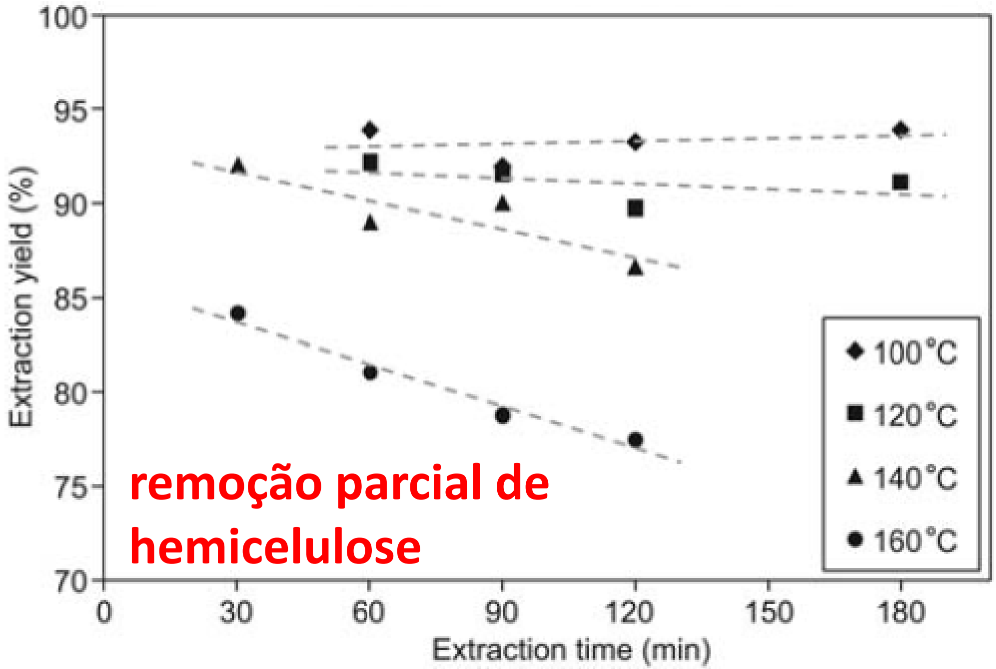
PSAQ-pulping

Larch pulp (~38%)

Hydrolysis

Fermentation

Lactic acid (~12%)

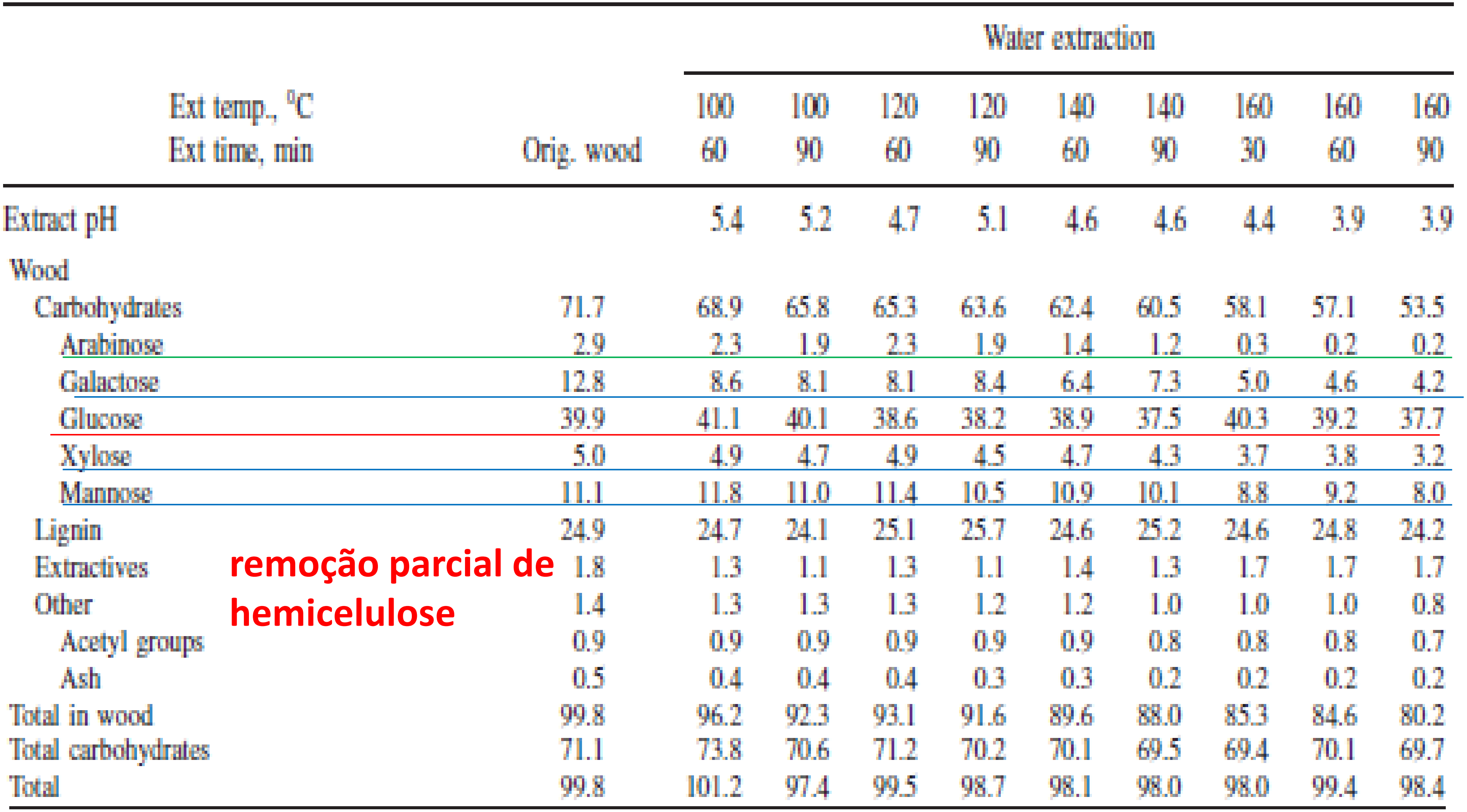


remoção parcial de hemicelulose

Figure 2 Yields from pre-extraction trials with Siberian larch (*L. sibirica*).

