AN OVERVIEW ON THE PULP AND PAPERMAKING PROCESS FROM AGROFORESTRY RESIDUES: A BIOREFINERY APPROACH

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Bioenergy III: Present and New Perspectives on Biorefineries
Lanzarote (Spain), May 25th, 2011

Outline

- **Introduction and Objectives**
- **Materials and Methods**
- **Results:**
  - Pulping process
  - Hydrothermal treatment
  - Active carbons from lignin
- **Conclusions**

Outline

- Introduction and Objectives

Introduction and objectives

- There is a need for new sources of low-cost virgin fibers
- The manufacture of cardboard requires up to circa 20% of virgin fibers
- Around 45% of all raw materials used in the Spanish pulp and paper industry (ca. 3 millions of tonnes) are destined to cardboard production (*)
- As of 2009, Spain is the 6th largest producer of pulp and paper (5.7 millions of tonnes) and the 4th largest exporter of paper pulp in the EU (2.8 millions of tonnes), (top ten worldwide) (**)

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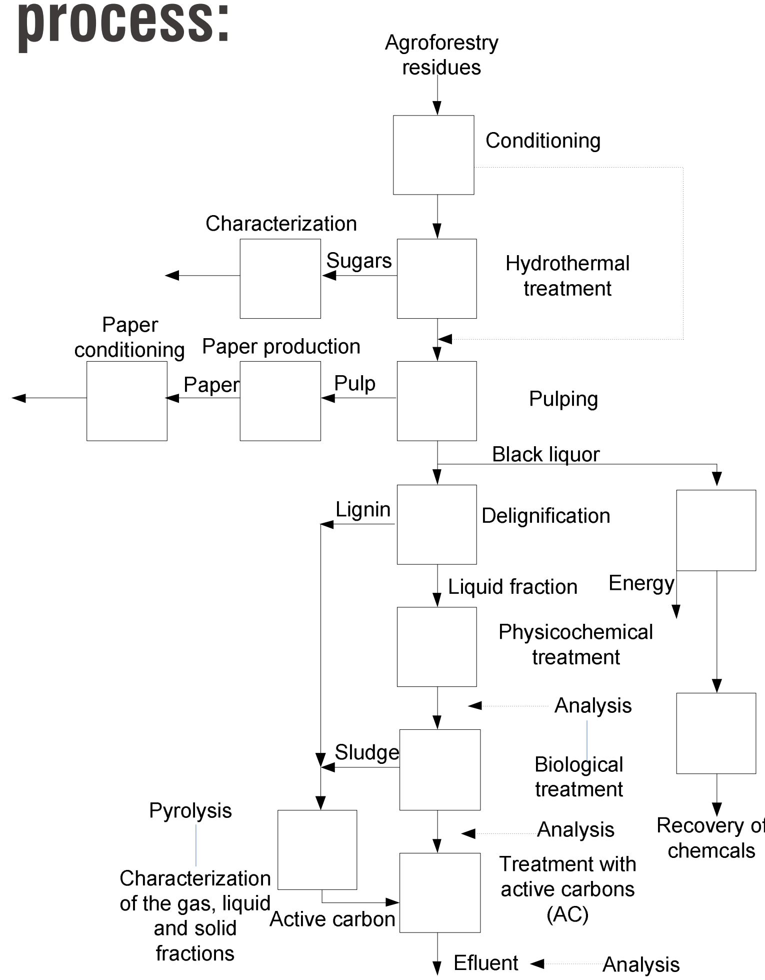
Alternative feedstocks must be sought for cardboard production

(*) Marín, F.; Sánchez, J. L.; Arauzo, J.; Fuertes, R.; Gonzalo, A. *Bioresource Technology*. 2009, *100*, 3933-3940

(**) ASPAPEL (Association of Spanish pulp and paper manufacturers), "Sustainability report – Update'09" (2009)

Introduction and objectives

- **The biorefinery approach applied to the pulp and papermaking process:**



Introduction and objectives

Main objective:

To value agroforestry residues via pulp and paper production following a biorefinery scheme

Introduction and objectives

Secondary objectives:

