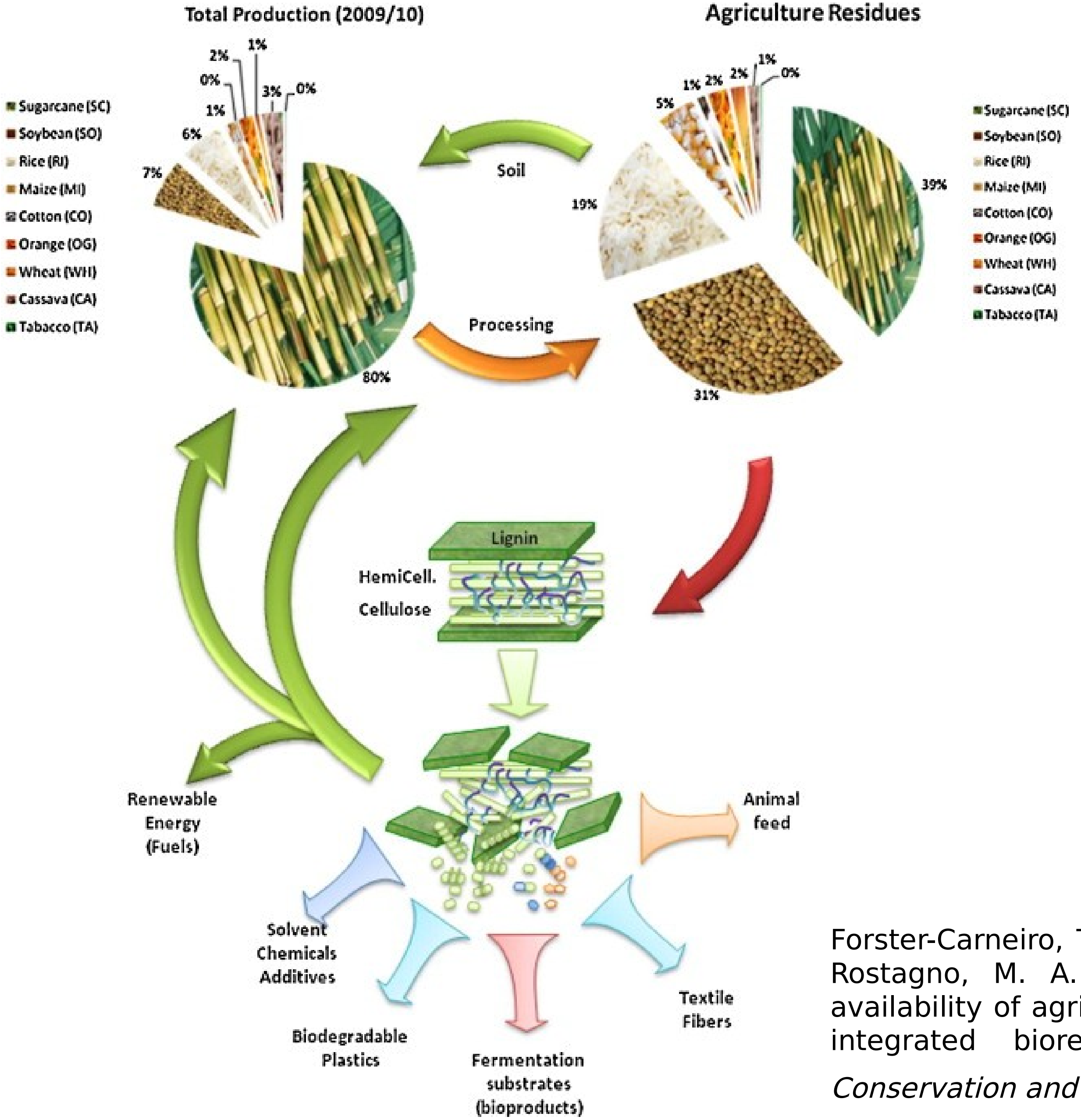
National Technical University of Athens
School of Chemical Engineering
Unit of Environmental Science & Technology