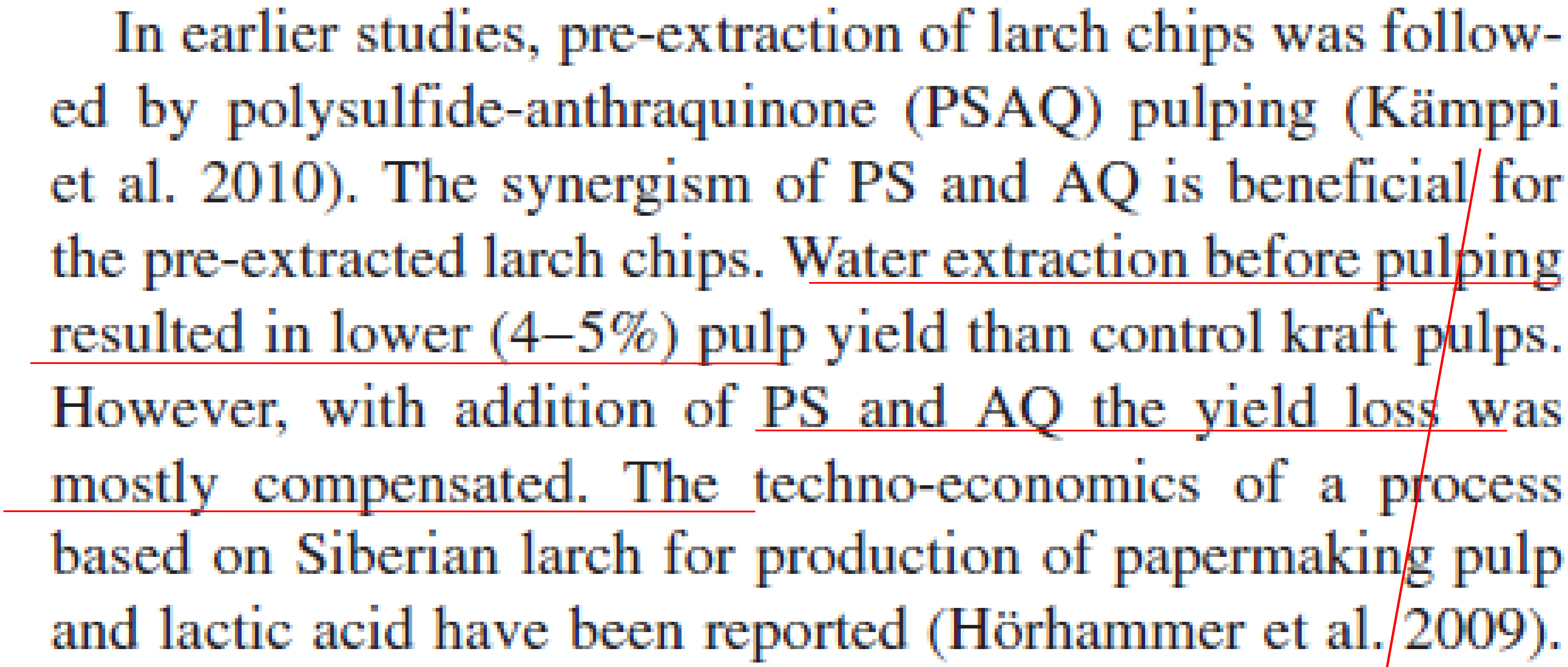
A larch based biorefinery: pre-extraction and extract fermentation to lactic acid

Balanço de massas dos componentes retidos na fração sólida



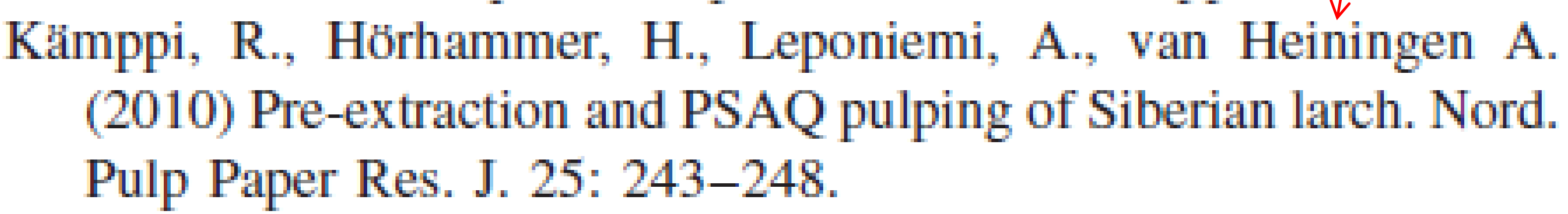
		Water extraction								
Ext temp., °C		100	100	120	120	140	140	160	160	160
Ext time, min	Orig. wood	60	90	60	90	60	90	30	60	90
Extract pH		5.4	5.2	4.7	5.1	4.6	4.6	4.4	3.9	3.9
Wood										
Carbohydrates	71.7	68.9	65.8	65.3	63.6	62.4	60.5	58.1	57.1	53.5
Arabinose	2.9	2.3	1.9	2.3	1.9	1.4	1.2	0.3	0.2	0.2
Galactose	12.8	8.6	8.1	8.1	8.4	6.4	7.3	5.0	4.6	4.2
Glucose	39.9	41.1	40.1	38.6	38.2	38.9	37.5	40.3	39.2	37.7
Xylose	5.0	4.9	4.7	4.9	4.5	4.7	4.3	3.7	3.8	3.2
Mannose	11.1	11.8	11.0	11.4	10.5	10.9	10.1	8.8	9.2	8.0
Lignin	24.9	24.7	24.1	25.1	25.7	24.6	25.2	24.6	24.8	24.2
Extractives	1.8	1.3	1.1	1.3	1.1	1.4	1.3	1.7	1.7	1.7
Other	1.4	1.3	1.3	1.3	1.2	1.2	1.0	1.0	1.0	0.8
Acetyl groups	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.7
Ash	0.5	0.4	0.4	0.4	0.3	0.3	0.2	0.2	0.2	0.2
Total in wood	99.8	96.2	92.3	93.1	91.6	89.6	88.0	85.3	84.6	80.2
Total carbohydrates	71.1	73.8	70.6	71.2	70.2	70.1	69.5	69.4	70.1	69.7
Total	99.8	101.2	97.4	99.5	98.7	98.1	98.0	98.0	99.4	98.4

remoção parcial de hemicelulose



In earlier studies, pre-extraction of larch chips was followed by polysulfide-anthraquinone (PSAQ) pulping (Kämppi et al. 2010). The synergism of PS and AQ is beneficial for the pre-extracted larch chips. Water extraction before pulping resulted in lower (4–5%) pulp yield than control kraft pulps. However, with addition of PS and AQ the yield loss was mostly compensated. The techno-economics of a process based on Siberian larch for production of papermaking pulp and lactic acid have been reported (Hörhammer et al. 2009).

Polpa ainda útil para fabricação de papéis



Kämppi, R., Hörhammer, H., Leponiemi, A., van Heiningen A. (2010) Pre-extraction and PSAQ pulping of Siberian larch. Nord. Pulp Paper Res. J. 25: 243–248.

