



Biomass pre-treatment: separation of cellulose, hemicellulose and lignin. Existing technologies and perspectives

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**Utilization of Biomass for the Production of Chemicals
or Fuels. The Concept of Biorefinery comes into
Operation.**

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Speaker : Anna Maria Raspolli Galletti, University of Pisa



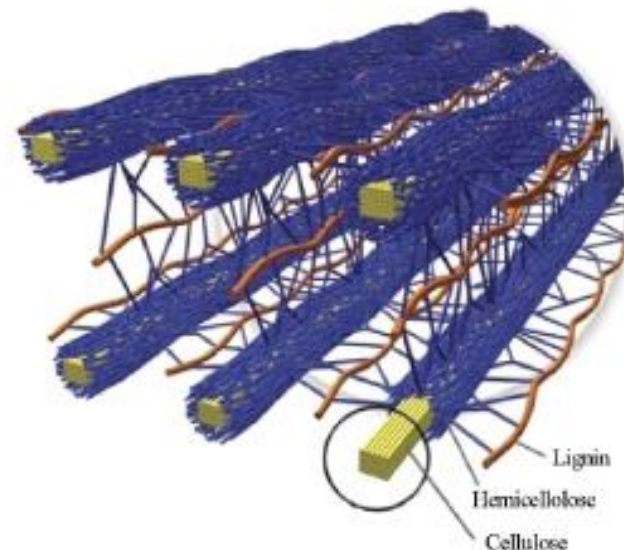
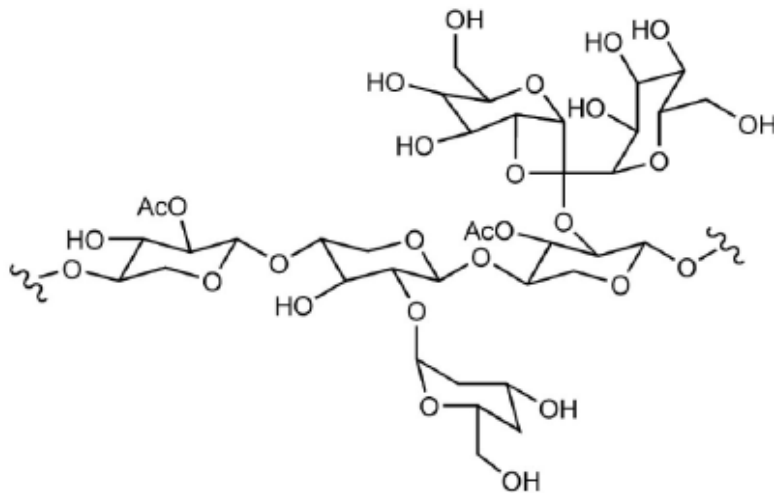
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Lignocellulosic biomass

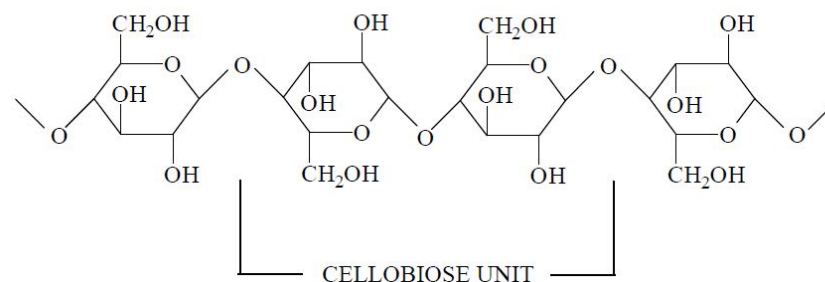
- Lignocellulosic biomass mainly consists of three polymeric components:
- **hemicellulose**,
- **cellulose**
- and **lignin**.
-

Hemicellulose is a complex, branched and heterogeneous polymeric network, based on pentoses such as xylose and arabinose, hexoses such as glucose, mannose and galactose, and sugar acids. **It has a lower molecular weight than cellulose and its role is to connect lignin and cellulose fibers.**



Lignocellulosic biomass

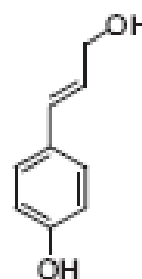
Cellulose is a long chain polysaccharide formed by D-glucose units, linked by β -1,4 glycosidic bonds: its structure has crystalline parts and amorphous ones.



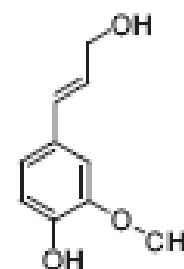
Lignin is an amorphous polymer made by different phenolic compounds and is the main component of cell walls:

Monolignol monomer species, (a) p-Coumaryl alcohol (4-hydroxyl phenyl, coniferyl alcohol (guaiacyl, G), (c) sinapyl alcohol (syringyl, S).

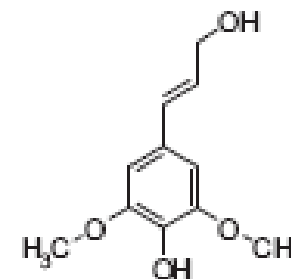
Lignin holds together cellulose and hemicellulose fibers and gives support, resistance and impermeability to the plant



(a)



(b)



(c)

Composition of common lignocellulosic raw materials and wastes (wt % on dry biomass)

	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40–55	20–40	18–25
Softwood stems	45–50	25–35	25–35
Rice straw	35–45	18–25	10–25
Wheat straw	38–45	20–32	7–10
Tobacco chops	22–30	15–20	15–25
Arundo donax	30–38	18–22	8–20
Miscanthus	35–40	16–20	20–25
Newspaper	40–55	25–40	15–30

Fractionation

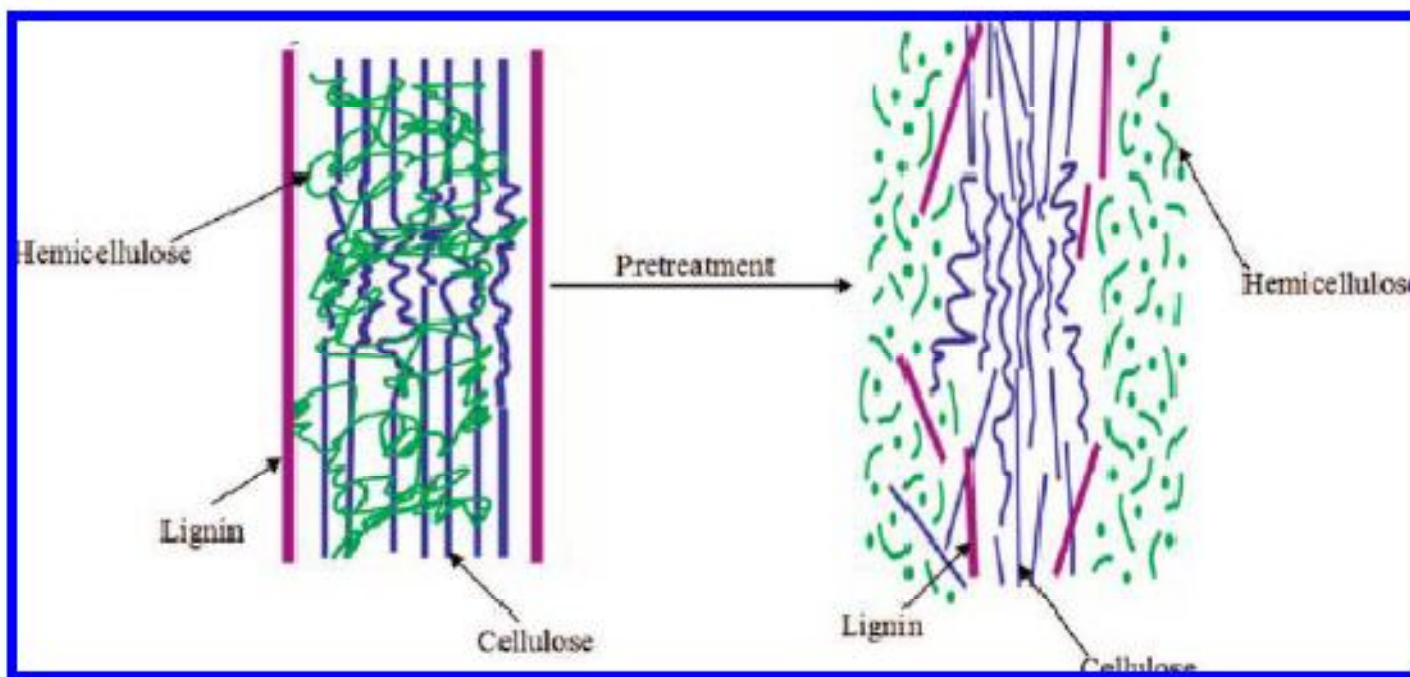
Biomass fractionation involves many different approaches:

An effective pretreatment should meet the following requirements:

- 1) overcome lignocellulosic biomass recalcitrance, deconstructing the three-dimensional structure of lignocellulose, and breaking down the semi-crystalline cellulose and hemicellulose
- 2) afford high yields to sugars or chemicals and/or give highly digestible pretreated solid;
- 3) avoid carbohydrates degradation and in particular preserve the utility of pentosan (hemicellulose) fraction;
- 4) avoid the formation of inhibitory toxic byproducts;
- 5) allow lignin recovery and exploitation to give valuable co-products;
- 6) be cost-effective, involving reasonable size reactors, low wastes amount and low energetic requirements

Alvira, P., et al. (2010) *Bioresour. Technol.* 101, 4851–4861.

Role of pretreatment



Schematic of the role of pretreatment in the conversion of biomass to fuel

P. Kumar et al., Ind. Eng. Chem. Res. 48 (2009) 3713-3729.

Biofuels by hydrolysis/fermentation

The separation of the three main components of lignocellulosic biomass is severely limited by many factors, such as lignin content, cellulose crystallinity, water content and available surface area which also influence the future exploitation of the pretreated materials, for conversion to ethanol or for fine chemicals synthesis.



Physical pretreatments of biomass

The purpose of physical pretreatments is the **increase of the accessible surface area and the size of pores of cellulose** and the **decrease of its crystallinity and its polymerization degree**.

Several types of physical processes have been developed, such as milling, grinding, extrusion, and irradiation (gamma rays, electron beam, ultrasounds, microwaves).

These methods are not very often satisfactory if used individually, and many times are employed **in combination with chemical ones** in order to improve the process efficiency.

The **power requirement** of these mechanical pretreatments is relatively **high** and depends on the type of biomass and on the final particle size: beyond a certain particle size, these pretreatments become economically unfeasible (Hendriks A.T.W.M., 2009)

Torrefaction

Biomass torrefaction is a thermal treatment consisting of biomass heating to a moderate temperature, generally between 200 and 300 °C, working under inert or nitrogen atmosphere (Prins M.J., 2006).

