Visegrad Fund

CTU CZECH TECHNICAL UNIVERSITY IN PRAGUE

CCUV4 Workshop in Prague

Research of Pretreatment of Lignocellulosic Biomass and cellulose pulp

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University of Cantabria

- Chemical Engineering (5 years)
- Industrial Chemistry (1 years)
- PhD. Industrial Engineering (3 years)

Czech technical university

- 2 year Post Doc position on mechanical pretreatment of biomass

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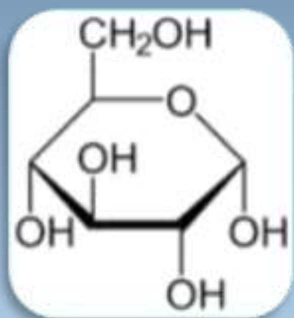
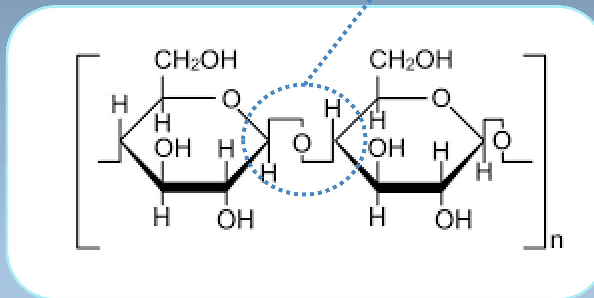
Cellulose Introduction



Glucose

β-(1->4) glycosidic bond

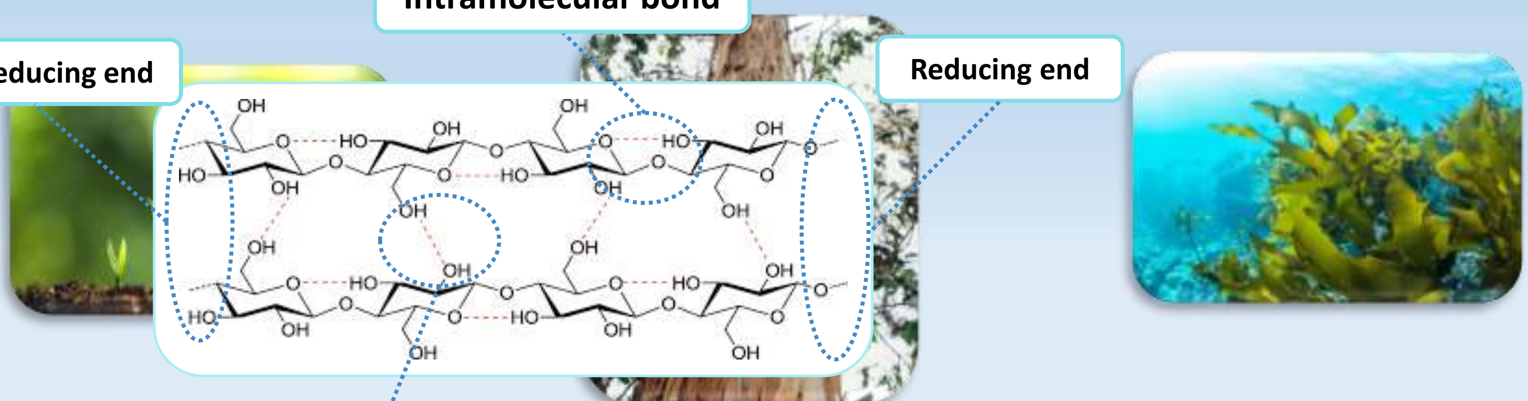


Cellulose

Intramolecular bond

Non-reducing end

Reducing end



Intermolecular bond

Cellulose Introduction

Cotton linters → **Dissolving Pulp production processes**

Dissolving Pulp is produced to compensate the cellulose gap

Several processes can be used:

- SO_2-etanol-water
- Pre-hydrolysis soda-anthraquinone
- Purification of paper grade
- Organosolv
- Pre-hydrolysis Kraft (PHK)
- Acid Sulfite (AS)

Acid sulfite

- Acidic liquor
- Only some hardwoods can be used
- High molecular weight distribution
- Production of lignosulfonates