NaOH ALKALINE PRETREATMENT FOR IMPROVEMENT OF ENZYMATIC DIGESTIBILITY OF WHEAT STRAW AS ALTERNATIVE SUGAR SOURCE

J. Novakovic, N. Kontogianni, E.M. Barampouti, S. Mai, D. Malamis, M. Loizidou

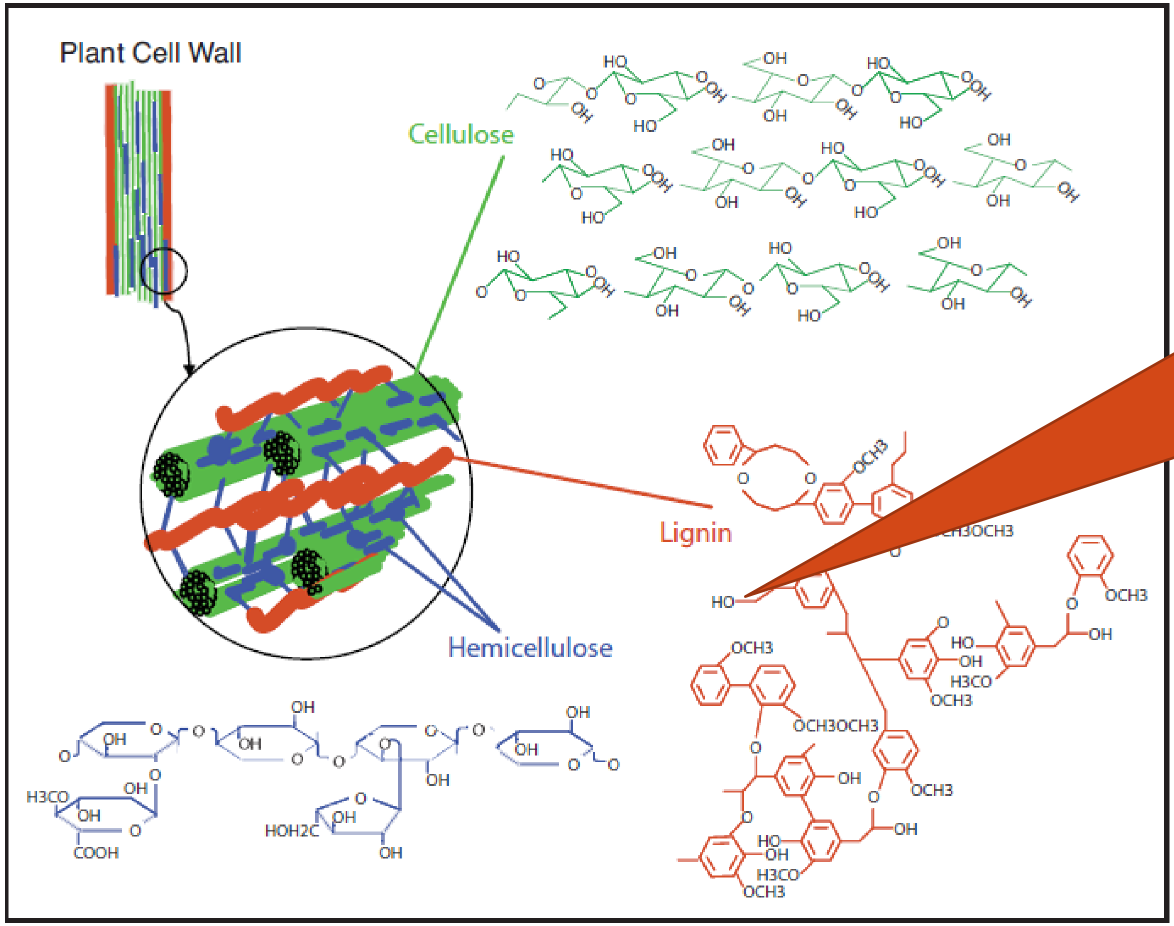
7th International Conference on Sustainable Solid Waste Management, 26-29 June 2019, Heraklion, Crete Island, Greece

Agricultural Waste Biorefinery



Forster-Carneiro, T., Berni, M. D., Dorileo, I. L., & Rostagno, M. A. (2013). Biorefinery study of availability of agriculture residues and wastes for integrated biorefineries in brazil. *Resources, Conservation and Recycling, 77*, 78-88.