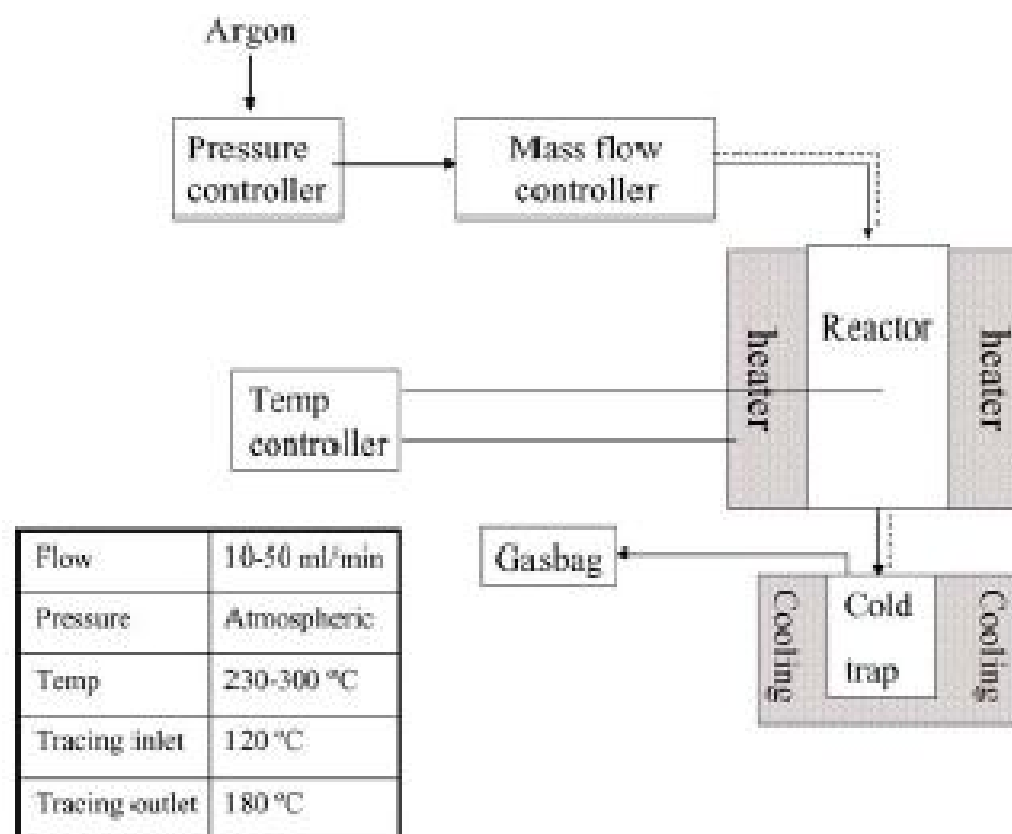
This thermal process mainly removes moisture and low weight organic components finally depolymerizing the long polysaccharides.

Three temperatures, around 220 °C, 250 °C and 290 °C, are applied for light, mild and severe torrefaction respectively.

Advantages

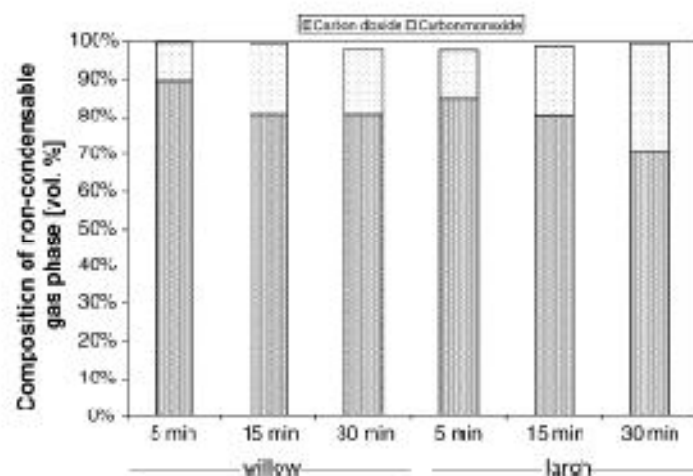
- the hygroscopic raw biomass is converted to hydrophobic material
- easier storage and delivery (herbaceous biomass...)
- easier grindability (energy saving)
- no inhibition in successive enzymatic hydrolysis

Torrefaction scheme



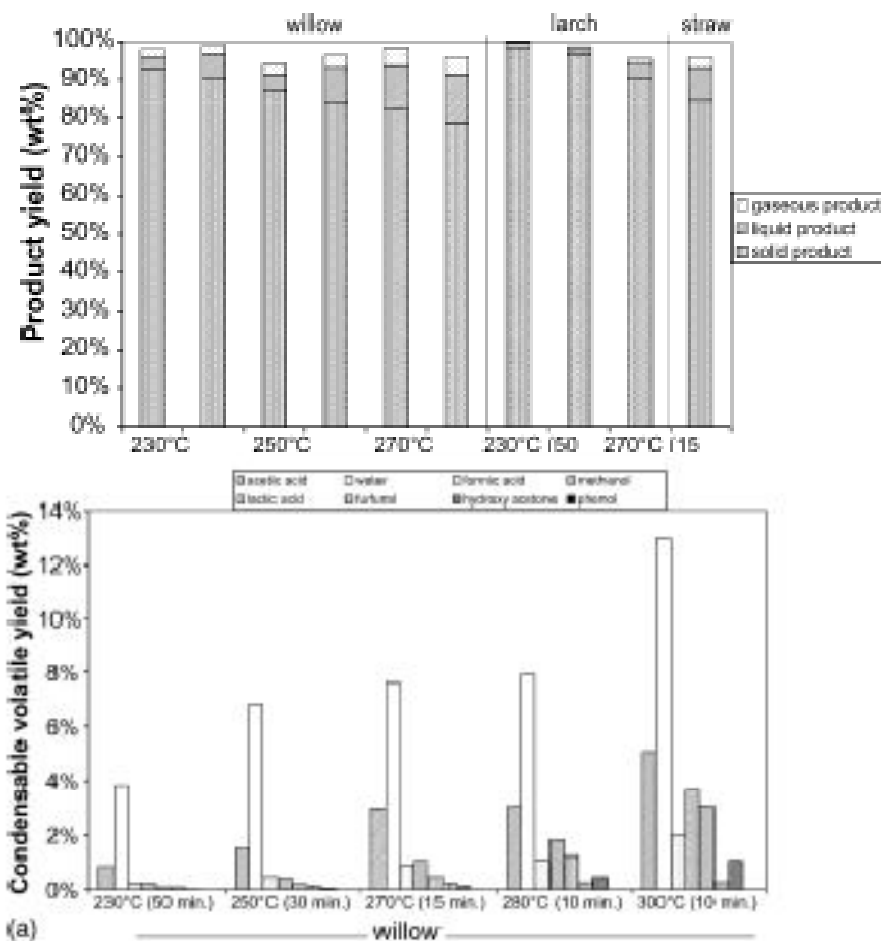
Torrefaction products

Gas composition : T: 250 °C; 30 min



Dehydration and decarboxylation reactions cause a mass loss of the wood and its friability is increased.

M.J. Prins et al., J. Anal. Appl. Pyrolysis 77 (2006) 35–40



Summary of torrefaction sensitivity of the tested materials.

	230°C	260°C	290°C
Hemicellulose	△	○	○
Cellulose	△	△	○
Lignin	△	△	△
Xylan	□	△	△
Dextran	△	□	□
Xylose	△	△	△
Glucose	△	△	△

△ : weakly active reaction (weight loss < 10 wt%).

□ : moderately active reaction (10 wt% ≤ weight loss ≤ 35 wt%).

○ : strongly active reaction (weight loss > 35 wt%).

W.-H. Chen, P.-C. Kuo / Energy 36 (2011) 803–811

Hemicellulose content was mainly influenced adopting light torrefaction, whereas in severe torrefaction there was a drastic depletion of lignocellulosic materials.

Steam Explosion (SE)

Steam Explosion (SE) is the most commonly used pretreatment of biomass and **uses both physical and chemical methods to break the structure of the lignocellulosic material** through an hydrothermal treatment. The biomass is treated with **high pressure steam at high temperature for a short time, then it is rapidly depressurized and the fibrils structure is destroyed by this explosive decompression.** This defibration and the remarkable autohydrolysis significantly improve the substrate digestibility and bioconversion as well as its reactivity toward other catalytic reactions. The successive sudden decompression reduces temperature, quenching the process.

Temperatures :160 °C - 260 °C

Pressures 0.7–5 Mpa

Residence times 1-10 min.

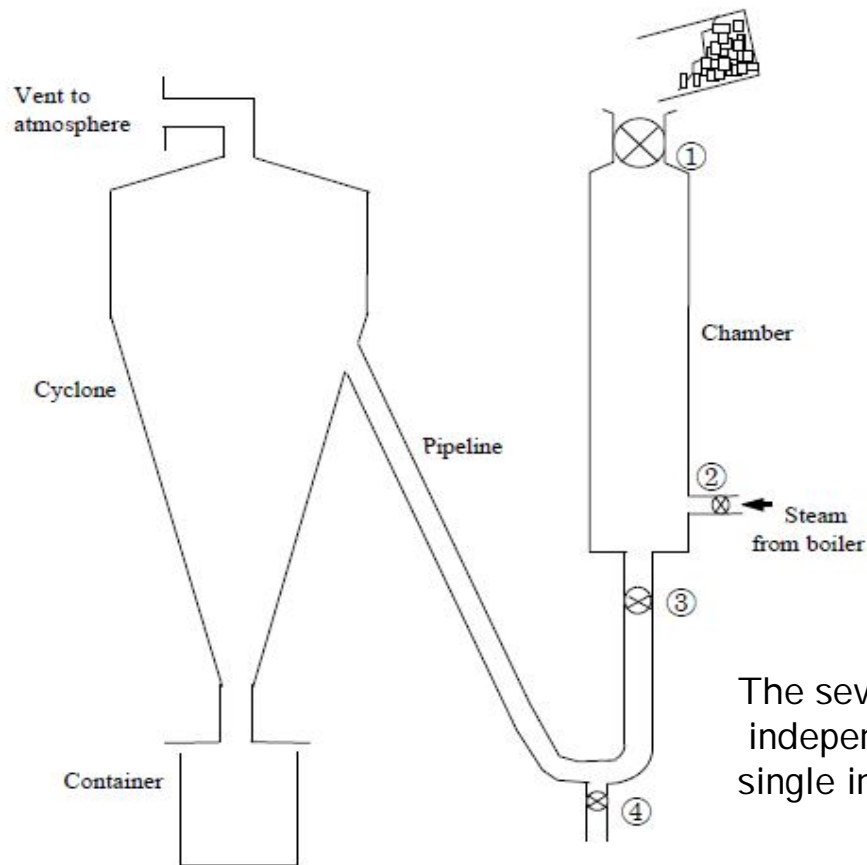
High solids concentrations (about 50%)

SE drawbacks

SE generates some **toxic derivatives** which can inhibit the successive hydrolysis and fermentation steps.

Furan derivatives, such as furaldehyde and 5-hydroxymethyl-2-furaldehyde, and phenolic compounds (deriving from lignin depolymerization) act as inhibitors.

To remove these inhibitors it is compulsive to wash the pretreated biomass with water, although this wash reduces the saccharification yields, removing soluble sugars, such as those deriving from hemicellulose hydrolysis .



1 : inlet valve; 2: steam inlet valve
3: release valve
P and T are controlled from boiler,
depending on required severity

$$R_o = \int_0^t \exp [(T_r - T_b) / 14.75] dt$$

R_o - severity

T_r - reaction temperature, °C

T_b - base temperature (100 °C)

t - retention time, minute

The severity index is an expression that combines the independent variables of temperature and time into a single independent variable.

Schematic batch steam explosion unit

SE parameters

SE main parameters are:

- temperature,
- residence time,
- particle size
- moisture content
- eventual addition of an acid (acid impregnation)

The optional addition of an acid in SE decreases contact times and temperatures.

Dilute acids (H_2SO_4 , but also SO_2 , oxalic acid and CO_2), generally 0.5–3.0 wt %, improve the hydrolysis step, leading to the complete removal of the hemicellulosic fraction, and decrease the formation of inhibitory compounds.

The addition of the acid catalyst results determinant for softwoods and to lower acetylated materials.

On the other hand, the addition of the acid causes many drawbacks related to equipment corrosion, higher amounts of degradation products and the necessary step of acid neutralization with consequent formation of wastes.