Pre-hydrolysis Kraft

- Alkaline liquor
- Any kind of lignocellulosic material can be used
- Uniform molecular weight distribution
- Recovery of lignin and energy valorization

56 % of the Pulp is produced by PHK and 42 % of the Pulp is produced by AS process

Pretreatment of cellulose pulp and LCB

Enzymatic

- Most used pre-tre
- High efficiency
- Xylanases purify p endoglucanases i of chemicals

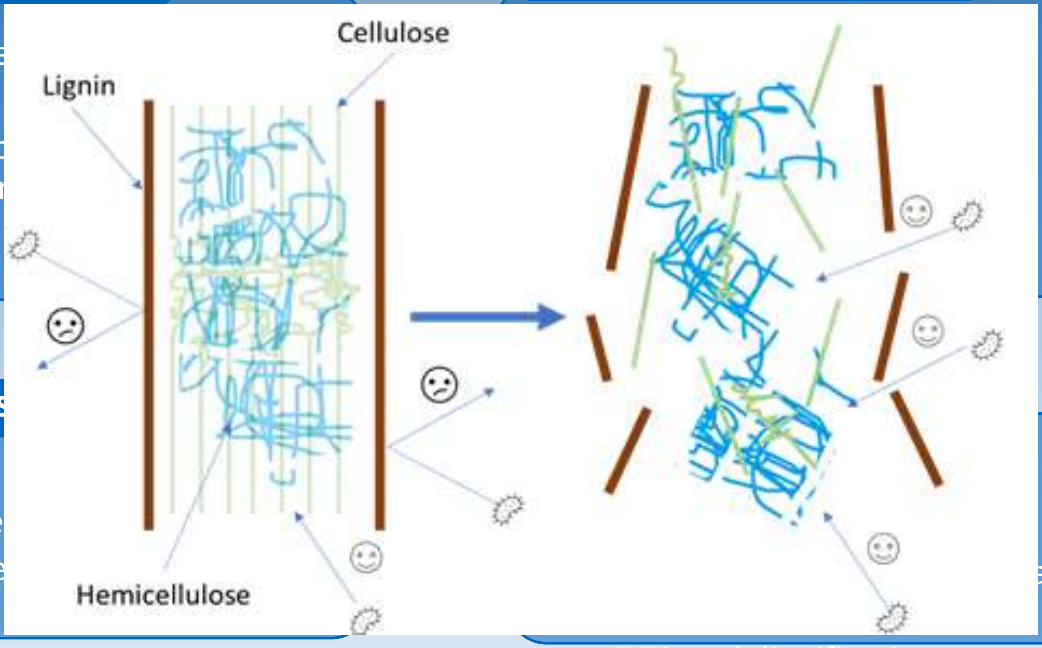
Mechanical

Acid treatments

- Hydrolization chains and he
- Chelation effe

am

- DES as delignification



Dissolving Pulp quality parameters

Lignin

- Phenolic polymer present in every lignocellulosic material
- Low content is needed

α-cellulose

- Represents the unaltered fraction of cellulose
- Higher than 90 % is needed

Pentosan

- Hetero polysaccharide of pentoses
- Low content is needed 3-4 %

Viscosity

- Related to the degree of polymerization and the MWD
- Should be between 400 and 600 mL/g

Brightness

- Reflectance at 457 nm
- Higher than 90 % ISO. Cotton linters can be lower

Fock's reactivity

- Ability of chemicals to react with cellulose
- The higher the better carefull with viscosity