-Lignocellulosic material

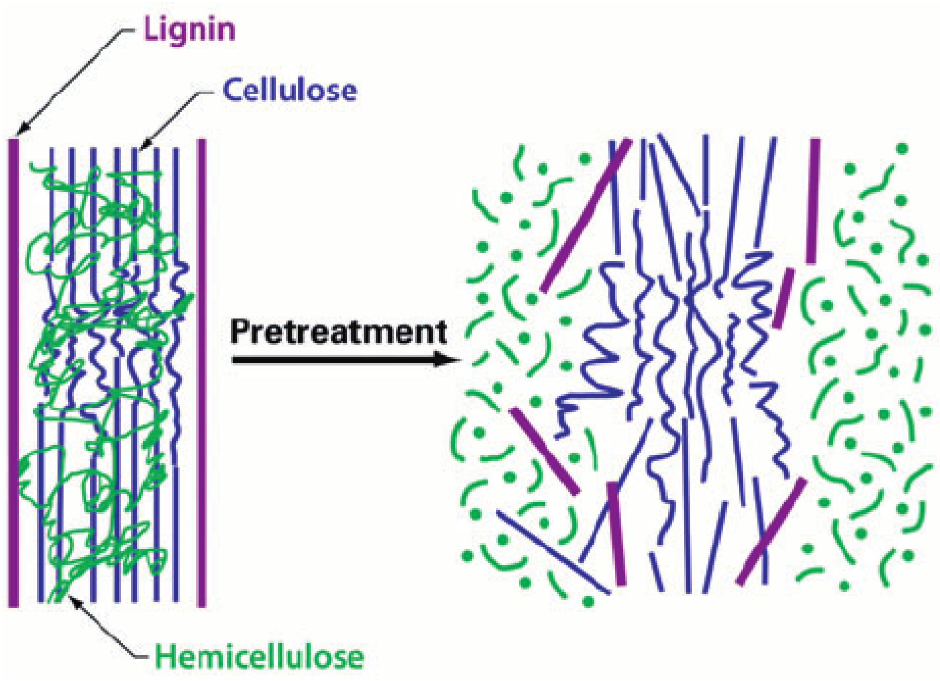


https://www.e-education.psu.edu/egee439/node/606

The major barrier to the enzymatic hydrolysis of carbohydrates towards the production of fermentable sugars