- Assessment of different crops as potential feedstocks for pulp and paper production
- Hydrothermal treatment of feedstocks for the extraction of high-added value products
- Preparation of active carbons from lignin

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Materials and Methods

- **Feedstocks:**
  - Residues from agricultural crops:
    - Pulping process: corn waste, sweet pepper, chilli, grean bean, bean, pea, tomato
    - Hydrothermal treatment: corn waste, sweet pepper, chilli, eucalyptus
    - Active carbons from lignin: sweet pepper

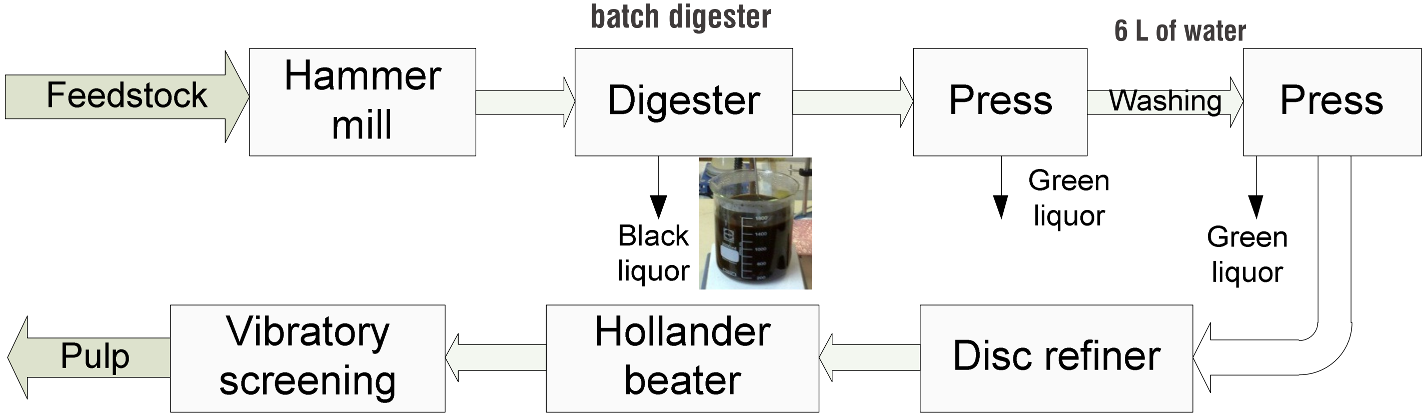
Materials and Methods

- **Pulping process:**

Soda semichemical pulping:

- 3 h at T = 98 ± 2 ºC
- Solid-to-liquid ratio = 1:10 (1 kg dry solid)
- Aqueous solution of NaOH (9.5 wt.% NaOH)

30 L stainless steel batch digester



2.5 – 3 wt.% consistency

Total refining time: 10 min

Marín, F.; Sánchez, J. L.; Arauzo, J.; Fuertes, R.; Gonzalo, A. *Bioresource Technology*. 2009, *100*, 3933-3940