These parameters need to be controlled to have good quality of pulp

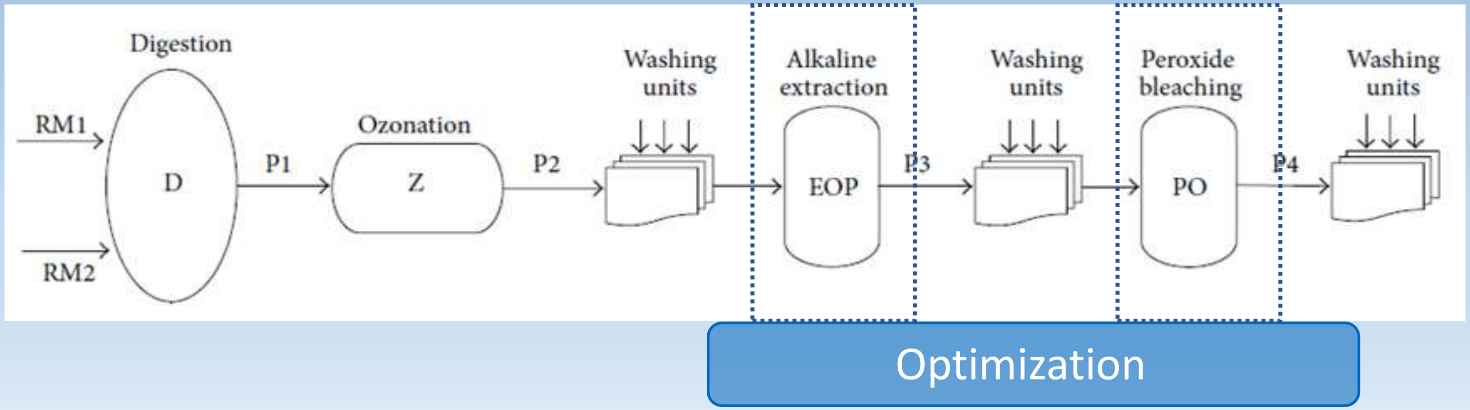
Bleaching process

Elemental chlorine
Elemental chlorine free

- Chlorine-based bleaching
- High selectivity towards impurities
- Environmentally harmful

Totally chlorine free

- Non cholrine-based compounds
- Low selectivity towards impurities
- Environmentally friendlier



Bleaching stage is needed not for brightness but to purify pulp further

Bleaching process

Independent Variables

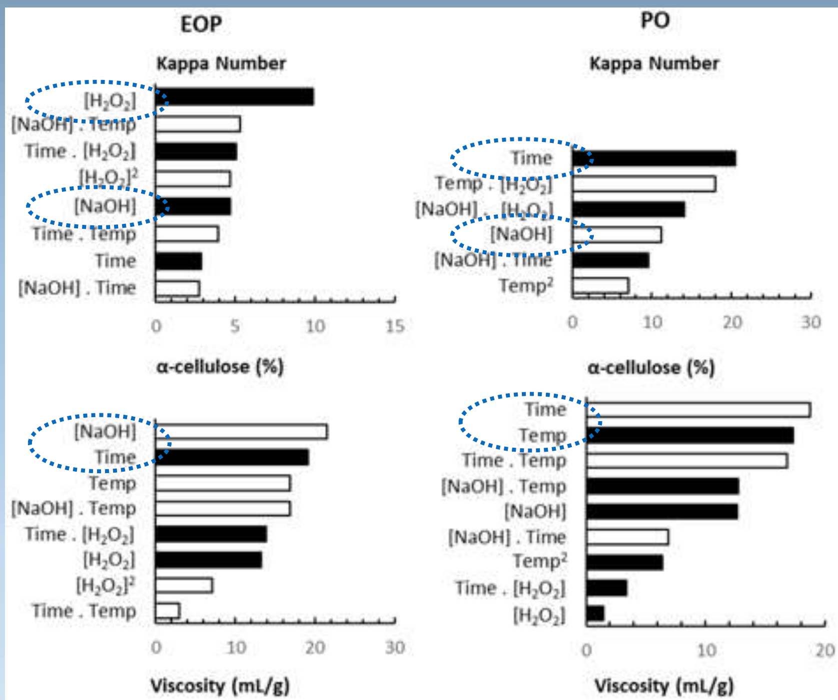
- NaOH dosage (Kg/ADT)
- H_2O_2 dosage (Kg/ADT)
- Time (min)
- Temperature (ºC)