Fermentação dos açúcares monoméricos liberados no extrato aquoso para produção de ácido lático

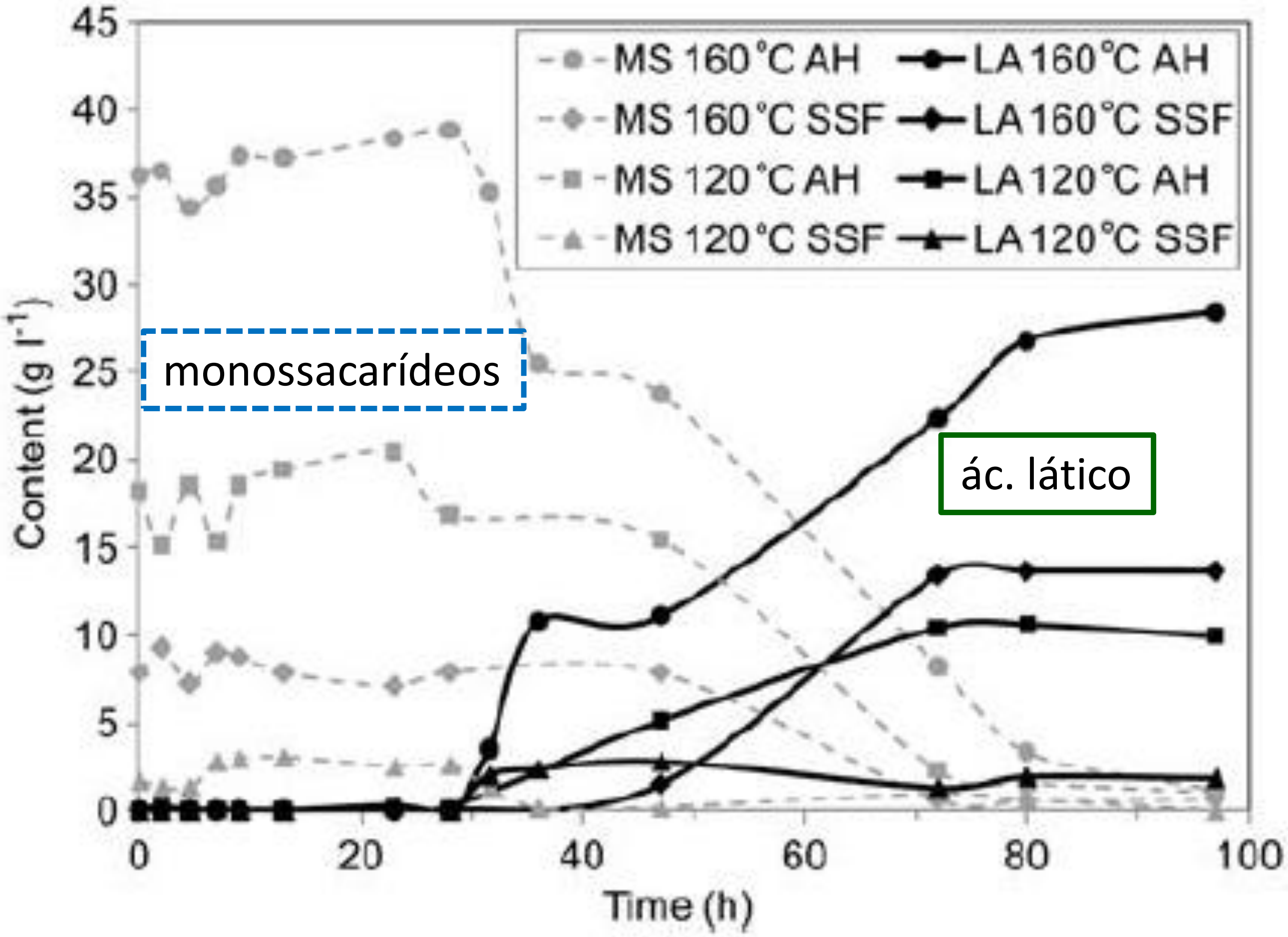


Figure 4 Lactic acid production through fermentation of larch (*L. sibirica*) extracts produced at 120°C and 160°C. Two different hydrolysis methods were tested; acid hydrolysis prior to fermentation (AH) and simultaneous enzymatic hydrolysis and fermentation (SSF). The consumption of monosugars (MS) and production of lactic acid (LA) are presented as a function of fermentation time.

Outra abordagem de biorrefinaria dentro do processo kraft

Recuperar a lignina na forma sólida

(usualmente por precipitação em meio ácido)

Visa minimizar o gasto energético necessário nas etapas de concentração do licor, além de proporcionar o desafogamento das indústrias na etapa de recuperação

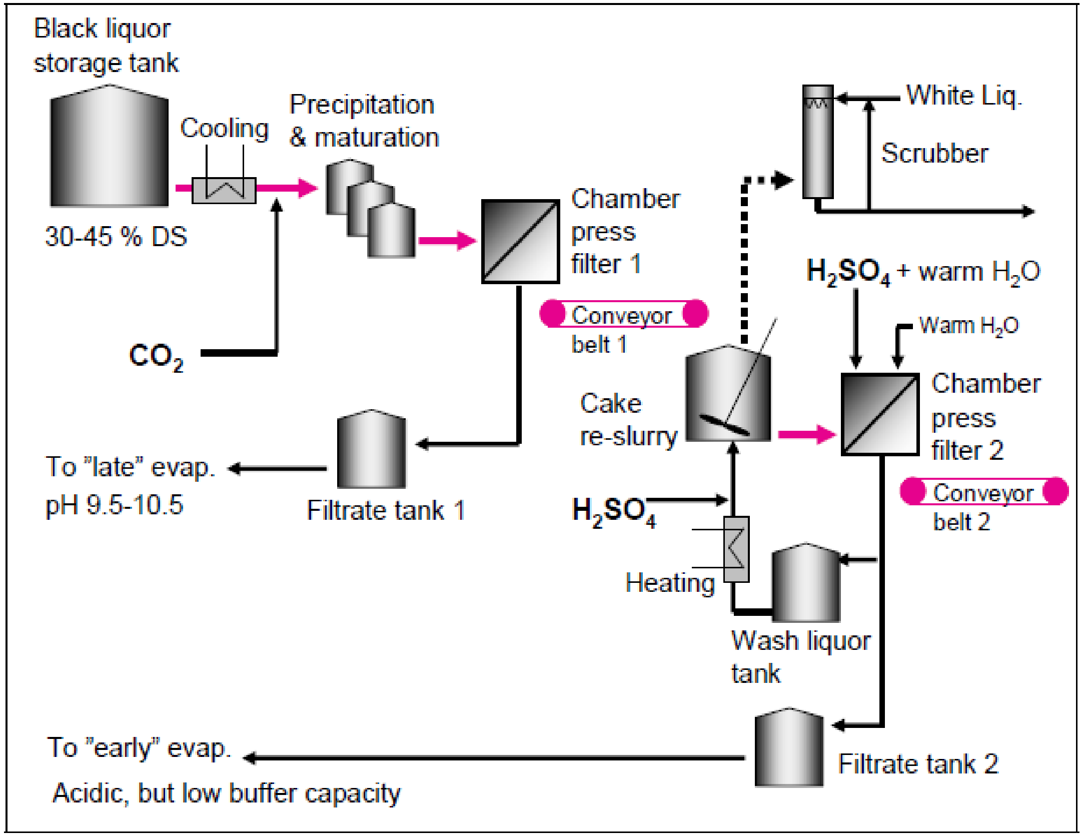


Figure 1 General layout of the lignin removal process (post-treatment, drying & pulverizing are excluded).