Materials and Methods

- **Hydrothermal treatment:**

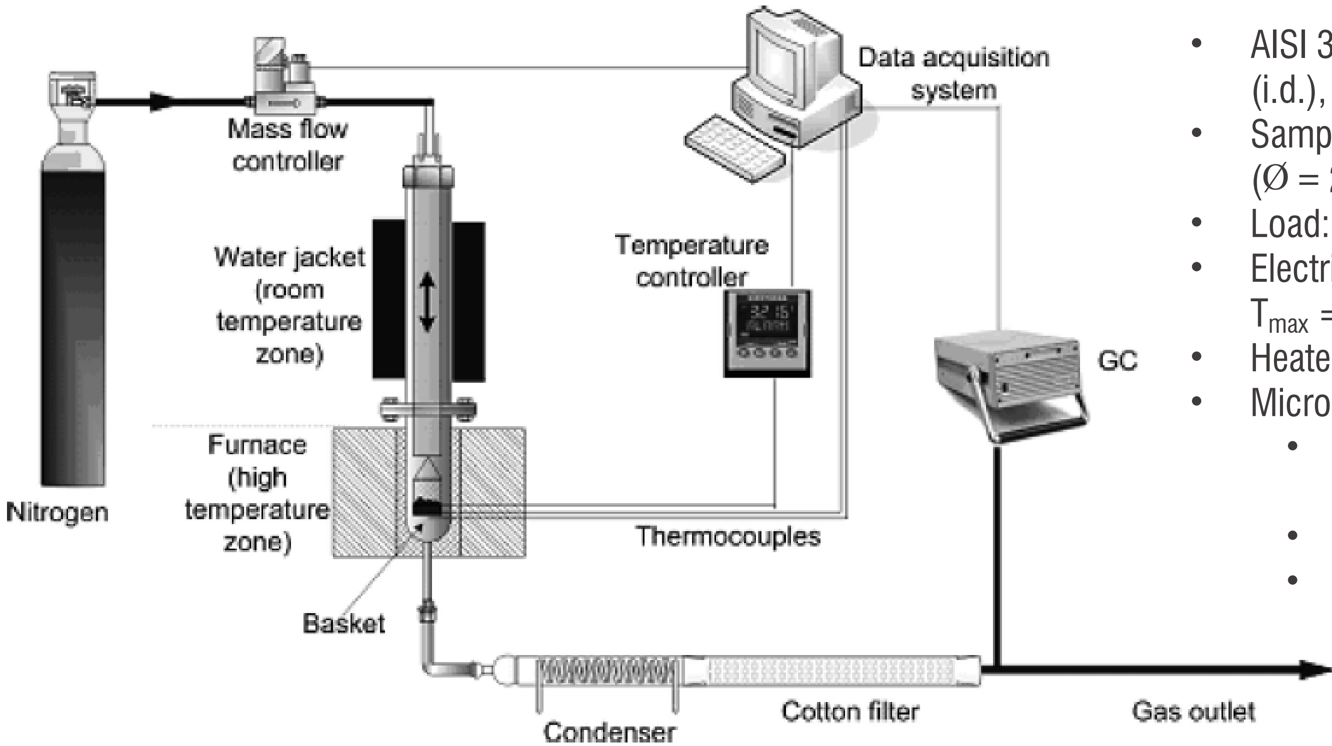
4 L stainless steel autoclave reactor (Autoclave Engineers)

Autohydrolysis conditions: T=180 ºC, 30 min
Solid: liquid ratio 1:20 (w/w)
Water as only reagent

Liquor posthydrolysis for sugars quantification (HPLC):
H_2SO_4 (5 % w/w), T=100 ºC, 60 min
Liquor: acid ratio 4:1 (v/v)

Materials and Methods

- **Active carbons from lignin:**



- AISI 316 Stainless steel reactor 2.5 cm (i.d.), 50 cm high.
- Sample held in an AISI 310 SS basket (Ø = 2 cm, 2.1 cm high).
- Load: 3 g.
- Electric furnace Watlow VC404A06T, T_{max} = 1100 ºC.
- Heated zone: 30 cm
- Micro GC Agilent M3000 (G2801A):
  - Plot-U column (Plot-Q precolumn)
  - Molsieve column.
  - TCD detectors

Ábrego, J.; Arauzo, J.; Sánchez, J. L.; Gonzalo, A.; Cordero, T.; Rodríguez-Mirasol, J., Ind. Eng. Chem. Res. 2009, 48, 3211-3221