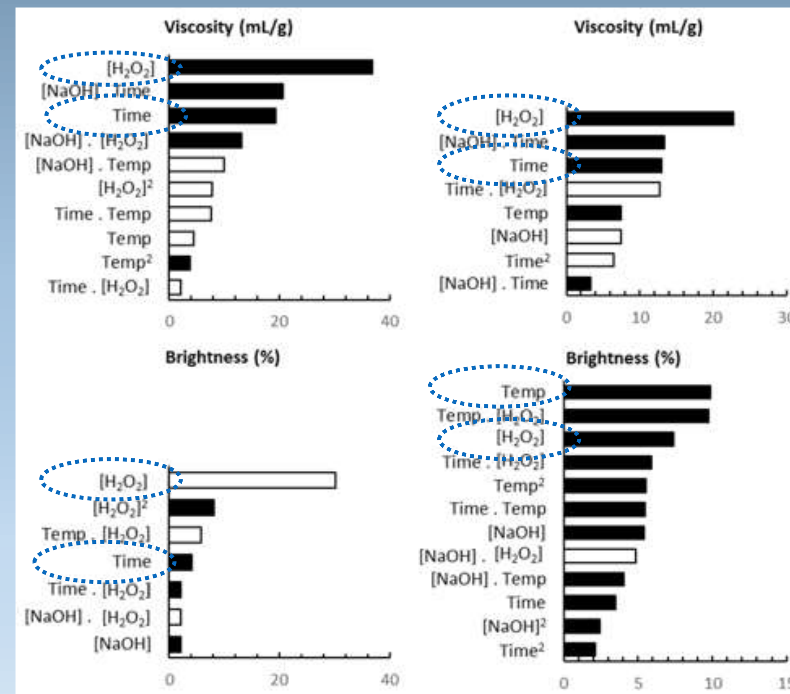
Response variables

- Lignin content (TAPPI UM 246)
- α-cellulose (TAPPI T203 cm-99)
- Brightness (TAPPI T452 OM-02)
- Viscosity (ISO 5351)

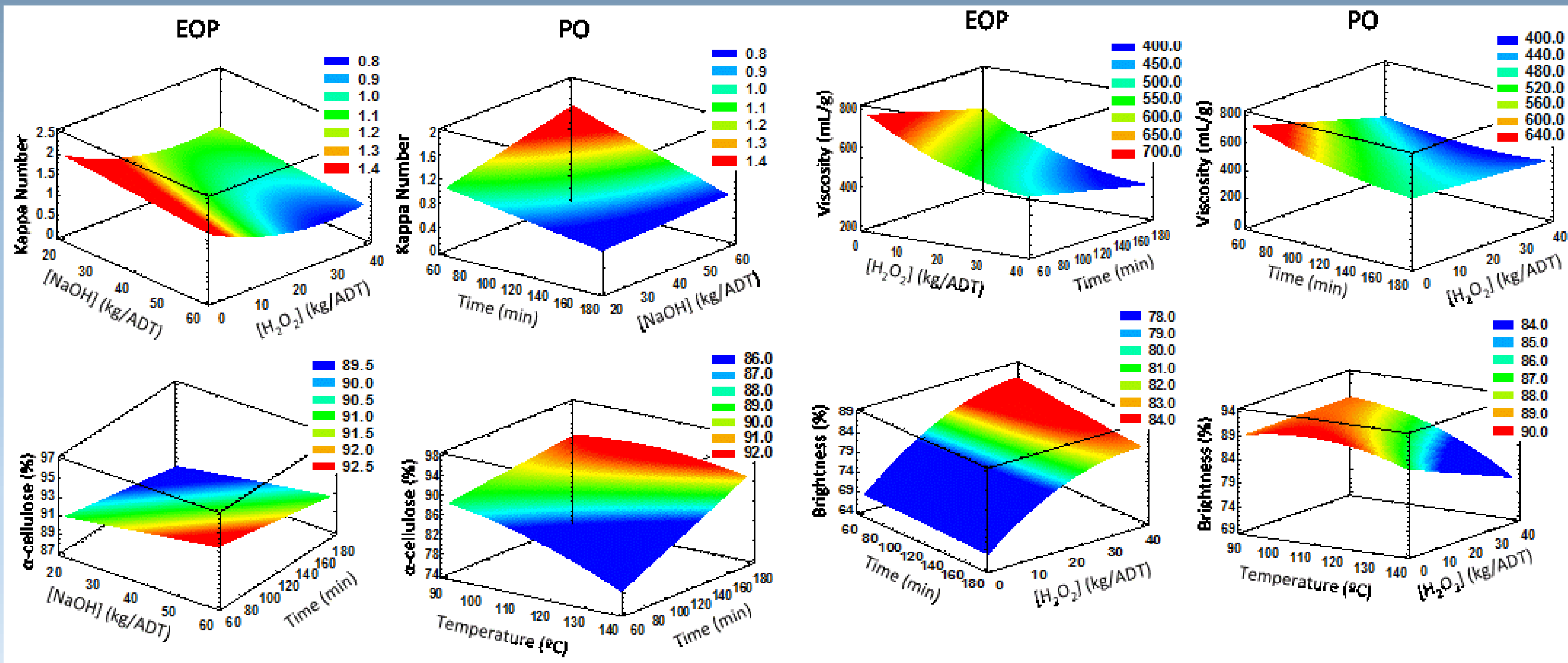
Washed pulp is weighed and chemicals are added → **Conditions of temperature, time and pressure (O_2) are set** → **Pulp is washed until pH of waste water is nearly 7** → **Pulp is analyzed after bleaching**