Lignoboost process
Inventia, Sweden

THE LIGNOBOOST PROCESS & USE OF LIGNIN AS A NEW BIO-FUEL

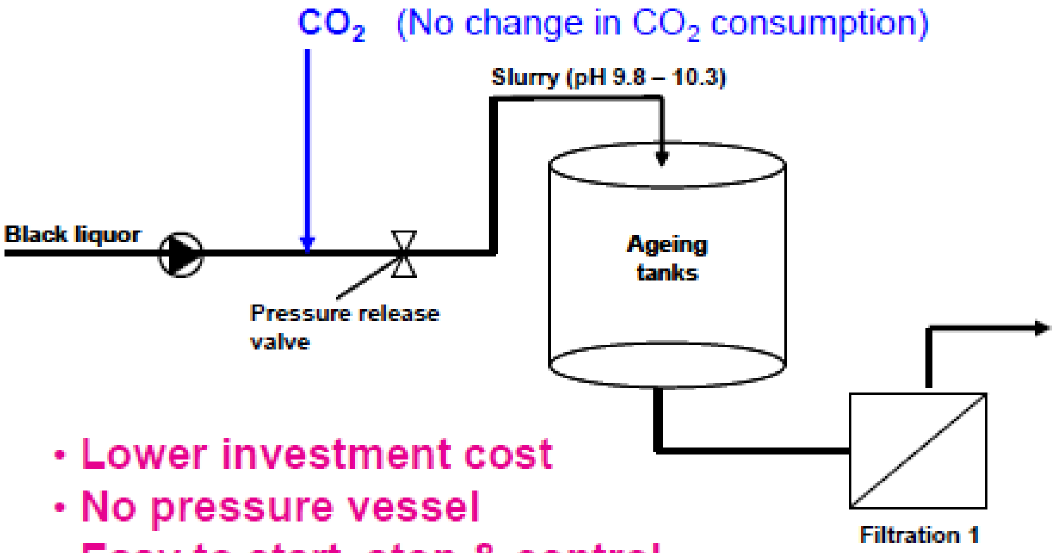
Per Tomani, Niklas Berglin, Peter Axegård

TAPPI Engineering, Pulping & Environmental Conference, October 11-14, 2009, Memphis, Tennessee

→ **Lignina**

Cellulose Chem. Technol., ***44*** *(1-3), 53-58 (2010)*

The NEW lignin precipitation process, 8 bar



CO_2 (No change in CO_2 consumption)

Slurry (pH 9.8 – 10.3)

Black liquor

Pressure release valve

Ageing tanks

Filtration 1

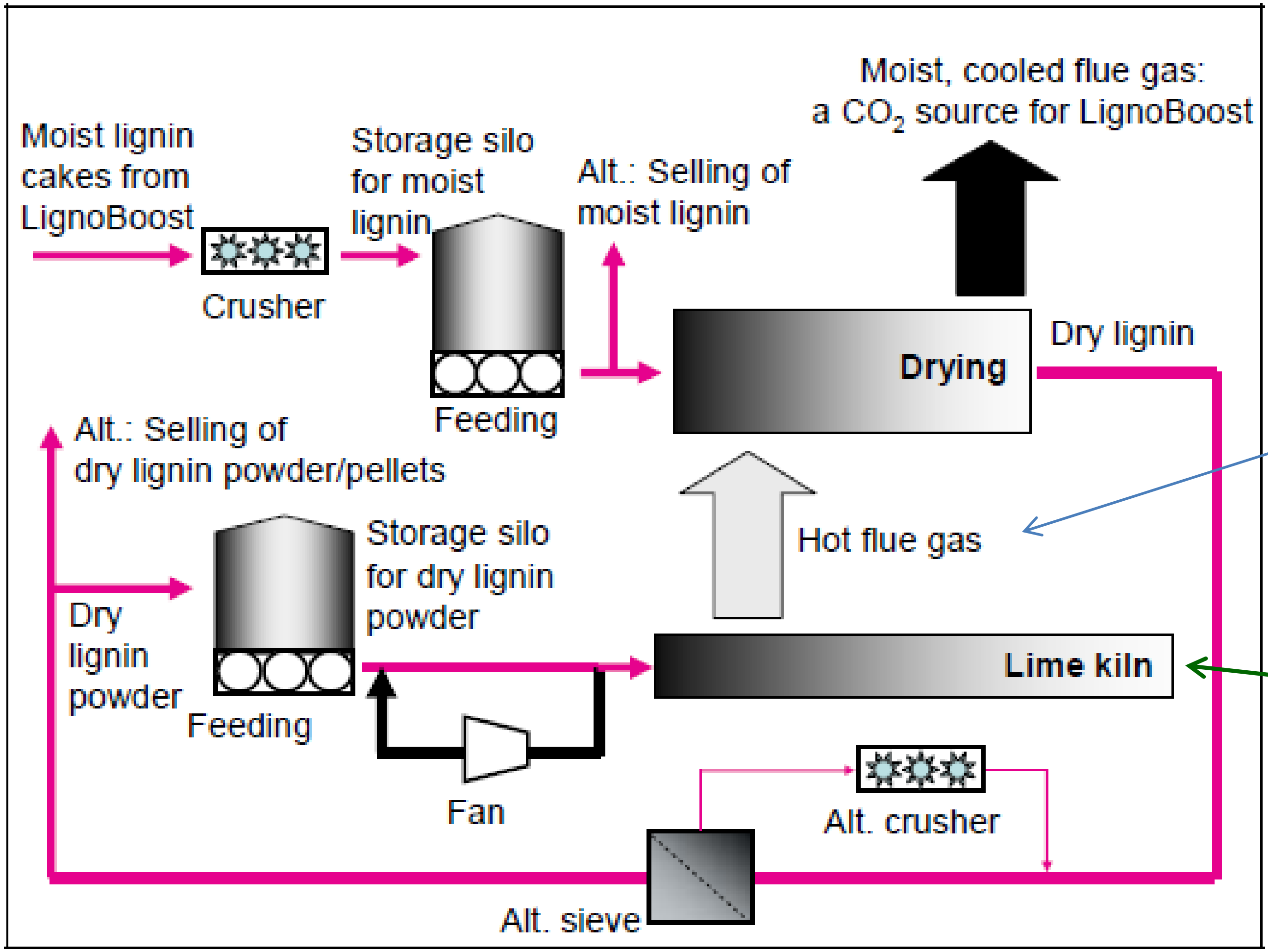
- Lower investment cost
- No pressure vessel
- Easy to start, stop & control
- Lower maintenance cost

Intermediate lignin filter cake from filtration stage 1

Dry solids: 65-70 %

ry-over of alkaline black
or effects the demand
cid in the last part of the
:ess.

ge amount of carry-over
acts the Na/S balance.