Materials and Methods

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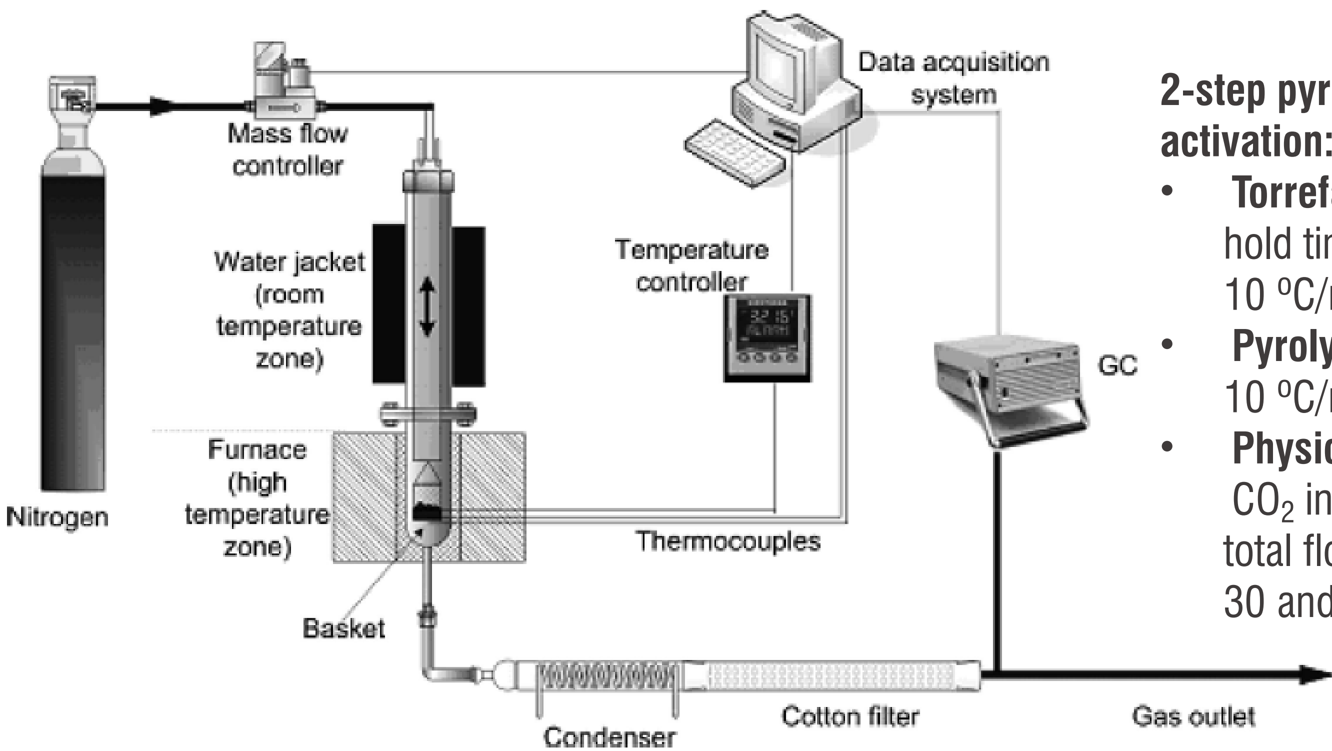

2-step pyrolysis followed by physical activation:

- **Torrefaction at 300 ºC**,
  hold time = 0 min
  10 ºC/min heating rate
- **Pyrolysis at 600 ºC** in N_2,
  10 ºC/min heating rate
- **Physical activation with CO_2** (10% CO_2 in N_2)
  total flow = 100 cm^3 STP/min
  30 and 120 min

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Results

Composition of agroforestry residues (wt.%, dry basis):

	Corn waste	Sweet pepper	Chilli	Eucalyptus
Ash (%)	9.27 ± 0.2	8.83 ± 0.5	7.88 ± 0.1	0.41 ± 0.05
Extractives (%)	1.08 ± 0.1	1.66 ± 0.2	2.18 ± 0.6	1.57 ± 0.20
Lignin (%)	17.18 ± 2.4	12.38 ± 0.0	16.93 ± 0.2	25.36 ± 0.98
Holocellulose (%)	74.79 ± 3.5	77.13 ± 0.9	72.93 ± 0.4	79.59 ± 1.94
Cellulose (%)	49.22 ± 2.7	62.80 ± 1.2	60.50 ± 0.8	57.23 ± 0.06
Hemicelluloses (%)	25.57 ± 0.7	14.33 ± 2.1	10.43 ± 0.4	22.36 ± 0.28

- ↑ % Lignin: eucalyptus chips: 25 %
- ↑ % Cellulose: pepper, chilli and eucalyptus chips: 57 % to 62 %
- ↑ % Hemicelluloses: corn waste and eucalyptus chips: 22 % to 25 %