corn stover on a field credit: USDOE-NRE
https://www.greenoptimistic.com

Pretreatments

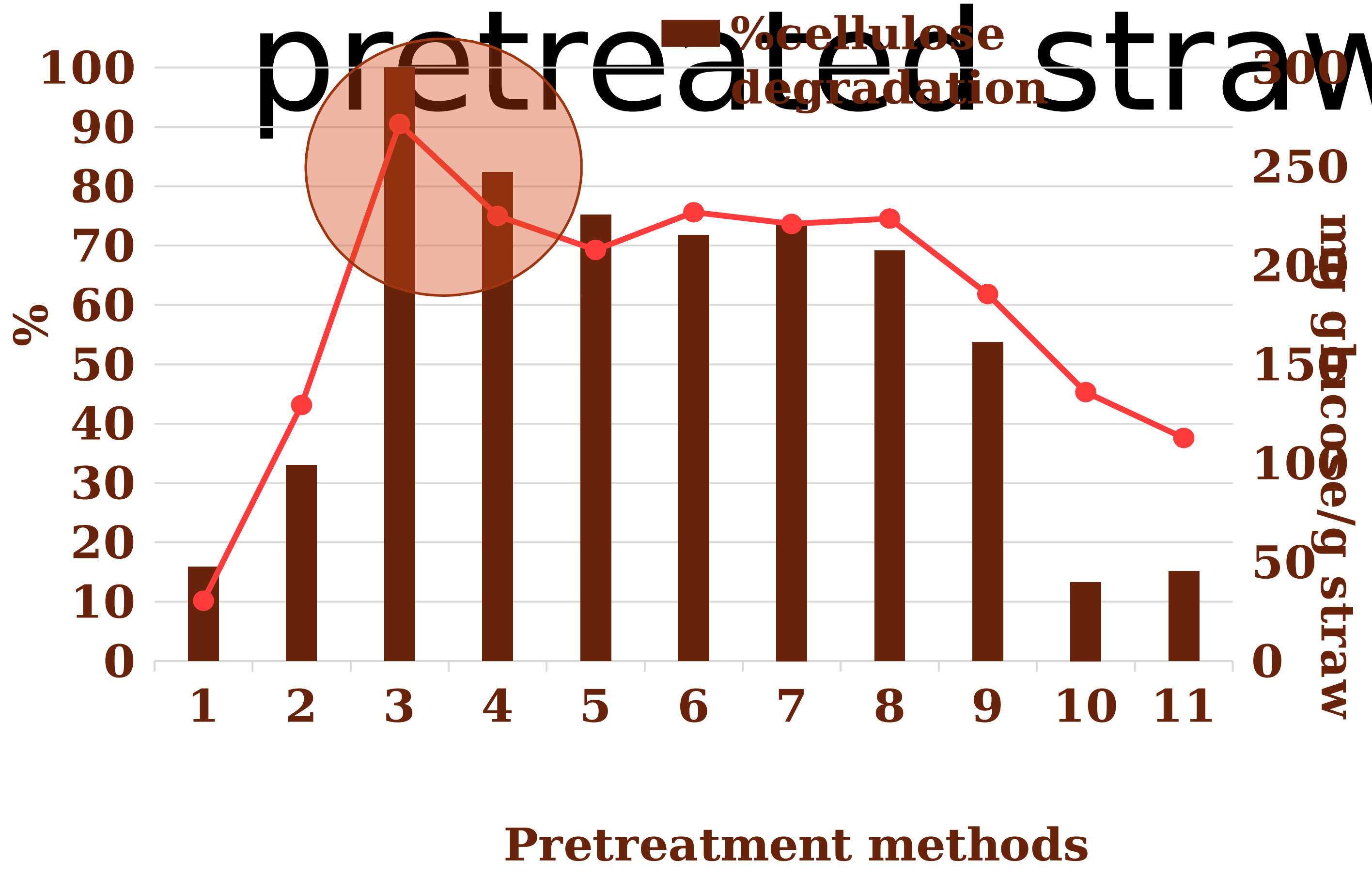


Removal of lignin is favorable to reducing the recalcitrance of lignocellulose for enzymatic attack.

tested

A/A	Reagent	T	Solid :Liquid (w/w)	Time
i	H_2O_2 (5%) NaOH (pH=11,5)	50°C	1:20	1h
ii	H_2O_2 (10%) NaOH (pH=11,5)	50°C	1:20	1h
iii	NaOH 0.5M	50°C	1:10	96 h
iv	NaOH 0.5M	121°C	1:10	1h
v	CH_5N 25 %w/w	50°C	1:10	96 h
vi	CH_5N 25 %w/w	121°C	1:10	1h
vii	Na_2CO_3 0.5M	50°C	1:10	96 h
viii	Na_2CO_3 0.5M	121°C	1:10	1h
ix	NH_3 25 %w/w	50°C	1:10	96 h
x	NH_3 25 %w/w	121°C	1:10	1h

Saccharification of alkaline pretreated straw



(i) alkaline peroxide 5%, **(ii) alkaline peroxide 10%, (iii) NaOH 0.5M**, (iv) NaOH 0.5M autoclaving, (v) methylamine 25 %w/w, (vi) methylamine 25 %w/w autoclaving, (vii) Na_2CO_3 0.5M, (viii) Na_2CO_3 0.5M autoclaving, (ix) ammonia 25 %w/w, (x) ammonia 25 %w/w autoclaving.

AIM

Optimisation of the NaOH pretreatment process along with the enzymatic hydrolysis in order to obtain more fermentable sugars and glucose recovery

Raw material - Wheat straw

Origin: From Aspropyrgos province, Greece

Parameter		Value (% w/w)
Cellulose		33.8
Hemicellulose		45.1
Lignin		16.4
	Klason lignin	15.4
	Acid-soluble lignin	1.0
Ash		4.7