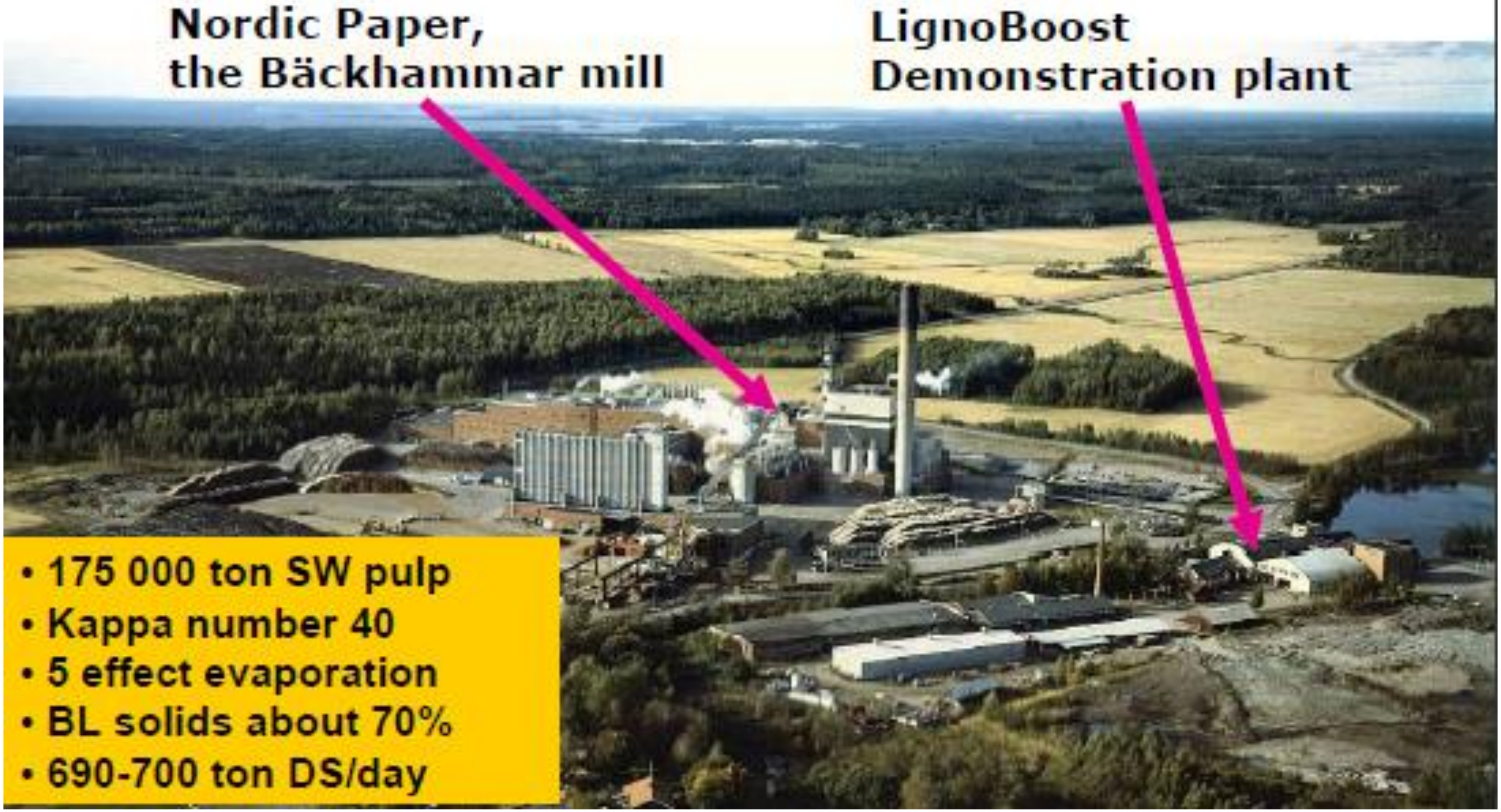


Aproveitamento do ar quente gerado >> secagem da lignina

Lignina **como fonte de energia para o forno de cal**: $CaCO_3$ >> $CaO + CO_2$

Figure 6. Lignin produced in the demonstration plant at Bäckhammar – filter cake and lignin pellets.

Demonstration in Bäckhammar by LignoBoost Demo AB



**Nordic Paper,
the Bäckhammar mill**

**LignoBoost
Demonstration plant**

- **175 000 ton SW pulp**
- **Kappa number 40**
- **5 effect evaporation**
- **BL solids about 70%**
- **690-700 ton DS/day**

The chamber pressfilter in Bäckhammar

Supplier: Metso Minerals

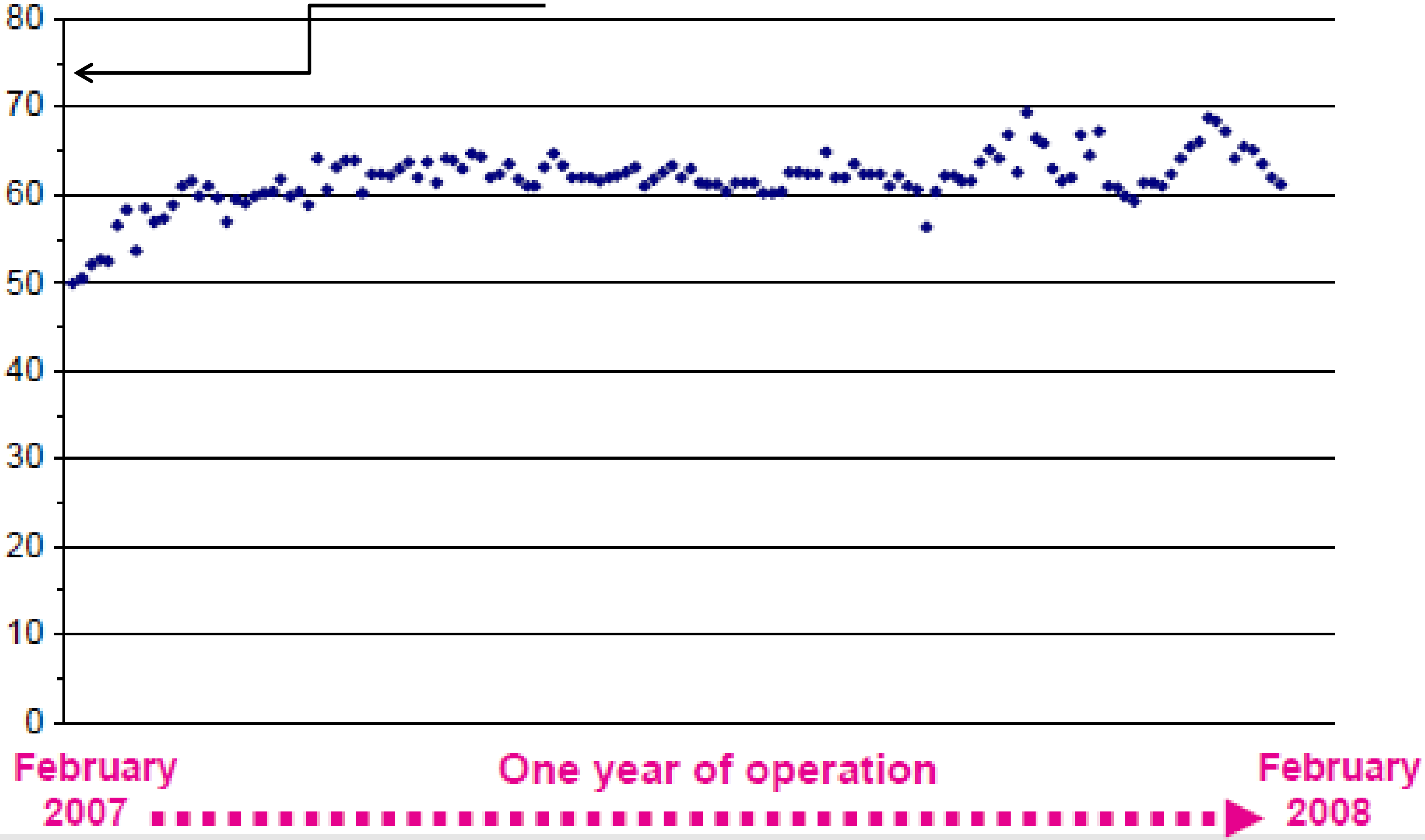
VPA 1040
24 chambers
1-1.2 tonnes lignin/h