Bleaching process





Bleaching process



Bleaching process

Optimization

$$Z = \sum costs_{energy} + \sum costs_{chemicals}$$

$$Cost^{EOP}_{energy}\,(€) = 0.00491 \cdot t^{EOP}_{R} \cdot \left(T^{EOP} - 65\right)$$

$$Cost^{PO}_{energy}(€)=0.00432 \cdot t^{PO}_{R} \cdot \left(T^{PO} - 65\right)$$

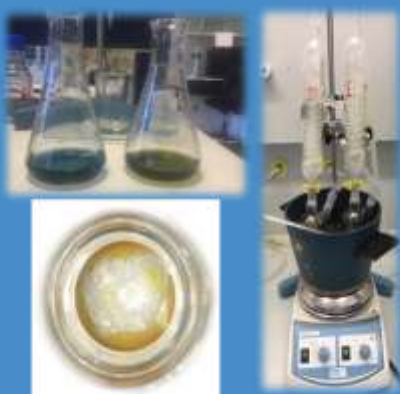
$$Cost^{EOP}_{chemicals}\,(€) = 0.0259 \cdot C^{EOP}_{NaOH} \cdot t^{EOP}_{R} + 0.0743 \cdot C^{EOP}_{H_2O_2} \cdot t^{EOP}_{R} + 0.0259 \cdot t^{EOP}_{R}$$

$$Cost^{PO}_{chemicals}\,(€) = 0.0228 \cdot C^{PO}_{NaOH} \cdot t^{PO}_{R} + 0.0653 \cdot C^{PO}_{H_2O_2} \cdot t^{PO}_{R} + 0.0228 \cdot t^{PO}_{R}$$

The optimization lead to cost reduction of 62.2 % when viscose was considered

Bleaching process

CS_2 Reduction



Quality pulp parameters

- Lignin content (TAPPI UM 246)
- α-cellulose (TAPPI T203 cm-99)
- Viscosity (ISO 5351)
- Reactivity (Fock's method)
- Pentosan content (Internal method)

CS_2 consumption calculation

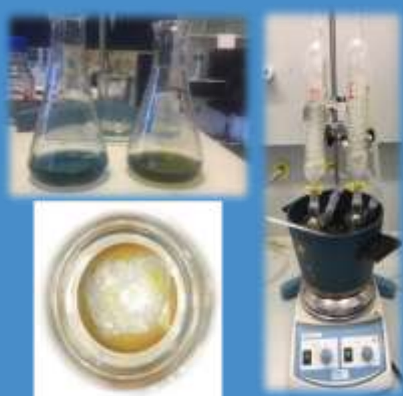
$$TF(\%) = \frac{\alpha\text{-cellulose }(\%) \cdot \text{Reactivity}(\%)}{100}$$