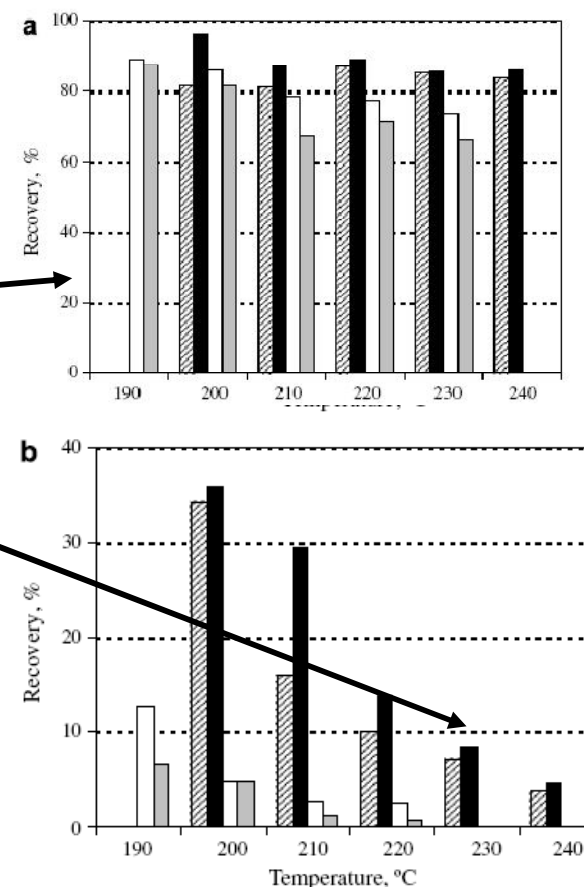
Effect of different SE pretreatments on olive tree pruning

In the production of fuel ethanol from olive tree pruning different SE pretreatments were tested (T: 190-240 °C; with or without impregnation by water or H₂SO₄ solutions):

Cellulose solubilization always occurs and is higher when acid and T > 210 °C were employed

Increase of steam temperature and acid presence give higher hemicellulose solubilization: it is complete at 230 °C for acid impregnated solids.

Fig. 1. Cellulose recovery (a) and hemicellulose recovery (b) in the solid pretreated residues at different pre-treatment conditions, expressed as a percentage of the initial content in the raw material. Impregnation conditions: none (▨), water (■), 1% H₂SO₄ (□), and 2% H₂SO₄ (▩).



C. Cara et al. Fuel 87 (2008) 692.

Effect of a water extraction stage previous to SE

Olive tree pruning contains about 25 wt % of extractives (resins and phenolics). It can be subjected to water extraction in autoclave (120 °C, 1h): significant improvement of sugars recovery can be reached if this water extraction stage previous to SE is adopted.

This extractives removal is determinant because their presence hinders the accessibility of cellulose lowering the successive enzymatic hydrolysis yield.

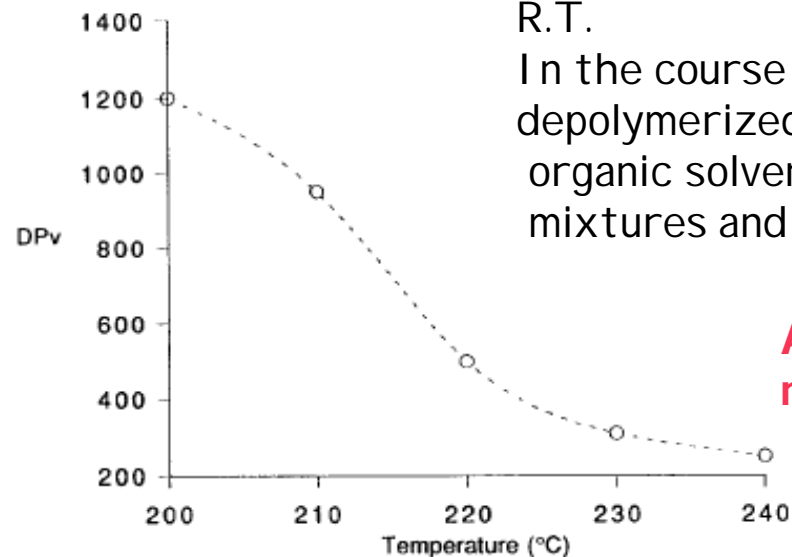
The SE products do not exert inhibitory effect on ethanol production.

Ballesteros I. et al., Bioresource Tech. 102 (2011) 6611.

Effect of SE on hemp

Hemp samples were soaked with 0.1 % H_2SO_4 solutions for 2 h at R.T.

In the course of steam treatment of hemp, lignin is partially depolymerized and modified, and becomes soluble in various organic solvents such as alcohols, acetone, dioxan-water mixtures and in alkaline solutions



At 240 °C degradation and fibre damage were noted!

Figure 8 Variation of the \overline{DP}_v values of exploded samples as a function of the STEX temperature

Steam explosion of woody hemp chènevotte; M. R. Vignon et al. (1995)

Liquid hot water (LHW) pre-treatment

LHW (aqueous fractionation, aquasolv or hydrothermolysis) is carried out at high temperatures (180–230 °C) and high pressures with contact times from few minutes to one hour and solids concentration < 20 wt %. In this process **biomass is immersed in liquid water**.

This chemical-free process dissolves about 50 % of the total biomass: almost **complete removal of hemicellulose**,
5–20 % removal of cellulose → cellulose digestibility increases
30–60 % removal of lignin.

Acetic acid and other released acid components catalyze the autohydrolysis, but LHW generates lower concentrations of inhibitory derivatives, due to higher water input ! It is a simple and environmental friendly approach.

Hendriks A.T.W.M. et al., Bioresour. Technol. 100 (2009) 10.

LHW pre-treatment of sugar cane bagasse for successive simultaneous saccharification and fermentation (SSF)

Solids concentration influenced many variables:

- Xylan recovery decreased and its dissolution increased
- Furfural concentration increased
- Inhibition of fermentation increased
- Hydrolyzate pH decreased
- SSF conversion increased

Xylan recovery, xylan dissolution, SSF conversion, hydrolyzate furfural concentration, and hydrolyzate pH as a function of solids concentration for LHW pretreatment at 220 °C and 2 min

Solids conc. (%)	Xylan recovery (%)	Xylan dissolution (%)	SSF conversion (%)	Hydrolyzate furfural conc. (g/l)	Hydrolyzate pH
1 ^a	91 ^a	79 ^a	75 ^a	0.1 ^a	3.8 ^a
2	83	85	84	0.2	3.7
3 ^b	64 ^b	93 ^b	94 ^b	0.5 ^b	3.4 ^b
8 ^b	41 ^b	98 ^b	92 ^b	0.6 ^b	3.3 ^b

^a Average of three pretreatment runs.

^b Average of two pretreatment runs.

R.L. Lynd et al., Bioresour. Technol. 81 (2002) 33.

Comparison of performances for LHW and SE of sugar cane bagasse SSF

For LHW pretreatment SSF conversion is favored by high temperature/short time conditions. Dissolved xylan is higher at high temperature/short time conditions.

For SE no significant differences existed between constant severity runs.

Comparison of pretreatment performance at constant severity with varying temperature and time for LHW and SE

Method	log Ro ^a	Temp. (°C)	Time (min)	Solids conc. (%)	pH	Dissolved xylan (%)	Xylan recovery (%)	SSF conversion ^b (%)
LHW	3.8	170	46	1	4.1	66	91	32
LHW	3.8	220	2	1	3.8	79	91	75
LHW	3.9	200	10	3	3.6	84	78	61
LHW	3.9	220	2	3	3.3	94	61	93
Steam	3.9	200	10	≥ 50	3.2	89	12	79
Steam	3.8	220	2	≥ 50	4.2	88	48	85

nd = not determined.

^a $Ro = t \exp((T - 100)/14.75)$; t = time (min); T = temperature (°C), (Overend and Chornet, 1987).

^b SSF conversion values based on residual cellulose.

R.L. Lynd et al., Bioresour. Technol. 81 (2002) 33.

LHW pretreatment of rye straw 10 wt %

At $T > 200\text{ }^{\circ}\text{C}$ **almost all hemicellulose can be recovered in the liquid fraction** whereas almost no glucose is detected.

At $T > 250\text{ }^{\circ}\text{C}$ the cellulose is depolymerized but glucose recovery is limited due to degradation.

LHW is a selective approach to separate hemicellulose from rye straw.

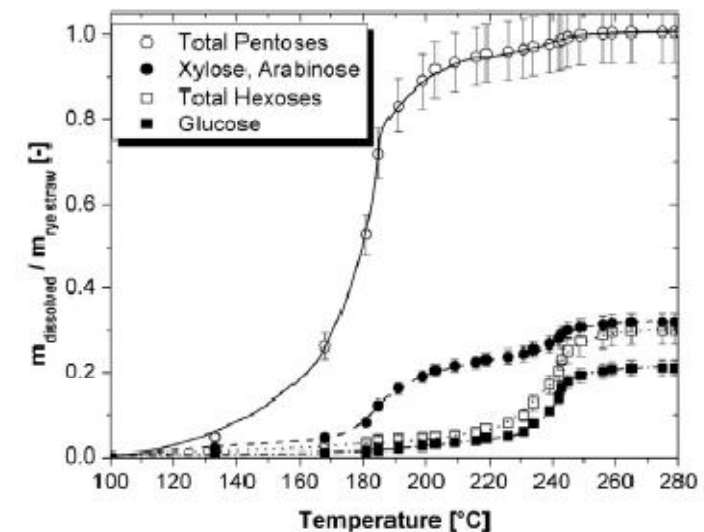


Fig. 2. Hydrolysis profile of rye straw in LHW; amount of dissolved mass related to the initial biomass with increasing temperatures (Ingram et al., 2009).

Ammonia fiber explosion (AFEX)

AFEX approach is similar to steam explosion: biomass is exposed to **liquid ammonia** (anhydrous or concentrated, > 70 %) under high temperature and pressure and then the pressure is quickly released, thus vaporizing the ammonia which is recovered and recycled

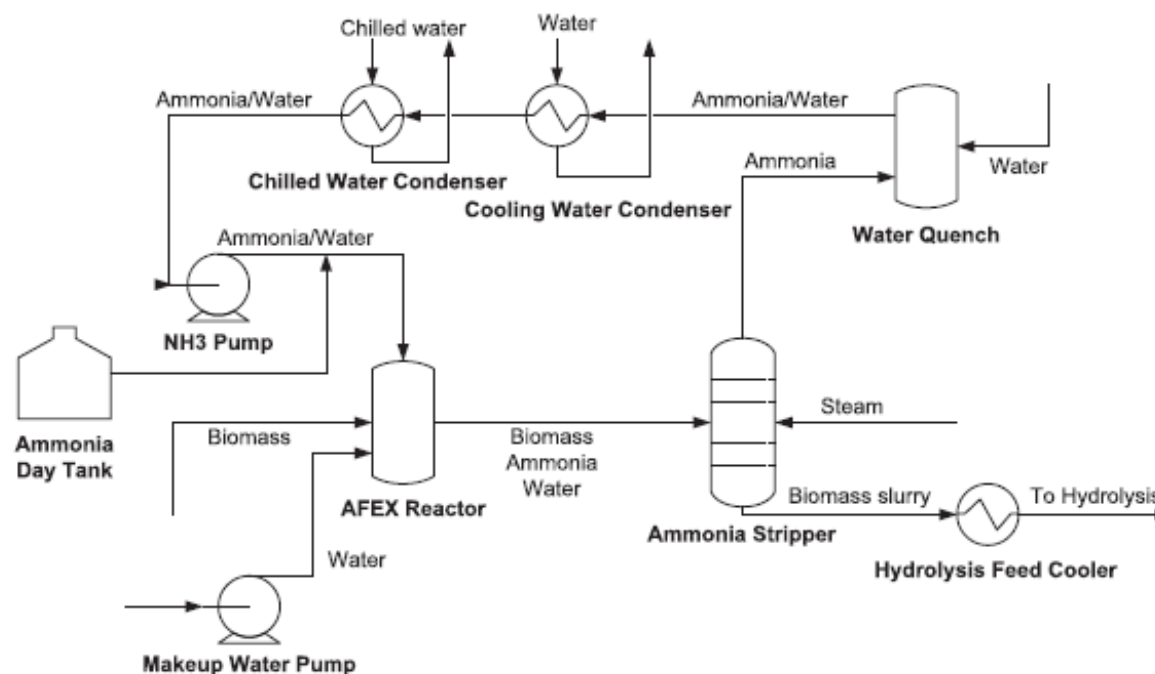


Fig. 1. Simplified process flow diagram of AFEX pretreatment and ammonia recovery system.

B. Bals, Bioresource Tech. 102 (2011) 1277-1283.

Ammonia fiber explosion (AFEX)

The main processing parameters are:

- Ammonia loading
- Water loading
- Residence time
- Temperature

Mild conditions (early maturity grasses, corn stover...): 1 kg of ammonia/Kg dry biomass; about 100 °C; 5-10 min residence time.