- **Max capacity: 10 000 tonnes/year**
- **190-210 kg lignin/ ton DS, but just a partial flow of BL**
- **Our production rate March 2007 to September 2008 :150-350 ton/month**
- **Today mainly R&D activities – not a commercial delivery of fuel**
- **Production manager & 4 process operators in Bäckhammar**
- **Technical & administrative management from INNVENTIA**

LignoBoost Demonstration plant

Samples from the first year of operation

Dry solids in the final lignin product, %



Poder calorífico da lignina produzida

HHV

highest heating value

(considera a energia liberada a uma temparatura suposta de 25oC >> água na forma líquida)

LHV

lowest heating value

desconta a energia consumida com a vaporização da >> água na forma vapor)

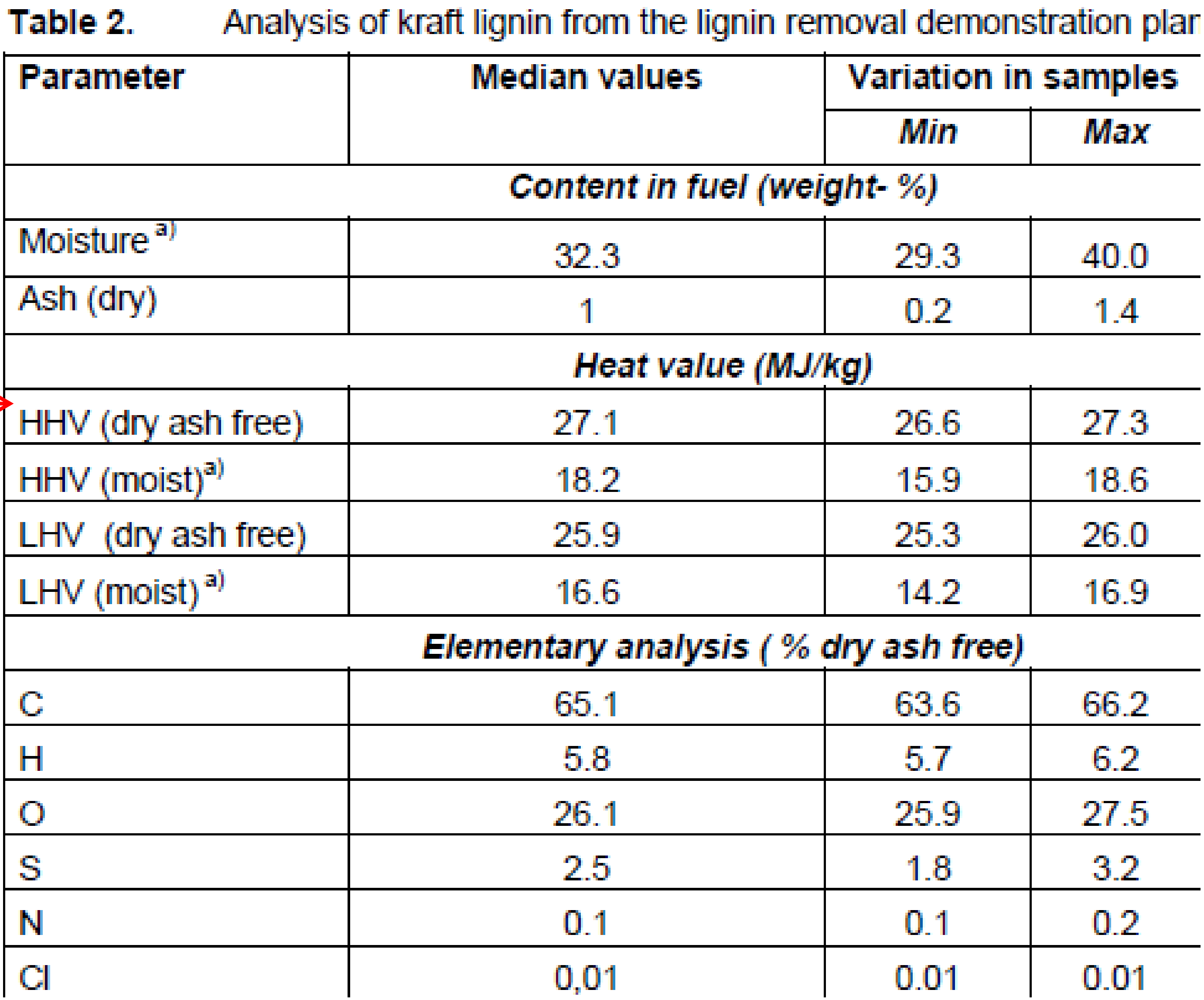


Table 2. Analysis of kraft lignin from the lignin removal demonstration plar

Parameter	**Median values**	**Variation in samples**	
		Min	***Max***
Content in fuel (weight- %)			
Moisture [a]	32.3	29.3	40.0
Ash (dry)	1	0.2	1.4
Heat value (MJ/kg)			
HHV (dry ash free)	27.1	26.6	27.3
HHV (moist)[a]	18.2	15.9	18.6
LHV (dry ash free)	25.9	25.3	26.0
LHV (moist) [a]	16.6	14.2	16.9
Elementary analysis (% dry ash free)			
C	65.1	63.6	66.2
H	5.8	5.7	6.2
O	26.1	25.9	27.5
S	2.5	1.8	3.2
N	0.1	0.1	0.2
Cl	0,01	0.01	0.01