$$CS_2\text{usage}(\%) = \frac{\alpha\text{-cellulose}(\%) \cdot 23.5}{100}$$

$$RCF = \frac{CS_2\text{usage}(\%)}{TF(\%)}$$

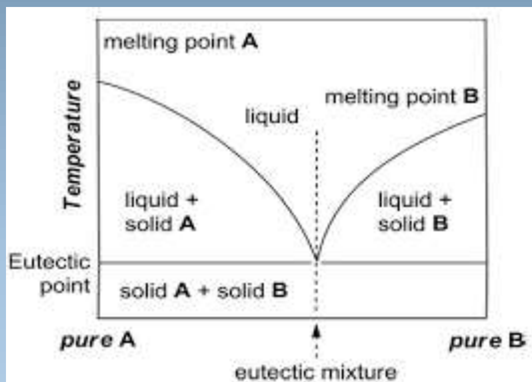
Bleaching process

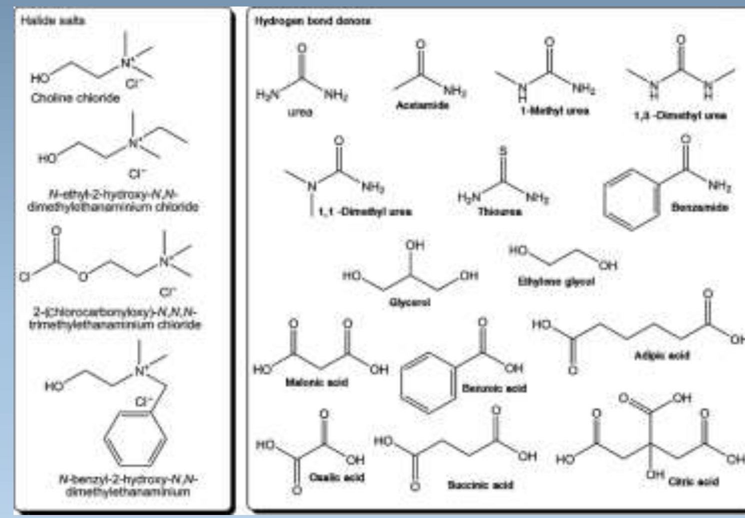
CS_2 Reduction

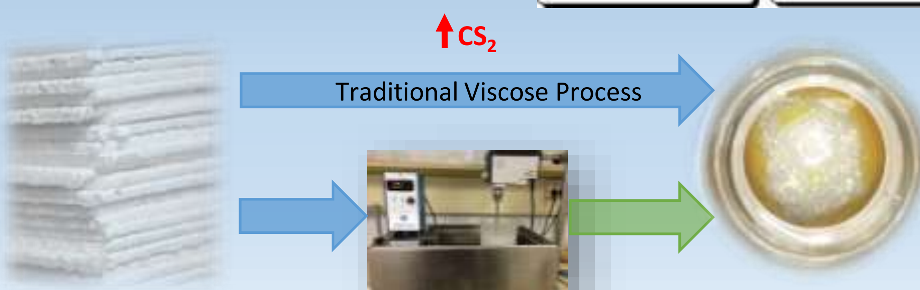


Experiment	NaOH-kg/ADT H_2O_2-kg/ADT Time-min Temperature-ºC	α-cellulose (%)	Reactivity (%)	CS_2 (%)	TF (%)	RCF	CS_2 reduction (%)
Commercial	-	91.52	83.98 ± 6.47	21.51	76.85	0.28	-
PO 1.1	0/0/180/90	88.51	97.35 ± 1.53	20.80	86.16	0.24	13.74
PO 1.2	20/0/180/90	92.02	84.63 ± 5.48	21.62	77.88	0.28	0.770
PO 1.3	60/0/180/90	90.81	85.37 ± 6.02	21.34	77.52	0.28	1.630
PO 1.4	80/0/180/90	92.68	85.07 ± 6.10	21.78	78.84	0.28	1.280
PO 2.1	0/30/15/90	91.40	56.02 ± 0.46	21.48	51.20	0.42	-49.91
PO 2.2	0/30/30/90	91.30	81.89 ± 4.85	21.46	74.77	0.29	-2.550
PO 2.3	0/90/90/90	91.75	85.42 ± 3.79	21.56	78.37	0.28	1.690
PO 2.4	0/30/210/90	88.19	93.53 ± 5.26	20.72	82.48	0.25	10.21
PO 3.1	0/30/180/70	89.62	79.32 ± 5.73	21.06	71.09	0.30	-5.870
PO 3.2	0/30/180/110	89.40	77.21 ± 5.47	21.01	69.03	0.30	-8.770
PO 3.3	0/30/180/140	89.74	96.89 ± 1.44	21.09	86.95	0.24	13.33
PO 3.4	0/30/180/160	89.81	89.94 ± 4.35	21.11	80.78	0.26	6.630
PO 4.1	0/5/180/90	88.58	78.33 ± 3.43	20.82	69.38	0.30	-7.210
PO 4.2	0/30/180/90	91.17	95.3 ± 0.46	21.42	86.89	0.25	11.88
PO 4.3	0/50/180/90	86.87	96.57 ± 1.37	20.41	83.89	0.24	13.04
PO 4.4	0/80/180/90	83.07	90.43 ± 4.80	19.52	75.12	0.26	7.130