⇩

Suitable to obtain high added value products and cellulose

Results

Pulping process:

Feedstock	Pulp yield (wt.%)	Schopper-Riegler drainability (ºSR)	Kajaani average fibre length (mm)
Hydrolysed sweet pepper	92	76	0.33
Non-hydrolysed sweet pepper	78	71	0.37
Chilli	65	81	0.42
Grean bean	61	77	0.22
Bean	70	86	0.31
Pea	43	81	0.35
Tomato	62	85	0.38
Corn waste	68	81	0.17

- Best yields obtained for hydrolysed and non-hydrolysed sweet pepper
- High ºSR values (> 70 ºSR) obtained in all cases → poor drainability
- Pulp mixtures with recovered paper required to enhance ºSR
- Best results in terms of fibre length obtained for chilli and sweet pepper

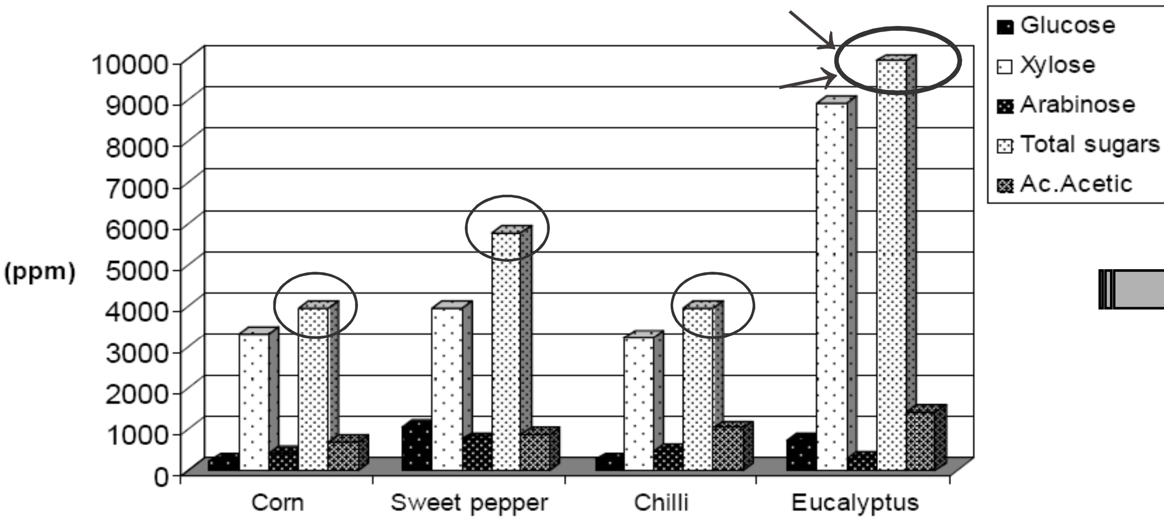
↓

Promising results for sweet pepper as a feedstock

Results

Hydrothermal treatment:

- Quantification of monomeric sugars and acetic acid:



Liquors rich in soluble sugars

suitable to obtain high added value products

- ↑[ ] Sugars: eucalyptus chips: 9.9 g/L→ 80% of hemicelluloses of raw material
- Pepper,corn waste,chilli:3.9 g/L to 5.8 g/L⟶27-73% hemicelluloses of raw material
- Xylose: 90 % of the total dissolved sugars in all liquors
- Arabinose and glucose: small quantities
- Acetic acid: 0.70 g/L to 1.40 g/L

Results

Active carbons from lignin:

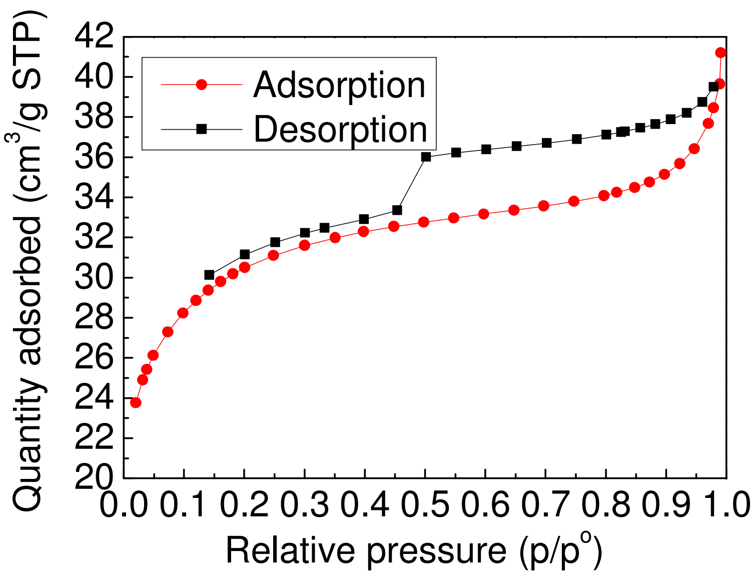
Material	BET surface area (m^2/g)
Lignin	2
Torrefied lignin produced at 300 °C	< 1
Char precursor produced at 600 °C	< 1
Carbon activated at 900 °C (10% CO_2 in N_2, 30 min)	51
Carbon activated at 900 °C (10% CO_2 in N_2, 120 min)	102

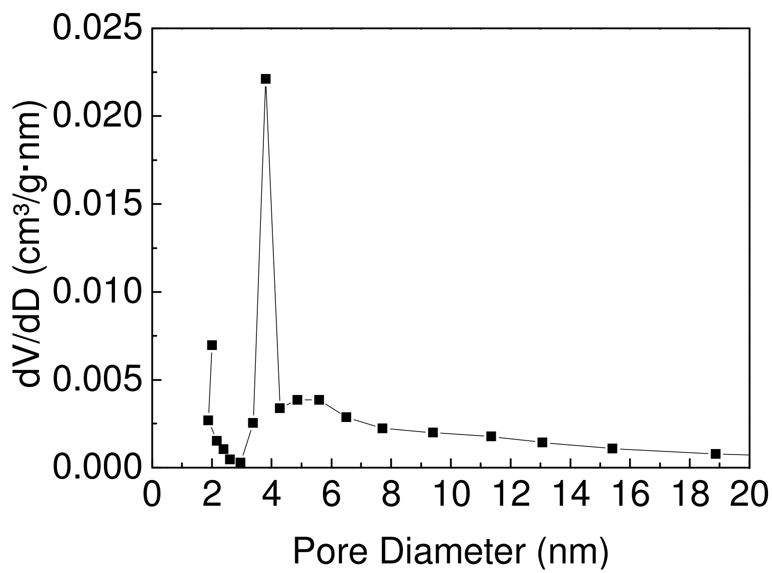
Low surface areas obtained compared to active carbons from kraft lignin (*)

(*) Suhas Carrott, P. J. M.; Carrott, M. M. L. R. Bioresource Technology. 2007, 98, 2301-2312

Results

Active carbons from lignin:





Mesoporosity of the material developed only during the activation stage.
Co-existence of micro and mesopores confirmed by N_2 adsorption.
Possible existence of “ink-bottle” like mesopores (*).

(*) Janssen, A.H.; Koster, A.J.; de Jong, K.P., J. Phys. Chem. B 106 (2002) 11905-11909

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Conclusions

- The valorisation of agroforestry residues is feasible via soda semichemical pulping for cardboard production
- A biorefinery approach for the process permits to minimize wastes and obtain high-added value products along with energy and chemicals recovery
- The best results in terms of pulp yield and fiber length were obtained for sweet pepper
- In order to enhance drainability, the pulp produced must be mixed with secondary fibers from recovered paper
- The hydrothermal treatment yields liquors rich in soluble sugars such as xylose along with acetic acid
- The preparation of active carbons from lignin by means of physical activation with CO_2 through a two-stage pyrolysis process yields mesoporous materials with low surface areas

Acknowledments

The authors express their gratitude to the Spanish Ministerio de Medio Ambiente y Medio Rural y Marino (MARM) (Research project 186/PC08/3.02-5) for providing financial support to this work.