Conceito do emprego da lignina como "óleo" bombeável

Pumpable lignin

33% lignin (on energy basis) in fuel oil 5

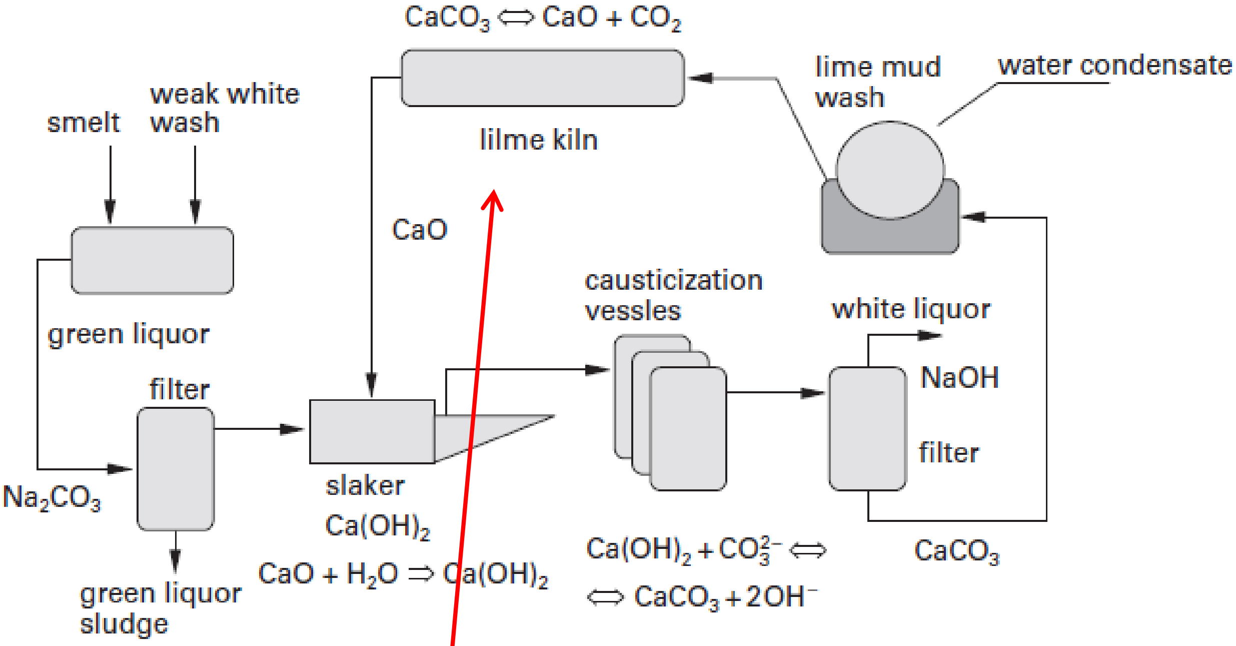
We have also sucessfully mixed lignin with glycerine (from bio-diesel production) and also with the tar oil from refining of crude tall-oil

Emprego da lignina no forno de cal

Full scale trial with lignin fuel as fuel in a lime kiln

Södra Cell Mönsterås 15-17 April 2008

- 37 tonne lignin to a lime kiln (275 ton lime/day) during 32 hours
- The lime kiln burner is designed for simultaneous co-firing of oil, bio-mass powder, gas (NCG) and methanol



Lignina como fonte de energia na calcinação no lugar de combustível fóssil

Lime product

Mesma qualidade como fonte de CaO


Reference lime before trial
(Sample K2)

Visible specks of lignin dust


Lime at 100 % lignin firing
(Sample K32)

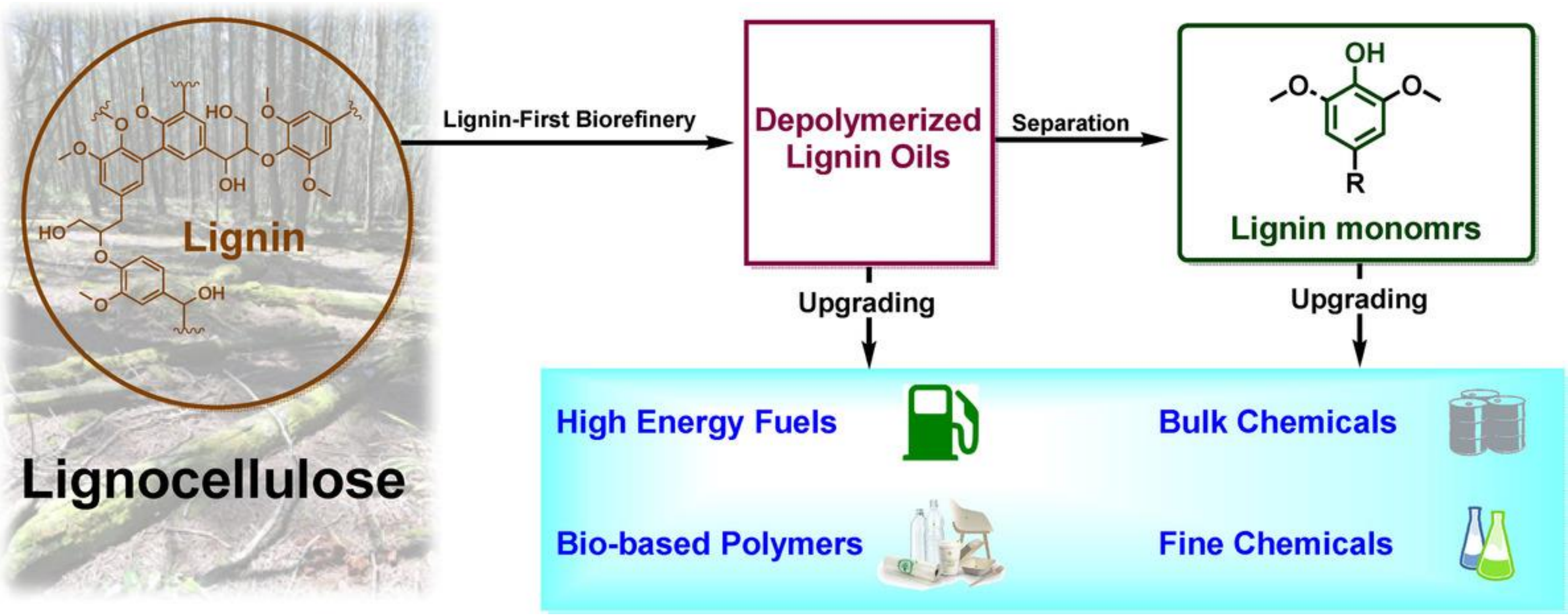
ChemSusChem
Chemistry-Sustainability-Energy-Materials
Chemistry Europe
European Chemical Societies Publishing