DES pre-treatment





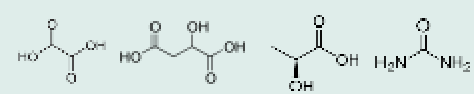


DES Pre-treatment ↓ CS_2

HBA

Choline Chloride

HBD



Oxalic acid | Malic Acid | Lactic Acid | Urea

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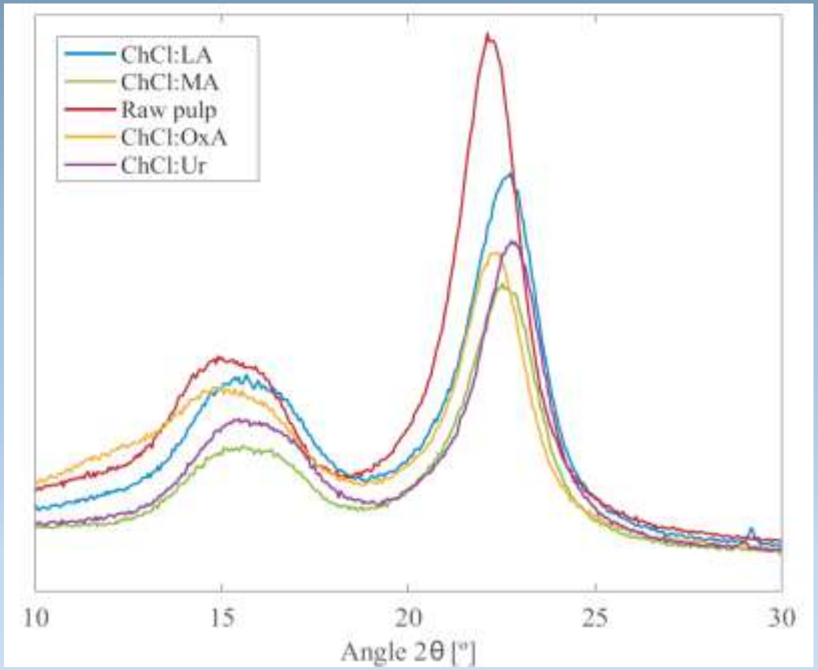
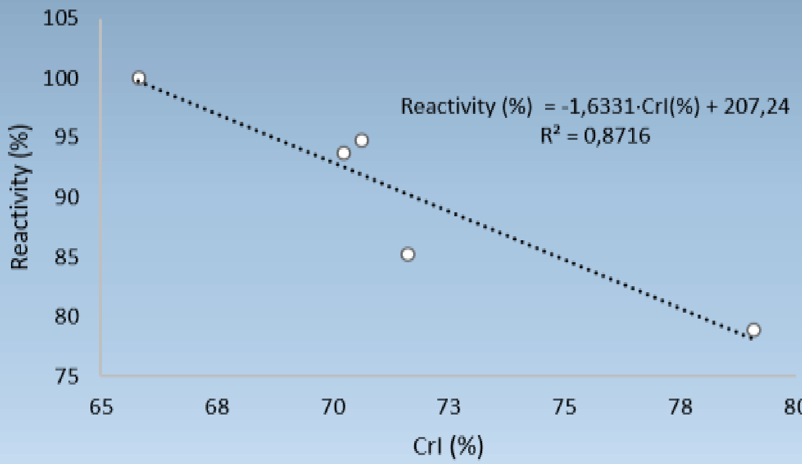
DES pre-treatment





Treatment	α-cellulose	Fock's reactivity(%)	CS_2(%)	TF(%)	RCF	CS_2 reduction (%)
Raw pulp	91.02	78.86	21.4	71.8	0.30	-
ChCl:LA	92.52	93.70	21.7	86.7	0.25	15.83
ChCl:Ur	91.28	94.81	21.5	86.5	0.25	16.82
ChCl:MA	91.88	85.18	21.6	78.3	0.28	7.416
ChCl:OxA	86.86	100.00	20.4	86.9	0.24	21.14