Severe conditions (mature grasses, woody materials...): up to 2 kg of ammonia/Kg dry biomass; about 200 °C; up to 30 min residence time.

AFEX effects:

almost complete solids recovery (no liquid dissolved fractions)

increased digestibility (cellulose decrystallization, cleavage of lignin-carbohydrate linkages, enhanced surface area and wettability)

AFEX severity

Levels used within the general full factorial model of AFEX pretreatment.

	Units	Low	Medium	High
Ammonia	g/g dry BM	0.5	1.25	2.0
Water	g/g dry BM	0.5	1.25	(2.0) ^a
Temperature	°C	80	140	(200) ^a
Residence time ^b	min	10	20	30

^a Levels dropped from factorial design due to lack of convergence by the Aspen model.

^b Factor dropped from equipment, energy, and material cost analysis due to only affecting one piece of equipment.

Operating costs

Ammonia loading and also residence time have the highest impact on the economics of the process. Ammonia must be recovered and recycled after the pretreatment and the cost of the recovery represents a severe limit for large scale applications. The electricity costs are the primary effect on the total variable operating costs of the biorefinery.

Impact of ammonia loading, water loading, and temperature on electricity usage within the biorefinery. A residence time of 10 min was used for this analysis. Only individual streams with a coefficient of variation >5% are shown.

	Average kWh/Mg	% LHV ^a (%)	C.V. ^b (%)	Impact of factors ^c		
				A	W	T
Total electricity	203.82	4.37	17.7	+++	—	—
Cooling tower system	4.37	0.09	28.6	+	+++	+++
Chilled water system	53.40	1.15	64.2	+++	—	—
Makeup water pump	0.02	0.00	79.9	—	+++	—
Recycle NH ₃ pump	1.48	0.03	41.9	+++	++	+
Hydrolysate feed pump	11.76	0.25	9.1	+	++	—
Cooling water pump	8.26	0.18	28.6	+	+++	+++
Process water circulation pump	1.38	0.03	7.9	+	++	+++

^a Electricity usage as a percentage of the entering biomass' lower heating value.

^b Coefficient of variation.

^c Qualitative assessment of the importance of ammonia loading (A), water loading (W), and temperature (T) on the costs of individual pieces of equipment or area. A+ represents an increase in price with an increase in level, A— represents a decrease of price with increase in level, and the number of + or — representing its relative importance.

B. Bals, Bioresource Tech. 102 (2011) 1277-1283

Makeup Ammonia

The amount of ammonia reacting with the biomass is dependent upon the composition and the structure of the biomass itself. Generally reacted ammonia is in form of acetamide (about 10 g of makeup ammonia/Kg dry biomass are necessary).

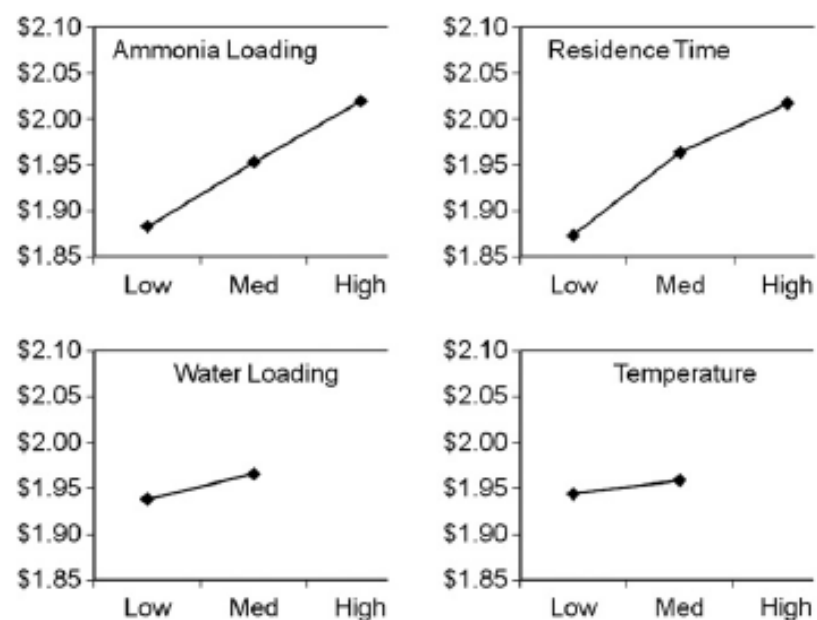


Fig. 2. Factor means for minimum ethanol selling price (MESP) at different levels of the four pretreatment factors studied. These factor means assume the amount of makeup ammonia required is constant at 10 g makeup ammonia per kg dry biomass.

LHW (sol/liq:1/6 wt/wt) vs mild AFEX for coastal Bermuda grass and subsequent enzymatic hydrolysis

Composition (mass %) of untreated CBG and pretreated CBG.

	Raw	AFEX						Autohydrolysis		
		80 °C 5 min	90 °C 5 min	100 °C 5 min	80 °C 30 min	90 °C 30 min	100 °C 30 min	150 °C 60 min	160 °C 30 min	170 °C 60 min
Holocellulose	55.7 ± 0.7	55.8 ± 0.2	56.1 ± 0.3	55.9 ± 0.5	56.2 ± 0.7	55.8 ± 0.1	56.6 ± 0.4	51.0 ± 0.9	42.9 ± 0.0	36.8 ± 1.2
Glucan	29.5 ± 0.5	29.1 ± 0.0	29.4 ± 0.1	29.3 ± 0.3	29.5 ± 0.4	29.2 ± 0.0	29.4 ± 0.3	33.6 ± 0.6	29.8 ± 0.3	31.8 ± 1.0
Hemicellulose	26.1 ± 0.2	26.7 ± 0.2	26.7 ± 0.2	26.6 ± 0.2	26.8 ± 0.3	26.6 ± 0.1	27.2 ± 0.1	17.4 ± 0.3	13.1 ± 0.3	4.5 ± 0.2
Xylan	19.8 ± 0.3	19.8 ± 0.2	19.9 ± 0.1	19.8 ± 0.2	19.8 ± 0.2	19.7 ± 0.0	20.1 ± 0.1	15.6 ± 0.2	12.2 ± 0.2	4.5 ± 0.2
Arabinan	4.5 ± 0.0	5.2 ± 0.0	5.0 ± 0.1	5.1 ± 0.0	5.2 ± 0.0	5.2 ± 0.0	5.4 ± 0.0	1.6 ± 0.0	0.8 ± 0.1	0.0 ± 0.0
Galactan	1.8 ± 0.0	1.8 ± 0.0	1.7 ± 0.1	1.8 ± 0.0	1.7 ± 0.0	1.7 ± 0.0	1.8 ± 0.0	0.2 ± 0.1	0.1 ± 0.0	0.0 ± 0.0
Total lignin	22.7 ± 0.4	21.9 ± 0.1	21.3 ± 0.5	22.0 ± 0.4	21.4 ± 0.0	21.9 ± 1.0	21.9 ± 0.2	19.2 ± 0.0	19.2 ± 0.6	23.1 ± 0.0
Acid-insoluble	17.6 ± 0.2	15.5 ± 0.1	15.3 ± 0.5	15.8 ± 0.3	14.8 ± 0.0	14.7 ± 0.3	15.1 ± 0.3	17.6 ± 0.0	17.8 ± 0.6	21.9 ± 0.1
Acid-soluble	5.0 ± 0.2	6.4 ± 0.0	6.0 ± 0.0	6.2 ± 0.1	6.6 ± 0.0	7.2 ± 0.7	6.8 ± 0.1	1.6 ± 0.0	1.4 ± 0.0	1.2 ± 0.1
Ash	4.9 ± 0.4	5.6 ± 0.1	6.2 ± 0.0	5.2 ± 0.6	7.0 ± 0.4	6.8 ± 0.9	7.8 ± 0.4	0.6 ± 0.0	1.1 ± 0.1	1.0 ± 0.0
Extractives	9.8 ± 0.3	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Others	7.0	16.8	16.4	16.9	15.3	15.5	13.8	29.2	36.8	39.1

N/D, not determined.

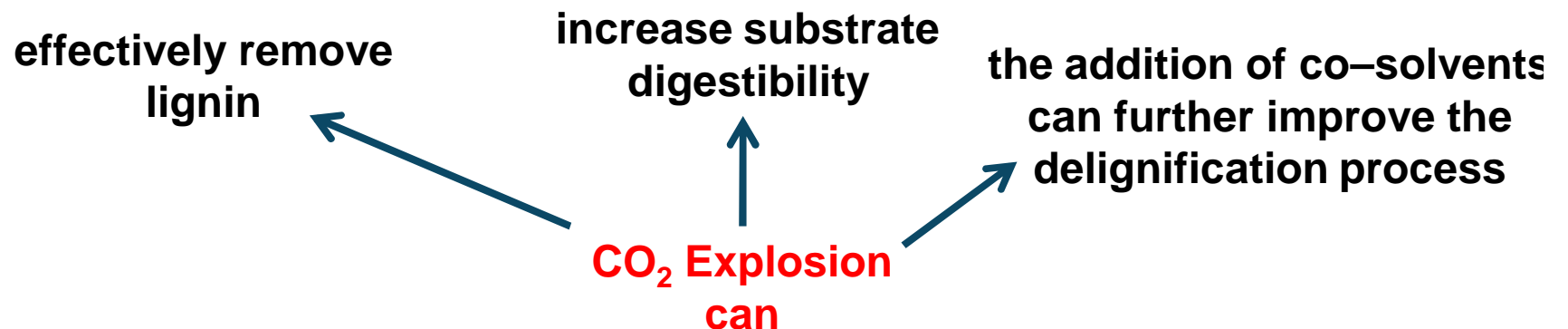
AFEX does not change the chemical composition of CBG and working at 100 °C for 30 min gives the highest sugar yield (94.8 % of theoretical possible).

LHW gives max 55 % sugar yield due to increased byproducts generation.

J.M. Lee et al., Bioresource Tech. 101 (2010) 5449-5458.

CO₂ Explosion

Carbon dioxide explosion is a biomass pretreatment which uses CO₂ as supercritical fluid (SC-CO₂) (Zheng Y., 1995). This technique was developed in order to adopt lower temperatures than those usually used in steam explosion and reduce the cost in comparison with AFEX (ammonia fiber explosion).

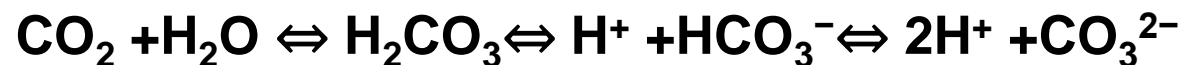


Pasquini D., Pimenta M.T.B., Ferreira, L.H., Curvelo A.A.D.S. *J. Supercrit. Fluids* (2005) 36, 31–39.

Advantages of Supercritical Carbon Dioxide

- availability at relatively low cost,
- non-toxicity,
- non-flammability,
- easy recovery after extraction,
- environmental acceptability (Schacht C., 2008).

In aqueous solution CO₂ forms carbonic acid which favours the biomass hydrolysis. CO₂ molecules are comparable in size to those of water and ammonia and thus they can penetrate in the same way the small pores of lignocellulose. This mechanism is facilitated by high pressures.



After the explosive release of CO₂ pressure, disruption of cellulose and hemicellulose structure is observed and consequently the accessible surface area for enzymatic attack increases.

Advantages of Supercritical Carbon Dioxide Explosion

- the employment of lower temperatures compared to those used in other pretreatments,
- the significant reduction of monosaccharides degradation,
- S-CO₂ is more cost effective than ammonia explosion,
- the formation of inhibitors is lower compared to that of steam explosion,
- the explosion affects the cellulose crystallinity and the glucose or ethanol yield from the subsequent enzymatic hydrolysis or simultaneous saccharification and fermentation,
- the possibility of using high solid concentrations in pretreated materials,
- the ability of increasing the accessible surface area,
- not-toxicity, non-flammability, easy recovery and low cost.

Srinivasan N., Ju L.K. *Bioresour. Technol.* (2010) 101, 9785–9791.

Kim T.H., Lee Y.Y. *Bioresour. Technol.* (2005) 96, 2007–2013.