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Materials and Methods

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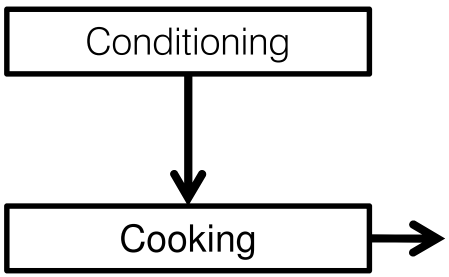

30 L stainless steel batch digester

Soda semichemical pulping:

- 3 h at T = 98 ± 2 ºC
- Solid-to-liquid ratio = 1:10 (1 kg dry solid)
- Aqueous solution of NaOH (9.5 wt.% NaOH)

Materials and Methods

- **Pulping process:**

Conditioning

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Cooking → Pressing and washing →

→ Black liquor

Pulp washed with 6 L of water

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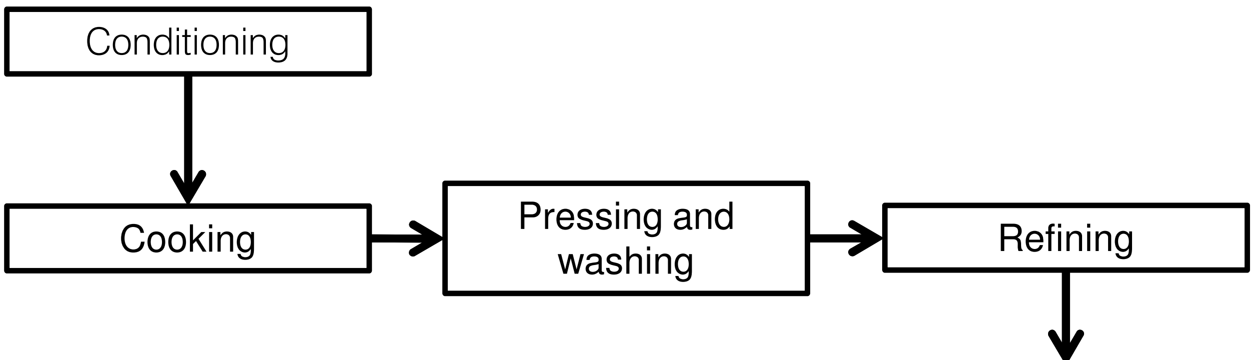
Green liquor

Materials and Methods

- **Pulping process:**



Total refining time: 10 min

Materials and Methods

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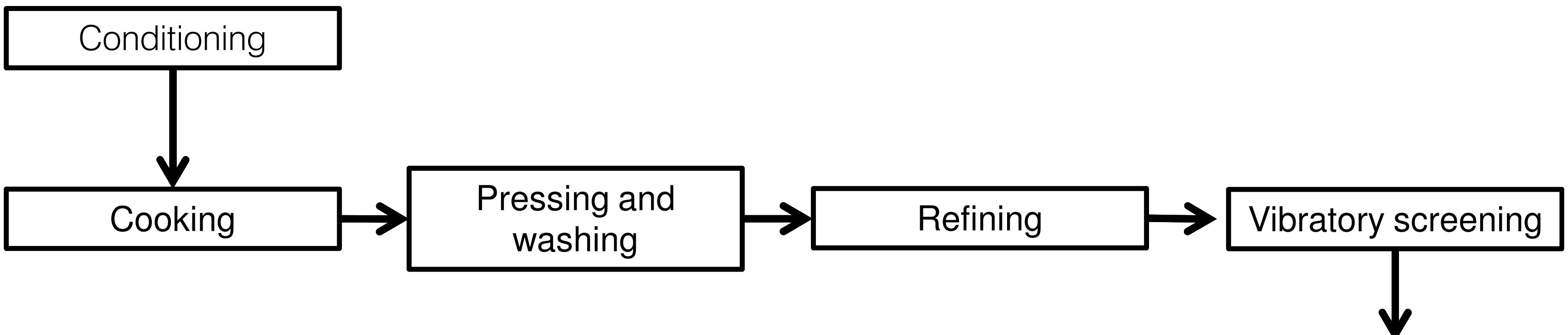
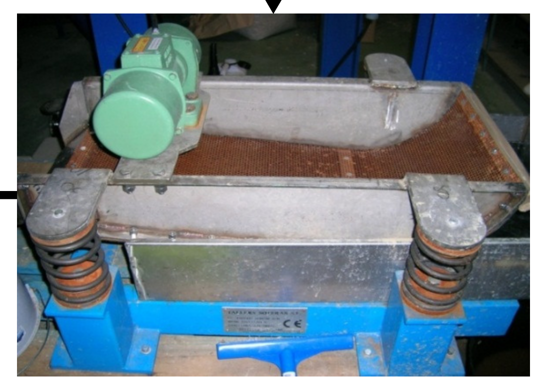
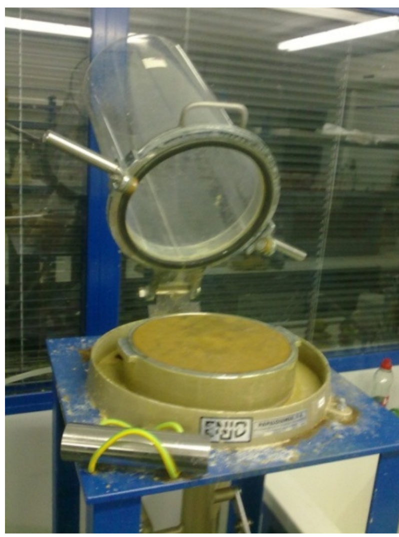