Optimisation Parameters

- Particle Size
- Enzyme loading

PARTICLE SIZE

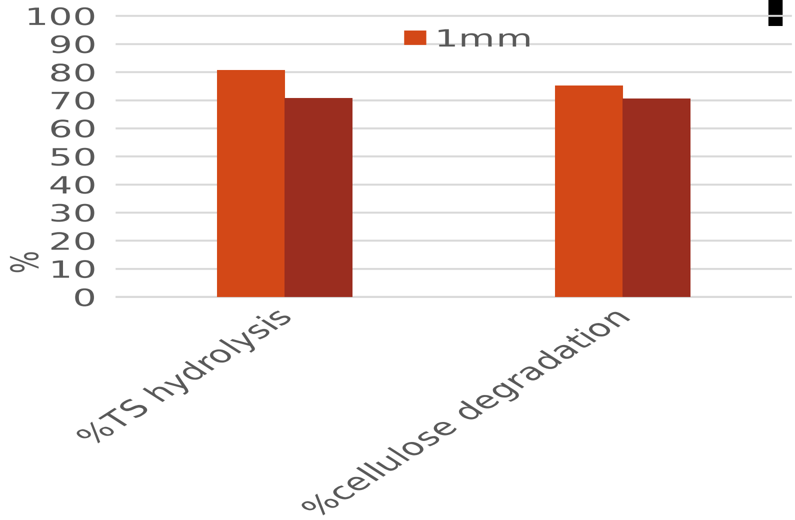
Particle Size- Experimental procedure

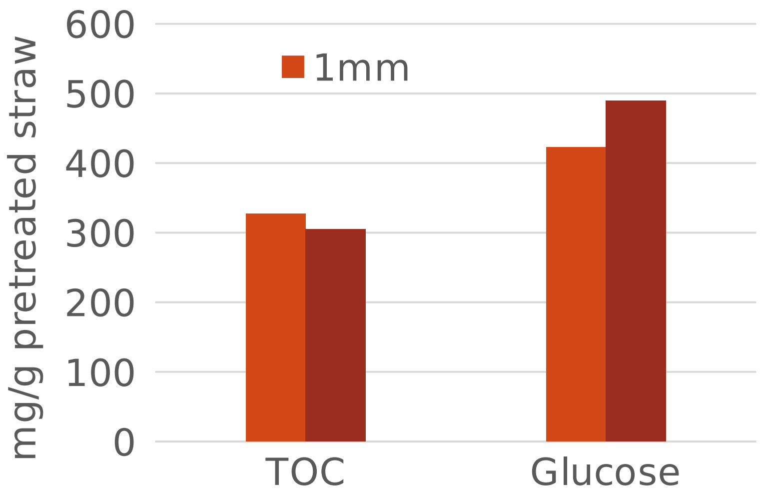
Comminution
- FRITSCH Cutting mill Pulverisette 15
- Particle size 1mm
- Particle size 10-20mm

NaOH pretretment
- NaOH 0.5M
- S/L: 1/10 w/w
- Autoclaved at 121°C for 1 h

Enzymatic Hydrolysis
- 10% w/w dry solid
- 15μL g^{-1} dry solid (CellicCTec2)
- 50°C and 300

Particle Size





Conclusion
The particle size in the range of 1 to 20mm didn't affect significantly the performance of the pretreatment scheme

Effect of particle size on enzymatic hydrolysis of pretreated straw

ENZYME LOADING

Enzyme Loading- Experimental procedure

Comminution
- Particle size 10-20mm

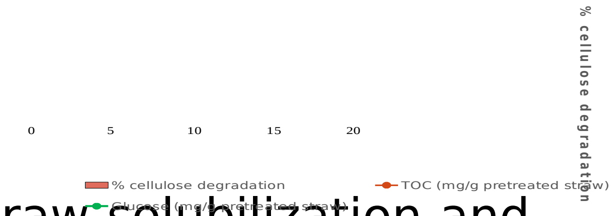
NaOH pretretment
- NaOH 0.5M
- S/L: 1/10 w/w
- Autoclaved at 121°C for 1 h

Enzymatic Hydrolysis
- 10% w/w dry solid
- 50°C and 300 rpm for 96 h
- **Cellic CTec2 5, 10, 15 and 20**

Enzyme Loading

Conclusion

15 μL/g pretreated straw was selected as the optimum cellulase dosage



Effect of enzyme loading on the straw solubilization and cellulose degradation during enzymatic hydrolysis

ALKALINE SOLUTION [illegible] RECYCLING

Alkaline solution Recycling- Experimental procedure

Comminution
- Particle size 10-20mm

NaOH pretretment
- NaOH solution recycled
- S/L: 1/10 w/w
- Autoclaved at 121°C for 1 h

Enzymatic Hydrolysis
- 10% w/w dry solid
- 50°C and 300 rpm for 96 h
- Cellic 15 μL/g pretreated

Alkaline solution Recycling

Cycle No	%TS hydrolysis			%cellulose degradation			%AIL degradation			%ASL degradation			%hemicellulose degradation		
1	36.61	±	0.12	2.74	±	0.26	86.36	±	2.16	99.54	±	2.84	51.71	±	2.59
2	30.16	±	0.21	4.12	±	1.47	79.51	±	3.58	99.48	±	2.93	26.34	±	2.31
3	26.80	±	0.32	7.34	±	1.61	72.21	±	5.23	99.41	±	3.65	15.67	±	3.26
4	30.08	±	0.78	8.50	±	2.44	76.47	±	2.45	99.41	±	5.62	44.02	±	6.19
5	14.03	±	0.13	5.05	±	2.63	65.96	±	1.36	99.38	±	3.18	23.65	±	4.36

Solid fractions' degradation after the different cycles of pretreatment of wheat straw.