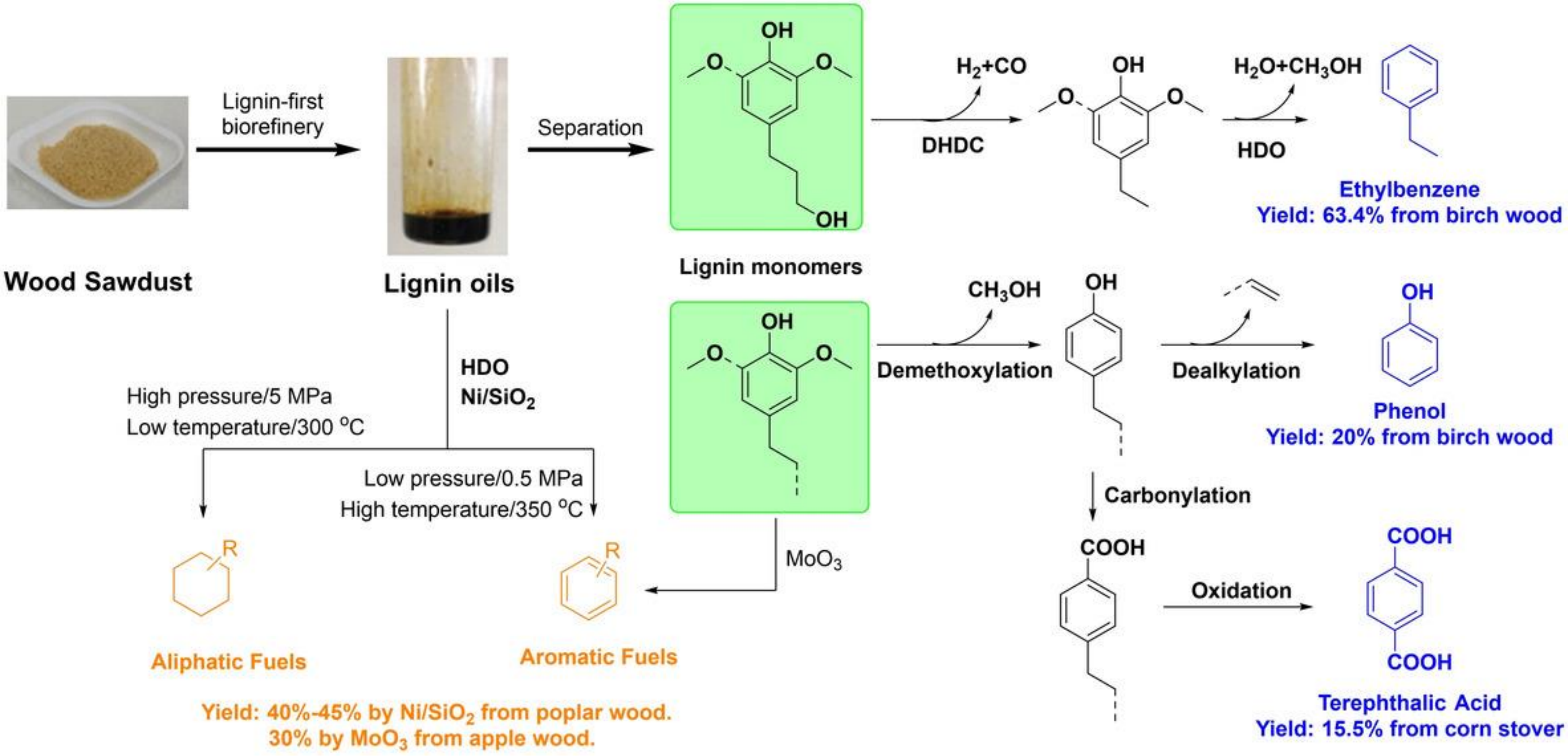
Minireview | Full Access

Downstream Processing Strategies for Lignin-First Biorefinery

Prof. Zhuohua Sun, Dr. Jinling Cheng, Prof. Dingsheng Wang, Prof. Tong-Qi Yuan, Prof. Guoyong Song, Prof. Katalin Barta

First published: 03 August 2020 | https://doi.org/10.1002/cssc.202001085 | Citations: 21



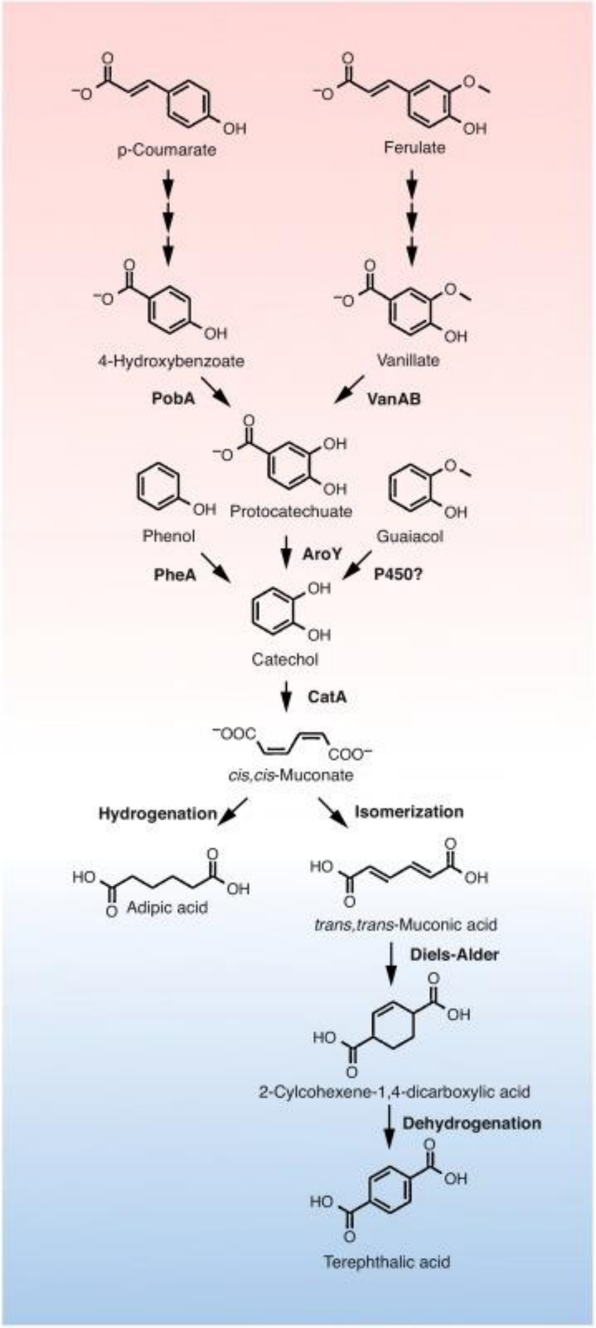

Wood Sawdust
Lignin-first biorefinery
Lignin oils
Separation
Lignin monomers
OH
OH
H2+CO
DHDC
H2O+CH3OH
HDO
Ethylbenzene
Yield: 63.4% from birch wood
CH3OH
Demethoxylation
Dealkylation
Phenol
Yield: 20% from birch wood
Carbonylation
COOH
Oxidation
Terephthalic Acid
Yield: 15.5% from corn stover
HDO
Ni/SiO2
High pressure/5 MPa
Low temperature/300 °C
Low pressure/0.5 MPa
High temperature/350 °C
MoO3
R
Aliphatic Fuels
Aromatic Fuels
Yield: 40%-45% by Ni/SiO2 from poplar wood.
30% by MoO3 from apple wood.

Current Opinion in Biotechnology
Volume 42, December 2016, Pages 40-53

Opportunities and challenges in biological lignin valorization

Gregg T Beckham ✉, Christopher W Johnson, Eric M Karp, Davinia Salvachúa, Derek R Vardon

Microbes capable of metabolizing aromatic monomers derived from depolymerized lignin, such as p-coumarate, ferulate, 4-hydroxybenzoate, vanillate, phenol, or guaiacol, convert these molecules through ‘upper pathways’ to two central intermediates, protocatechuate and catechol. Protocatechuate can be decarboxylated by AroY to form catechol, which is then subjected to ring-opening to form cis–cis-muconate by CatA, a catechol 1,2-dioxygenase. Subsequently, muconic acid can be chemo-catalytically converted to (a) adipic acid via hydrogenation, or (b) terephthalic acid via isomerization, Diels–Alder reaction with ethylene, and dehydrogenation.



Current Opinion in Biotechnology

Próxima aula

Integração de um processo de produção de etanol desde sacarose (1G) e de celulose e demais polissacarídeos (2G)