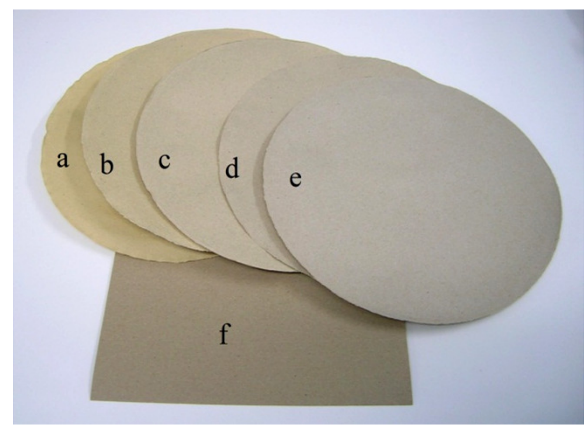


2.5 – 3 wt.% consistency

Etapas

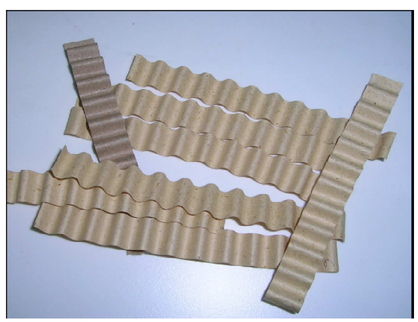
Acondicionamiento materia prima → Cocción → Prensado y lavado → Refino de la pasta → Depuración → Análisis de la pasta → Preparación hojas de papel





Etapas

Acondicionamiento materia prima → Cocción → Prensado y lavado → Refino de la pasta → Depuración → Análisis de la pasta → Preparación hojas de papel → Realización de los ensayos



Procesos de producción de pasta papelera

Proceso	Tipo de pasta	Descripción
Físico	Mecánica	Desfibrado mediante la acción de dos discos que giran en sentido contrario
	Termomecánica	Procedimiento mecánico, con aplicación de calor para debilitar la unión de entre fibras
Químico	Kraft o al sulfato	Degradación de la lignina mediante una mezcla de sulfuro e hidróxido sódicos
	Sulfito	Degradación de la lignina mediante mezclas de sulfito sódico con distintas bases
	Termoquímica	Procedimiento mecánico, con adición de agentes químicos y aplicación de calor
Semiquímico	Sulfito neutro (NSSC)	Tratamiento químico (adición de sulfito y bicarbonato sódicos) previo al desfibrado mecánico
	Alcalina	degradación de la lignina mediante la acción del hidróxido sódico