Luterbacher J.S., Tester J.W., Walker L.P. *Biotechnol. Bioeng.* (2010) 107, 3, 451–460.

Unfortunately, this method does not guarantee economic viability yet

In particular, the high capital cost for high–pressure equipment may represent an obstacle to the commercialization of this lignocellulosic pretreatment.

An example: Luterbacher and coworkers developed a high pressure (200 bar) CO₂–H₂O process for pretreating several lignocellulosic biomass (hardwood, switchgrass, corn stover, big bluestem, and mixed perennial grasses (a co-culture of big bluestem and switchgrass)) at high-solid contents.

Temperatures: from 150 °C to 250°C;

Residence Times: from 20 seconds to 60 minutes.

Samples were then enzymatically hydrolyzed.

Luterbacher J.S., Tester J.W., Walker L.P. *Biotechnol. Bioeng.* (2010) 107, 3, 451–460.

Obtained Yields

Total yields, defined as the fraction of the theoretical maximum, were determined for glucose, hemicellulose sugars, and two degradation products: furfural and 5-hydroxymethylfurfural. Response surfaces of yield as a function of temperature and residence time were compared for different moisture contents and biomass species.

Table II. Biomass yields for different species and pretreatment conditions.

	No pretreatment		Pretreatment at 160°C for 1 h				Pretreatment at 170°C for 1 h			
	Glucan yield [%]	Hemicellulose sugars yield [%]	Glucan yield [%]	Hemicellulose sugars yield [%]	5-HMF yield [%]	Furfural yield [%]	Glucan yield [%]	Hemicellulose sugars yield [%]	5-HMF yield [%]	Furfural yield [%]
Mixed hardwood (20 wt.%)	5.1 ± 0.3	3.9 ± 0.8	57 ± 2	28 ± 1	0.6 ± 0.1	11.6 ± 0.2	77 ± 4	27 ± 3	1.1 ± 0.1	21.7 ± 0.3
Mixed hardwood (40 wt.%)			67 ± 2	18 ± 3	1.3 ± 0.1	16.6 ± 0.3	73 ± 5	14 ± 2	1.9 ± 0.3	16 ± 1
Switchgrass	10.4 ± 0.4	6.6 ± 0.4	81 ± 1	13 ± 1	0.8 ± 0.2	11.8 ± 0.5	79 ± 1	12 ± 1	0.9 ± 0.1	13.1 ± 0.6
Big bluestem	17 ± 1	5.0 ± 0.4	56 ± 2	9.9 ± 0.3	0.9 ± 0.3	14 ± 1	66 ± 2	13 ± 1	1.0 ± 0.2	15 ± 1
Corn stover	36 ± 1	17 ± 1	85 ± 2	10 ± 1	1.3 ± 0.1	11.2 ± 0.5	67 ± 2	10 ± 2	1.2 ± 0.1	9.1 ± 0.2
Mixed perennial grasses	12.2 ± 0.4	3.5 ± 0.3	65 ± 2	8.7 ± 0.4	0.6 ± 0.1	5.5 ± 0.2	68 ± 1	6.2 ± 0.3	1 ± 0.1	12 ± 0.1

NDF, neutral detergent fiber; ADF, acid detergent fiber.

All measurements are provided with a range representing their 90% confidence interval.

Biphasic CO₂-H₂O pretreatment can produce glucan yields of **73% for wood, 81% for switchgrass, and 85% for corn stover** using very similar experimental conditions 160–170 °C and a 60 min residence time, high-solid contents (40 wt.%) and no additional chemicals.

However, further improvements are needed to increase hemicellulose sugar yields and reduce furfural formation.

Alkaline hydrolysis

This treatment employs alkaline solutions, such as **sodium hydroxide, calcium hydroxide or ammonia** for the treatment of biomass, **in order to remove lignin and part of hemicellulose** and **to efficiently increase the accessibility of cellulose**: it is basically a delignification process, where a significant amount of hemicellulose is also solubilized.

In particular, the use of an alkali causes

- the degradation of ester and glycosidic side chains, resulting in structural alteration of lignin, cellulose swelling, partial decrystallization of cellulose and partial solvation of hemicellulose.

Ibrahim M.M., El-Zawawy W.K., Abdel-Fattah Y.R., Soliman N.A., Agblevor, F.A. *Carbohydr. Polym.* (2011) 83, 2, 720–726.

Sills D.L., Gossett J.M. *Bioresour. Technol.* (2011) 102, 2, 1389–1398.

Alkaline pretreatment of lignocellulosic materials causes

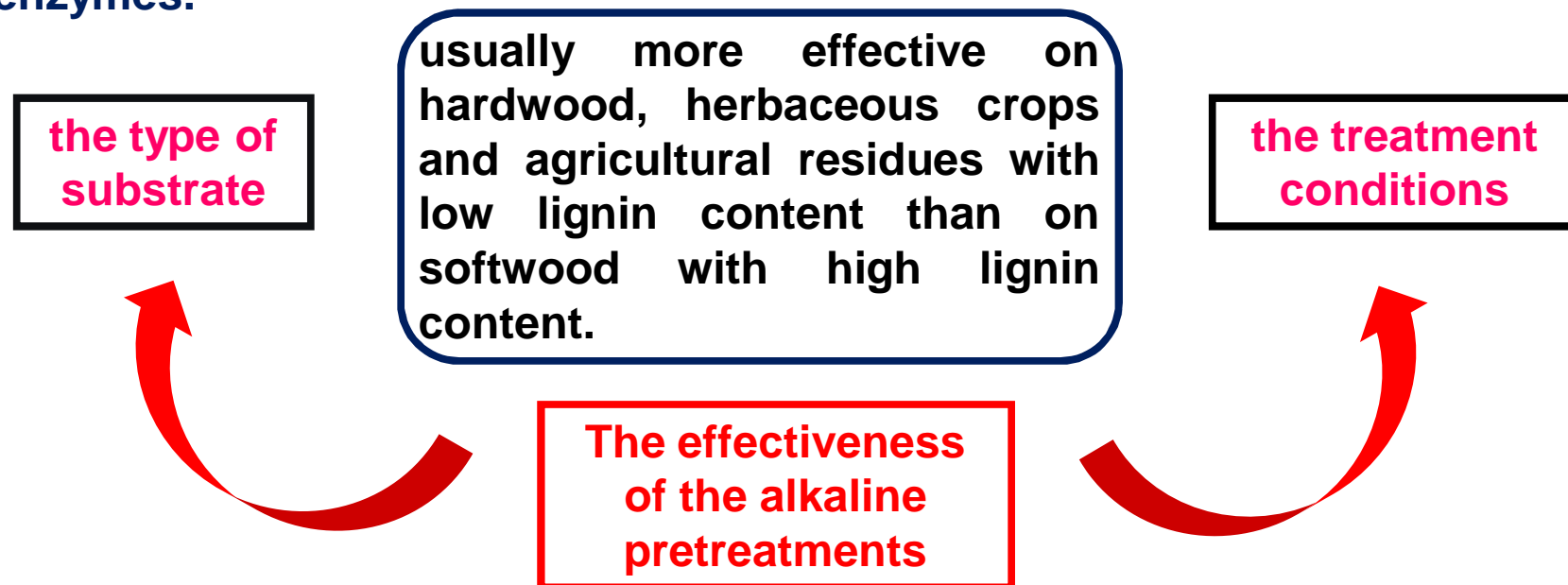
- cellulose swelling,
- decrease of polymerization degree and crystallinity,
- increase of internal surface area,
- disruption of the lignin structure,
- separation of structural linkages between lignin and carbohydrates.

Advantages of Alkaline pretreatment:

- the employment of lower temperatures and pressures than other pretreatment technologies,
- in comparison with acid processes, alkaline ones cause less sugar degradation,
- many of the caustic salts can be recovered and/or regenerated.

Disavantages of alkaline pretreatment:

- if performed at room temperature, long times and high concentrations of base are required,
- alkaline reagents can also remove acetyl and various acid substitutions on hemicellulose, thus reducing the accessibility of hemicellulose and cellulose to enzymes.



Sodium hydroxide pretreatment

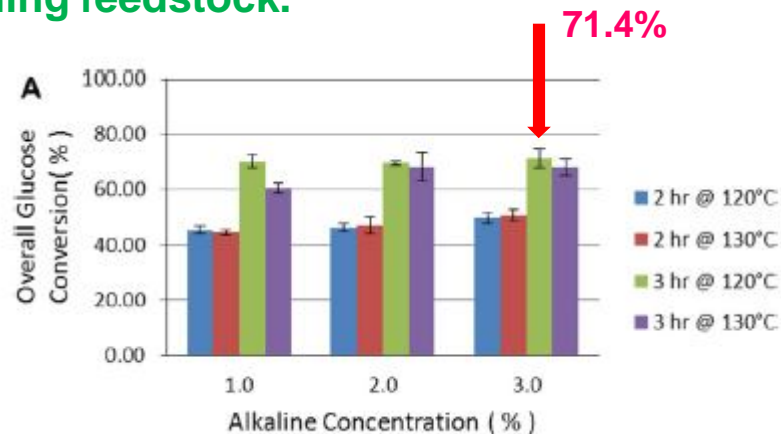
This pretreatment is able to improve the enzymatic digestibility of solid digestate fibers, enhancing glucose and ethanol yields from enzymatic hydrolysis and fermentation steps (Teater C., 2011).

The authors studied the most effective alkaline pretreatment for solid digestable (AD fiber) from a completely stirred tank reactor (CSTR) anaerobic digester, for switchgrass and agricultural residue of corn stover, employed for ethanol production, showing the first one as a suitable biorefining feedstock.

In particular for AD fiber:

Overall glucose conversion

The overall glucose conversion (the ratio of glucose produced to the total cellulose in the original fiber samples)

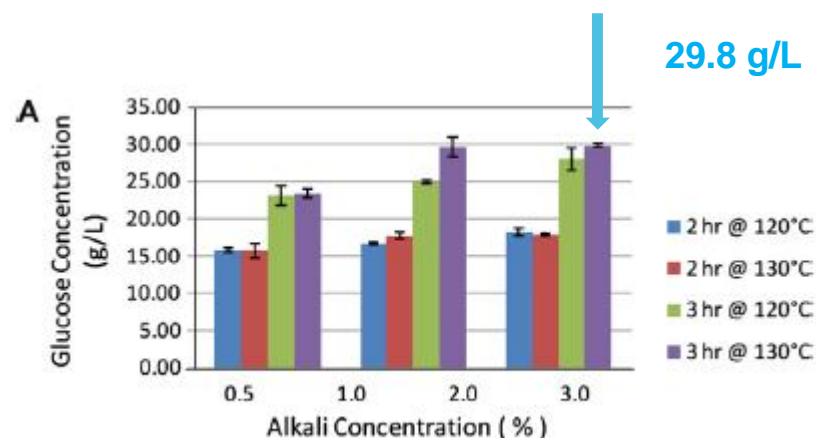


The pretreatment conditions of 120 °C and 3% NaOH for 3 h had the highest overall glucose conversion (71.4%) of AD fiber.

Teater C., Yue Z., MacLellan J., Liu Y., Liao W. *Bioresource Technology* (2011) 102, 1856–1862.

Glucose Concentration

Glucose concentrations from enzymatic hydrolysis of all pretreated samples were investigated: the results for AD fiber are shown.



The highest glucose concentration was 29.8 g/L for the reaction conditions of 130 °C and 3% NaOH for 3 h.

Glucose concentration and overall glucose conversion of enzymatic hydrolysis (5% solids) with the most effective pretreatment conditions.

Feedstock	Glucose concentration (g/L)	Glucose conversion (%)	Xylose concentration (g/L)	Hemicellulose-sugar conversion (%)
CSTR AD fiber ^a	29.7 ± 1.3	68.2 ± 5.2	10.1 ± 0.5	49.1 ± 4.0
Switchgrass ^b	25.1 ± 0.1	66.6 ± 0.9	8.8 ± 0.1	27.4 ± 1.1
Com stover ^c	28.9 ± 4.9	67.6 ± 14.1	8.7 ± 1.6	28.5 ± 5.5

^a The most effective pretreatment conditions for CSTR AD fiber were 130 °C and 2% NaOH for 3 h.