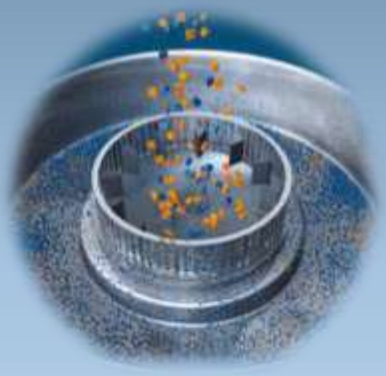
A linear corelation between CrI and reactivity was found

DES employed did not change the configuration of cellulose chain and reduced crystallinity of cellulose

Mechanical pretreatment

Knife milling

Ball milling



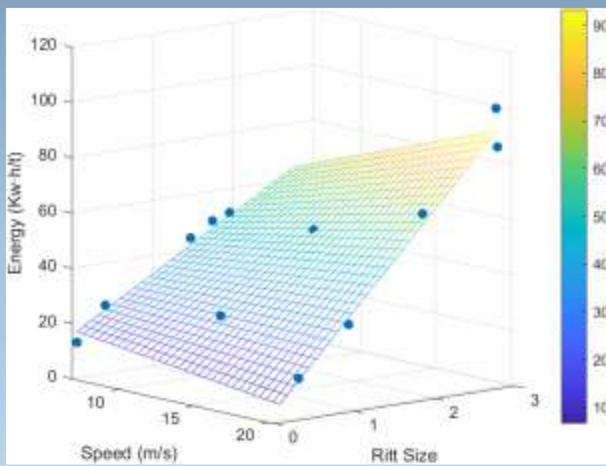
Centrifugal milling

Predict and optimize the energy consumed in these pretreatments to achieve a certain particle size, when LCB is used

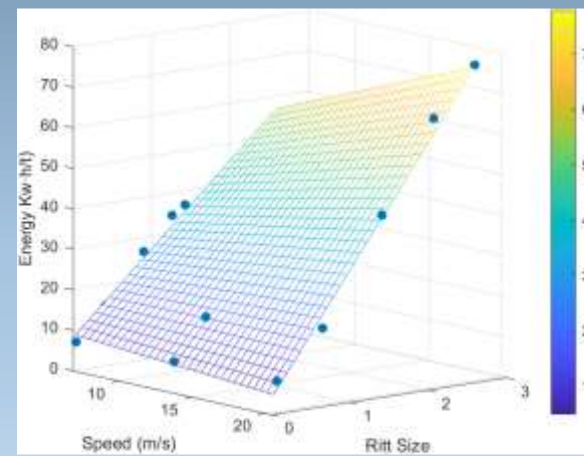
There are equations that predict the energy consumption but were developed for minerals not for biomass

Mechanical pretreatment

LINEAR ROTOR

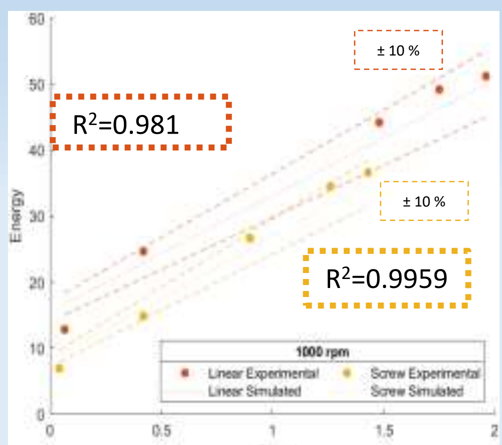


SCREW ROTOR



$$E_{linear} = 21.16 - 0.82 \cdot \mathbf{Rev} + 10.27 \cdot \boldsymbol{Size} + 1.07 \cdot \mathbf{Rev} \cdot \boldsymbol{Size}$$

$$E_{Screw} = 10.154 - 0.3131 \cdot \mathbf{Rev} + 13.9854 \cdot \boldsymbol{Size} + 0.723 \cdot \mathbf{Rev} \cdot \boldsymbol{Size}$$



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Acknowledgements

CCUV4 - Green Deal strategies for V4 countries: The needs and challenges to reach low-carbon industry.

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