^b The most effective pretreatment conditions for switchgrass were 130 °C and 1% NaOH for 2 h.

^c The most effective pretreatment conditions for com stover were 130 °C and 1% NaOH for 2 h.



Ethanol Production

Ethanol concentration and conversion of samples

Feedstock	Ethanol concentration (g/L)	Ethanol conversion (%)
CSTR AD fiber ^a	14.7 ± 0.7	80.3 ± 3.2
Switchgrass ^b	16.6 ± 1.7	83.1 ± 2.7
Corn stover ^c	18.1 ± 0.5	78.0 ± 2.1
Pure glucose	18.9 ± 0.1	59.5 ± 1.1

^a The most effective pretreatment conditions for CSTR AD fiber were 130 °C and 2% NaOH for 3 h.

^b The most effective pretreatment conditions for switchgrass were 130 °C and 1% NaOH for 2 h.

^c The most effective pretreatment conditions for corn stover were 130 °C and 1% NaOH for 2 h.

An 80.3% ethanol yield was obtained from CSTR AD fiber, which was consistent with switchgrass (78.0%) and corn stover (83.0%) hydrolysates, and significantly greater than pure glucose (59.5%). Ethanol concentrations of 14.7, 16.6, 18.1, and 18.9 g/L were produced from CSTR AD fiber, corn stover, switchgrass, and pure glucose, with initial fermentation glucose concentrations of 36.6, 38.8, 45.8, and 59.4 g/L respectively.



The AD fiber is a suitable biorefining feedstock and the integrated process of anaerobic digestion and bioethanol production is able to utilize the main components of the biomass in a robust manner.

Calcium hydroxide (lime pre-treatment)

The process of lime pretreatment requires slurrying the lime with water, spraying it onto the biomass material and accumulating the material in a pile for a period from hours to weeks. After the treatment, the particle sizes of the biomass are typically 10 mm or less. Elevated temperatures can reduce contact times. Also in this case lignin removal improves enzyme effectiveness by eliminating non productive adsorption sites and by increasing access to cellulose and hemicellulose (Fu Z., 2011; Nachiappan B., 2011).

Nachiappan B., Fu Z., Holtzapple M.T. *Bioresource Technology* (2011) 102, 4210–4217.
Fu Z., Holtzapple M.T. *Appl. Microbiol. Biotechnol.* (2011) 90, 1669–1679.

Ammonia pretreatment

This method has also been used as a pretreatment reagent to remove lignin. The main effect of ammonia treatment of biomass is delignification without significant effect on carbohydrate contents. It is a very promising pretreatment reagent, in particular for substrates with low lignin contents, such as agricultural residues and herbaceous feedstock. The ammonia method is suitable for simultaneous saccharification and cofermentation because the treated biomass does not lose cellulose and hemicellulose. Ammonia is a proven delignification reagent and the lignin content of the biomass can decrease to a very low level (Kim T.H., 2009).

Ammonia treatment does not cause substantial loss of carbohydrates and its use leads to the fractionation of biomass, by separation of lignin from biomass. It is also important to underline that this lignin is sulphur- and sodium-free, unlike that obtained from other pretreatment processes. It is generally of high quality and thus it is considered as a higher value byproduct.

Some disadvantages:

- the consumption of ammonia due to the interaction with lignin,
- the ammonia neutralization by acetates and other buffering agents present in the biomass.

Most of the ammonia is recovered and reused in the process: in general, only ammonia equivalent to 2–5 % of dry biomass is irreversibly consumed during the pretreatment.

The most widely used ammonia pretreatments are

- 1) the ammonia recycle percolation, (ARP), which is a high severity, low contact time process ;
- 2) the soaking in aqueous ammonia, (SAA), which is a low severity, high contact time process.

Combined approaches

Sometimes, the alkaline pretreatment is carried out in combination with irradiation, such as **microwaves** and radio–frequency.

In particular, the microwave–based alkali pretreatment of switchgrass and coastal bermudagrass was investigated in order to improve the production of fermentable sugars from enzymatic hydrolysis.

Pretreatments were carried out by immersing the biomass in dilute alkali reagents and exposing the slurry to microwave radiation at 250 watt for residence times ranging from 5 minutes to 20 minutes. Sodium hydroxide resulted the most effective base for MW pretreatment of switchgrass and coastal bermudagrass (Keshwani D.R., 2010).

Keshwani D.R., Cheng J.J. *Biotechnol. Progr.* (2010) 26, 3, 644–652.

Conclusions about Alkaline pretreatment:

To sum up, it is possible to conclude that, in comparison with other pretreatment technologies, alkali pretreatment usually involves **lower temperatures and pressures, even up to room conditions**. Pretreatment time, however, is recorded in terms of **hours or days**, a duration much longer than those of other pretreatment processes. Another considerable drawback of alkaline pretreatment is **the conversion of alkali into irrecoverable salts and/or the incorporation of salts into the biomass** during the pretreatment reactions, making the treatment of a large amount of salts a challenging issue for alkaline approach.

Acid hydrolysis

- Acid pretreatment can be performed with **diluted** or **concentrated** acids, but these last are more hazardous, highly corrosive for reactors and equipments and must be recovered after the pretreatment.
- If the pretreatment is preceding to enzymatic hydrolysis, drastic acid conditions favour the formation of degradation and inhibiting compounds.

H₂SO₄ (generally < 4 wt %) is the most commonly employed acid: an efficient mild acid pretreatment completely solubilizes the hemicellulosic component of the biomass and only a little part of cellulose (at low acid concentration), thus making undissolved cellulose more accessible to enzymes.

Other types of acids have also been applied, such as **HCl**, **HNO₃** and **H₃PO₄** and also organic acids (as **maleic and oxalic acid**) have been tested

Acid pretreatment of olive tree pruning for EtOH production

The main issue is to solubilize hemicellulose keeping cellulose in the pretreated solid

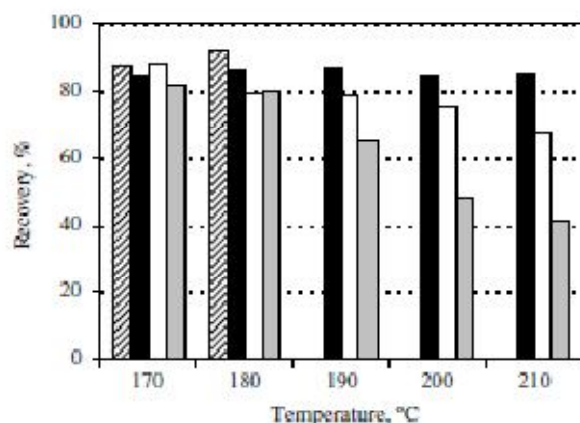


Fig. 1. Cellulose recovery in the water-insoluble solid (WIS) at different pretreatment conditions, expressed as a percentage of the initial content in the raw material. Sulphuric acid concentration (% w/w): 0.2 (▨), 0.6 (■), 1.0 (□) and 1.4 (▩).

Cellulose solubilization reaches near 60 % at 210 °C and 1.4 % acid concentration. Cellulose recovery decreases with T and Acid concentration.

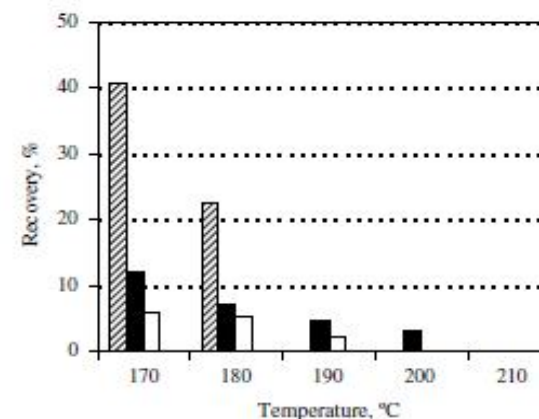


Fig. 2. Hemicellulose recovery in the water-insoluble solid (WIS) at different pretreatment conditions, expressed as a percentage of the initial content in the raw material. Sulphuric acid concentration (% w/w): 0.2 (▨), 0.6 (■), 1.0 (□) and 1.4 (▩).

Hemicellulose is completely dissolved at any T with 1.4 % acid concentration and above 210 °C at any acid conc.



180 °C and 1 wt % of acid conc. were adopted for the best saccharification yield

Dicarboxylic organic acids vs. Sulfuric

The effect of different acid catalysts on the hydrolysis and degradation of corncob when each was used at the same combined severity factor (CSF) values during pretreatment.

Then ethanol production with pretreated biomass by SSF was evaluated.

pH and acid concentrations used for each calculated severity factor (CSF)^a.

CSF	pH ^b	Acid (g/l)		
		Sulfuric	Oxalic	Maleic
1.8	1.5	1.67	3.67	5.33
1.9	1.4	3.00	5.00	9.10
2.0	1.3	4.67	6.67	11.67
2.1	1.2	6.67	8.67	15.33

^a All reaction conditions used 170 °C for 18 min.
^b Acid added to adjust pH as theoretical and then confirmed the pH value during making acid solution with pH meter.

0.23 g EtOH/l/h (pointing to CSF 1.8, Oxalic)

0.27 g EtOH/l/h (pointing to CSF 1.9, Oxalic)

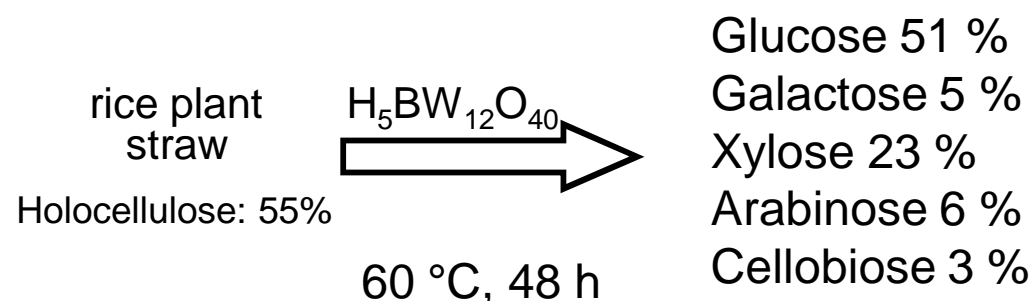
0.21 g EtOH/l/h (pointing to CSF 2.1, Sulfuric)

Maleic and oxalic acid can release more sugars in the hydrolysate and more ethanol can be produced from the residual solids than can be achieved with sulfuric acid when each is used at the same CSF

Heteropolyacids (HPAs) for biomass saccharification

HPAs are emerging strong homogeneous acid catalysts. $H_5BW_{12}O_{40}$ in solution gives highly negatively charged anions. These heteropolyanions have strong hydrogen-bond accepting abilities due to external oxygen atoms which have an important role in cellulose dissolution at low T (60 °C).

Saccharification of natural biomass resulted very efficient even in the presence of lignin, extractives and ash (yield based on holocellulose):



On the other hand too long reaction times are involved and HPAs are expensive !!!

Y. Ogasawara et al. ChemSusChem 4 (2011) 519-525.

Dilute acid/MW assisted heating for sugarcane bagasse

Microwaves are able to penetrate into the solutions and can provide a rapid and energy-efficient heating on biomass pretreatment. The treatment time with dilute sulfuric acid is **reduced to 5-10 min.**

The content of hemicellulose in bagasse drops markedly when the dilute acid pretreatment is performed.

When the reaction temperature is increased to 160 and 190 °C, some lignin in the bagasse is also solubilized by the acid. The crystalline structure of cellulose is destroyed.

Microwave heating at 190 °C with 5 min is an appropriate operating condition for the pretreatment of bagasse, from the viewpoint of lignocellulosic structural disruption!!!

Fiber analysis of raw bagasse and pretreated materials as well as pH values of the liquid solution.

Raw bagasse		Hemicellulose: 25.97; Cellulose: 52.45; Lignin: 12.72; Ash: 1.01; Others: 7.85		
Reaction temperature (°C)		130	160	190
5 ^a (min)				
Fiber analysis ^b (wt%)	Hemicellulose	9.86	7.64	0.8
	Cellulose	53.17	61.44	67.31
	Lignin	28.89	24.33	15.67
	Ash	1.3	2.71	2.93
	Other	3.78	3.86	13.29
pH(—)		0.43	0.26	0.25
10 ^a (min)				
Fiber analysis ^b (wt%)	Hemicellulose	9.64	5.17	0.59
	Cellulose	53.31	65.02	68.43
	Lignin	26.94	16.47	14.14
	Ash	2.05	2.36	3.66
	Others	8.06	10.97	13.18
pH(—)		0.47	0.38	0.17

^a Heating time.

^b The relative differences among the measurements were below 5%.

Ozonolysis

Pretreatment of lignocellulosic materials can be carried out using ozone, which can effectively degrade lignin and part of hemicellulose. In fact, ozone is a powerful oxidant, soluble in water and readily available. In addition, it is also highly reactive toward conjugated double bonds and functional groups with high electron density. Therefore, the moiety most likely to be oxidized in ozonization of lignocellulosic materials is lignin, because of its high content of C=C bonds. Ozone attacks lignin releasing soluble compounds of low molecular weight, such as organic acids, formic and acetic ones, which can cause a decrease in pH from 6.5 to 2 (García-Cubero M.T., 2009).

**The main factors which
affect the ozonolysis
pretreatment**

- the moisture content of the sample,
- the particle size,
- the ozone concentration in the gas flow.

The most significant parameter: the percentage of water in the feed

This aspect is important because it has a significant effect on the solubilization. The optimum water content was found to be around 30 %, corresponding to the saturation point of the fibers.

In particular, García–Cubero et al. studied the pretreatment with ozone of wheat and rye straw in order to enhance the enzymatic hydrolysis extent of potentially fermentable sugars. More specifically, they studied the influence of five operating parameters:

- moisture content,
- particle size,
- ozone concentration,
- type of biomass
- air/ozone flow rate

on ozonization pretreatment of straw in a fixed bed reactor under room conditions.

García–Cubero M.T., González–Benito G., Indacoechea I., Coca M., Bolado S. *Bioresour. Technol.* (2009) 100, 1608–1613.

In this case

The acid insoluble lignin content of the biomass was reduced in all experiments involving hemicellulose degradation. Operating in a fixed bed reactor, moisture content and type of biomass showed the most significant effects on ozonolysis. Moisture is a reaction controlling parameter for values below 30%. Wheat straw proved to be easier hydrolyzed than rye, although a similar content of residual lignin after ozone pretreatment was obtained for both samples.

wheat	29 %	Enzymatic hydrolysis yields		88.6 %
rye straw	16 %			57 %
non-ozonated samples				ozonated samples

Ozonolysis is an efficient pretreatment for cereal straw. Ozone degrades and/or solubilizes lignin and slightly solubilizes the hemicellulose fraction, improving subsequent enzymatic hydrolysis. Negligible losses of cellulose were detected.

The main advantages of ozonolysis are

- the lack of any degradation product which might obstruct the subsequent hydrolysis or fermentation,
- the efficient removal of lignin,
- the absence of toxic residues for the downstream processes,
- the possibility of carrying out the reaction at room temperature and pressure,
- the fact that ozone can be easily decomposed by using a catalytic bed or increasing the temperature, minimizing in this way the environmental pollution (Sun Y., 2002).

The main drawback consists

- in the demand of large amount of ozone, making, at the moment, the process expensive and not so suitable for application on an industrial scale.

Organosolvation (organosolv) treatment

Organosolv is a very promising approach for **solubilizing lignin in an organic medium**, thus providing a residual cellulose suitable for enzymatic hydrolysis.

After precipitation, the recovered lignin (organosolv lignin) is a sulfur-free lignin, with high purity and low molecular weight, to be used for many purposes.

The solvents more frequently used in organosolv processes are acetone, methanol, ethanol, phenols, ethylene glycol and tetrahydrofurfuryl alcohol.

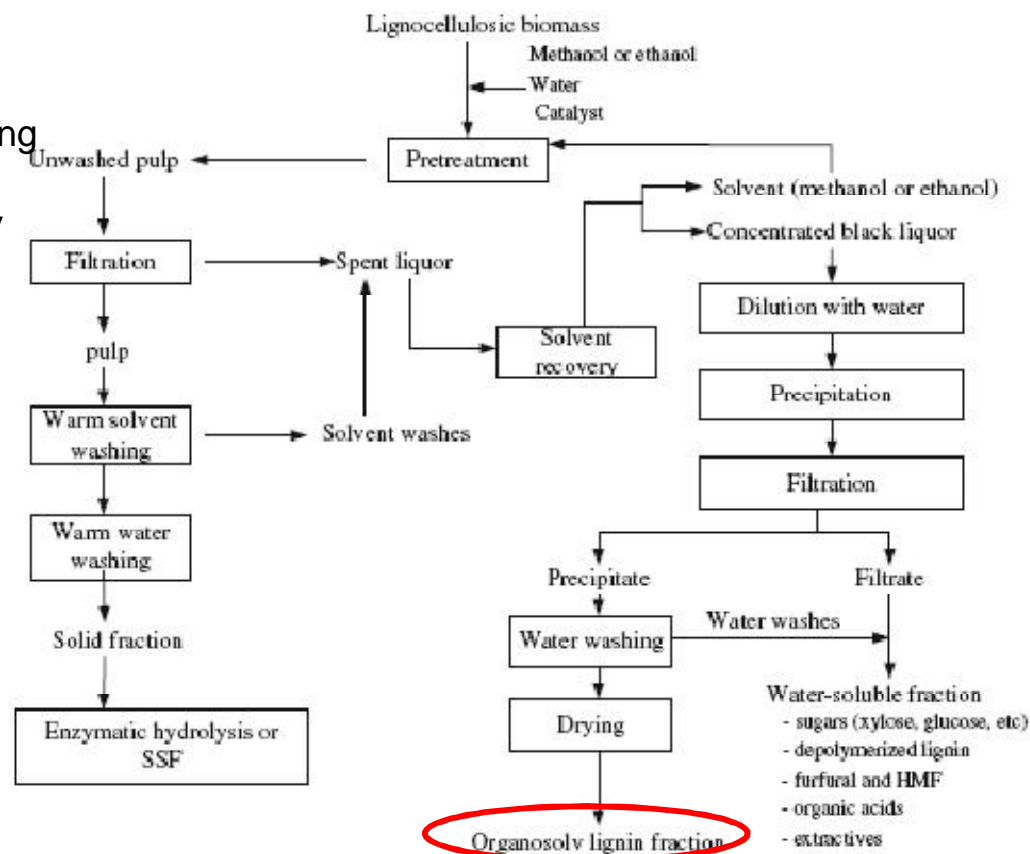
For economic reasons **aqueous ethanol** is generally the preferred solvent, having low boiling point, toxicity and cost, but the pretreatment process is always conducted under **high pressure** with increase of the equipment cost.

Organosolv

Flow-sheet of methanol or ethanol treatment

The advantage of employing cheap low boiling point alcohol (mainly methanol and ethanol) is of their low boiling point, ease of recovery by simple distillation with concomitant low energy requirement for their recovery

Biomass is treated with addition of acid catalyst at low temperature (below 180°C) or without catalyst (auto-catalysis) at higher temperatures (185–210°C).



Zhao, X. et al., Appl. Microbiol. Biotechnol. 82 (2009), 815–827.

Organosolv

The main products from pretreatment are the following:

1. Cellulosic fibers, which contain the original cellulose component and varying amounts of hemicellulose and residual lignin.
2. Solid lignin, obtained after removal of the volatile solvent from the black liquor by distillation. It may contain lipophilic extractives from the original lignocellulosic feedstock.
3. An aqueous solution of the hemicellulose sugars, which consists mainly of xylose in the case of hardwoods or agricultural residues. This solution is the filtrate of the previous solvent-evaporated liquor in which the lignin fraction was precipitated.

Organosolv treatment of pine sawdust

Temperatures less than 150 °C were not sufficient to obtain a reasonable degree of delignification. The delignification operation at 180 °C resulted in a “lignin” yield of ca. 26 wt.%, almost the total lignin content in the feedstock (28.4 wt.%).

Above 200 °C, the “lignin” yield continuously increased up to 40 wt.% at 250 °C, owing to the formation of the degraded products from cellulose: the temperature of 180 °C appeared to be optimal for the lignin extraction.

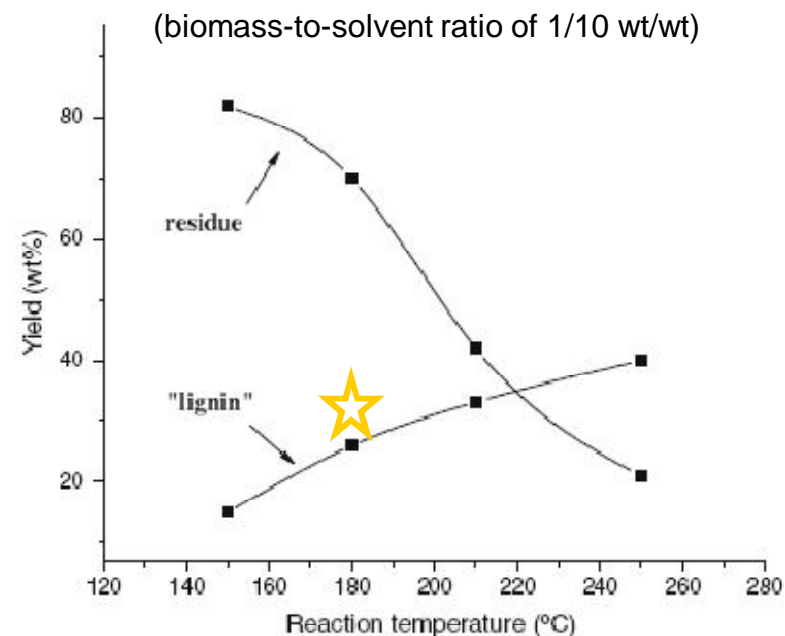


Fig. 1. Effects of reaction temperature on the lignin extraction with the ethanol–water (1:1 wt/wt) co-solvent for 4 h.

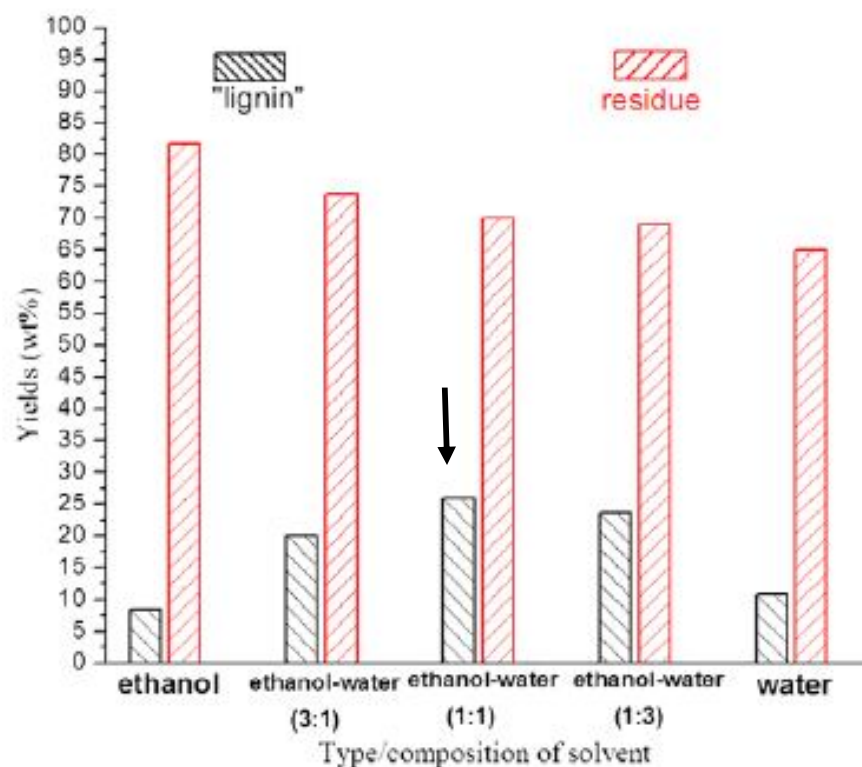
M. Wang et al., European Polymer Journal 45 (2009) 3380–3388

Organosolv treatment of pine sawdust

50 wt.% ethanol water solution appears to be the optimal co-solvent for biomass Delignification.

Water and ethanol played synergistic roles in the delignification process.

Water could act as a nucleophile to attack and promote the cleavage of lignin, and ethanol could act as impregnating reagent and carry the degraded lignin fragments away from the wood texture into the ethanol solution.



Effects of type and composition of solvent on the lignin extraction at 180 C for 4 h

Organosolv treatment

Liquid-to-solid ratio (LSR) used in the pretreatment also should be optimized.

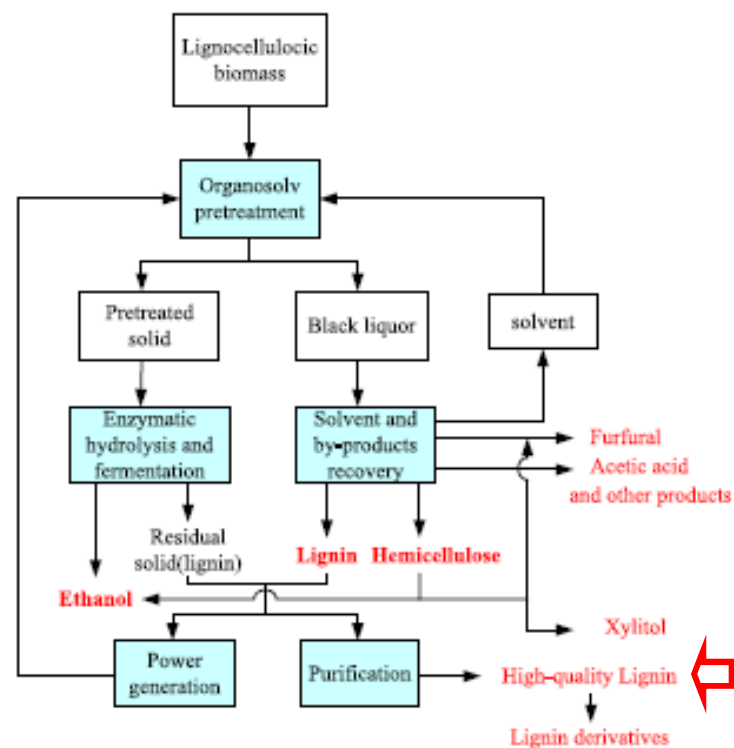
- Low LSR reduces the amounts of water and solvent in the system, with reduction of **capital costs** (smaller tanks and pumps are required for the same quantities of feedstock).
- **Operating costs** (especially energy for pumping and solvent recovery) are also reduced when low LSR is selected.

BUT...

- separation equipment, specially filters and centrifuges, must work more efficiently since inlet and outlet solid concentrations are much higher.
- at a very low LSR (below 4:1) reprecipitation of dissolved lignin onto the cellulose fiber can take place, thus limiting its successive enzymatic hydrolysis

Organosolv: integrated utilization of the biomass components

Further development of organosolv pretreatment should be focused on the integrated utilization of all the biomass components !



Ionic liquids (ILs) pretreatments

ILs are salts generally formed by large organic cations and small inorganic anions, which are liquid at low temperature and can be used as non–aqueous alternatives to traditional organic solvents.

Advantages

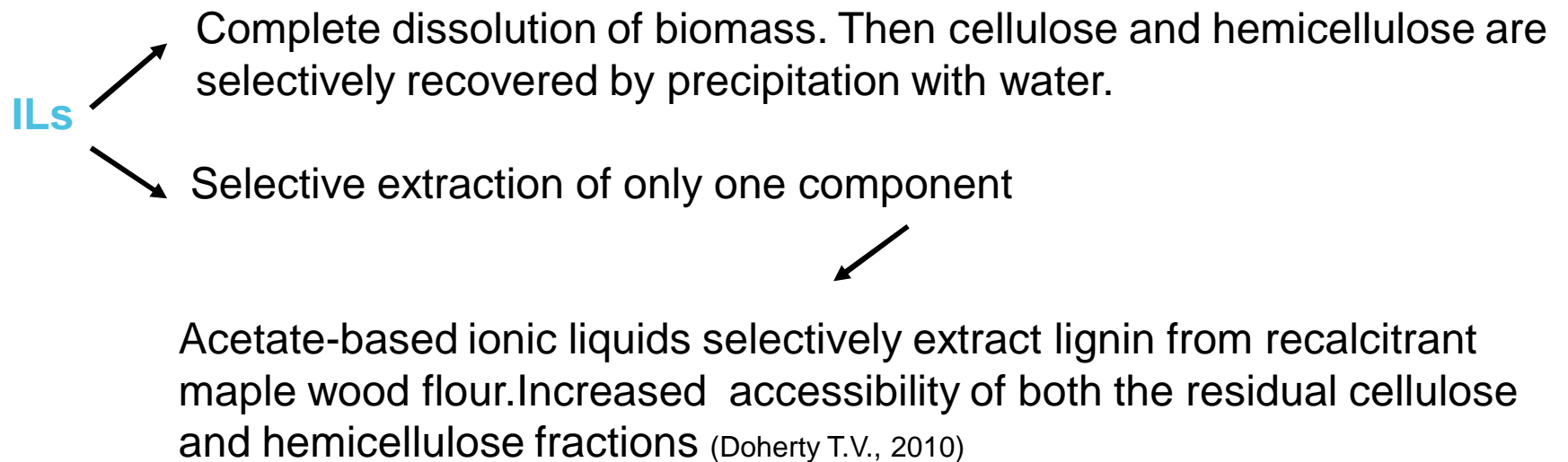
- Tunable properties (e.g., viscosity, melting point, polarity, and hydrogen bond basicity) depending on the selection of the anion and cation.
- high chemical and thermal stability
- non–flammability
- low vapour pressures (they remain liquid in a wide range of T)
- good (selective) solvation properties due to the swelling of the plant cell wall, with disruption of inter– and intra–molecular hydrogen bonding between lignin and cellulose, and also to the possible electronic interaction of the organic cations and the aromatic rings of lignin (Zavrel M., 2009).

Drawbacks

- high viscosity (a serious limit to mass and phase transfer)
- toxicity and corrosivity to be better considered (?)
- Expensive and only Kg scale production

Ionic liquids (ILs)

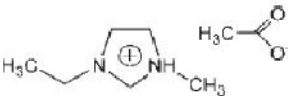

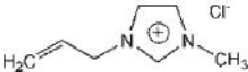
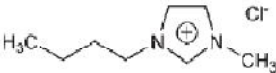
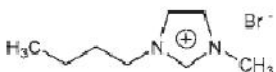
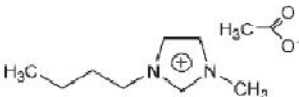
Tunable behaviour



After the extraction removal of lignin and other extractives is **critical**, requiring a potentially complex set of steps including precipitation by antisolvents such as deionized water or alcohols.

Mora-Pale, M. et al., Bioresour. Bioeng. 108 (2011) 1229–1245.

ILs for biomass extraction

RTIL	Structure	Uses
1-Ethyl-3-methylimidazolium acetate [EMIM]OAc		Dissolution of cellulose (Kosan et al., 2008; Vitz et al., 2009; Zavrel et al., 2009) Extraction of lignin from maple wood flour (Lee et al., 2009) Dissolution of a variety of carbohydrates such as sugars, starch, and cellulose (Zhao et al., 2008)
1-Ethyl-3-methylimidazolium chloride [EMIM]Cl		Dissolution of cellulose (Kosan et al., 2008; Vitz et al., 2009; Zavrel et al., 2009)
1-Allyl-3-methylimidazolium chloride [AMIM]Cl		Dissolution of cellulose (Fukaya et al., 2008; Zavrel et al., 2009; Zhang et al., 2005) Dissolution of hard wood and softwoods (Kilpelainen et al., 2007) Extraction of lignin from maple wood flour (Lee et al., 2009)
1-Butyl-3-methylimidazolium chloride [BMIM]Cl		Dissolution of cellulose (Erdmenger et al., 2007; Heinze et al., 2005; Kosan et al., 2008; Swatoski et al., 2002; Vitz et al., 2009; Zavrel et al., 2009) Pretreatment of cellulose for enhancing enzymatic hydrolysis (Dadi et al., 2006) Dissolution of hard wood and softwoods (Fort et al., 2007; Kilpelainen et al., 2007) Extraction of lignin from maple wood flour (Lee et al., 2009)
1-Butyl-3-methylimidazolium bromide [BMIM]Br		Dissolution of cellulose (Swatoski et al., 2002; Vitz et al., 2009; Zavrel et al., 2009) Dissolution of lignin (Pu et al., 2007)
1-Butyl-3-methylimidazolium acetate [BMIM]OAc		Extraction of lignin from maple wood flour (Doherty et al., 2010)

Mora-Pale, M. et al., Bioresour. Bioeng. 108 (2011) 1229–1245.

ILs future perspectives

- The high cost of RTILs necessitates **efficient recycling and regeneration**, particularly for the extremely large volumes required for biomass pretreatment.
- After selective precipitation of the different biomass components the following steps are applied:
 - filtration,
 - adsorption of impurities by activated carbon,
 - organic solvent washing and evaporation,
 - eventual purification with neutral-activated alumina
- Too steps represent a critical problem (options: use of anion exchange resins for isolation of the ionic liquid as a salt, use of supercritical fluids to extract ILs-soluble polymers...)

Overview

Influence of the main pretreatment processes on lignocellulose structure

	Milling	Torrefact.	S.E.	LHW	AFEX	CO ₂ expl	Alkaline	Acid	O ₃	Organo -solv	ILs
Increase of accessible surface area	H	H	H	H	H	H	H	H	H	H	H/-
Cellulose decrystallization	H	n.d.	-	n.d.	H	L	H	-	n.d.	n.d.	H/-
Hemicellulose solubilization	-	L	H	H	L	L	L	H	H	H	H/L
Lignin solubilization	-	-	L	L	L	L/-	H	L	H	H	H/-
Generation of inhibitors	-	-	H	L	L	-	L	H	-	-	-
Alteration lignin structure	-	L	H	L	H	L/-	H	H	H	H	H/-

H: high effect; L: minor effect; n.d.: not determined.

Overview

	Main advantages	Main disadvantages
Milling	Reduces cellulose crystallinity; increase surface area	Need of combination with other treatments; high energy consumptions
Torrefaction	Easier biomass storage; no formation of inhibitors; moderate energy consumption; easier grindability	Need of combination with other treatments; still incomplete investigation
Steam explosion	Increase of accessible surface area; higher substrate digestibility; depolymerization of lignin; solubilization of hemicellulose	Need of combination with other treatments; formation of inhibitors;
LHW	Enhanced substrate digestibility; low formation of inhibitors; low-cost plant	High energetic requirements; high water input
AFEX	Low formation of inhibitors; increase of accessible surface area	High cost of plant and ammonia
CO₂ explosion	No toxicity; easy recovery; increase of accessible surface area; efficient hydrolysis of hemicellulose	High cost of plant; high pressure involved lignin remains
Alkaline	Hemicellulose and lignin hydrolysis; mild conditions; increased substrate digestibility	Long reaction times; salts formation and incorporation; base consumption
Acid	Increased substrate digestibility; hemicellulose solubilization	Formation of degradation products; formation of inhibitors; corrosion; need of acid recovery
Ozonolysis	No toxicity; no formation of inhibitors; lignin solubilization	High cost of ozone
Organosolv	Hemicellulose and lignin solubilization	High cost for plant and solvents
ILs	Low toxicity and flammability; high selective solubilization of biomass components	High cost for plant and ILs; high viscosity

In conclusion...

The optimum conditions of pre-treatment strictly depend on **the characteristics of each raw material** (composition, harvesting time, water content...) as well as on **the final purpose of the process itself (biofuels, chemicals production...).**

Techno-economic studies which compare the different technologies have been reported only for bioethanol production from different lignocellulosic materials.

Thank you for your kind attention!