Conclusion

The alkaline solution could be recirculated at least 4 times before being "saturated" although after each experiment it needed to be supplemented with some fresh solution.

PRETREATMENT KINETICS

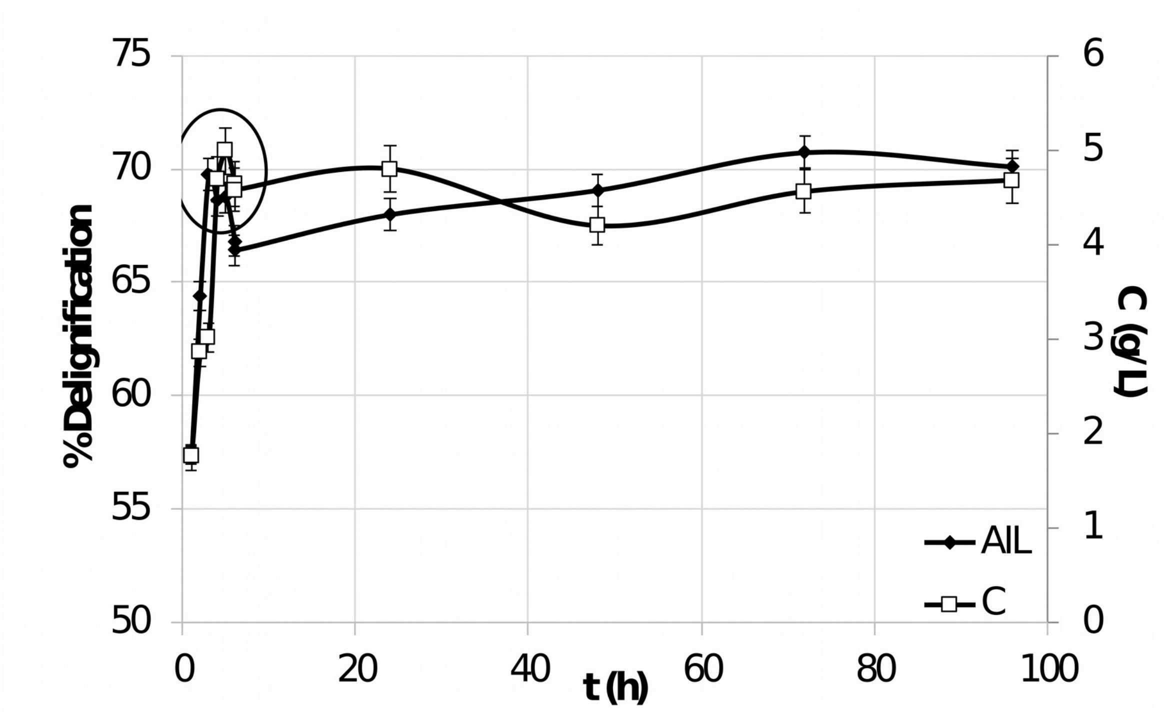
Pretreatment Kinetics - Experimental procedure

Comminution
- Particle size 10-20mm

NaOH pretretment
- NaOH 0.5M
- S/L: 1/10 w/w
- 50°C for **0-96 h**

Enzymatic Hydrolysis
- 10% w/w dry solid
- 50°C and 300 rpm for 96 h
- Cellic 15 μL/g pretreated

Pretreatment Kinetics



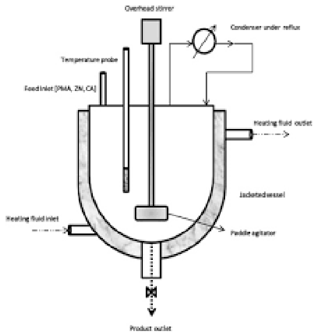
Timeline of total organic carbon (g/L) and delignification efficiency (%) during NaOH 0.5M pretreatment at 50°C

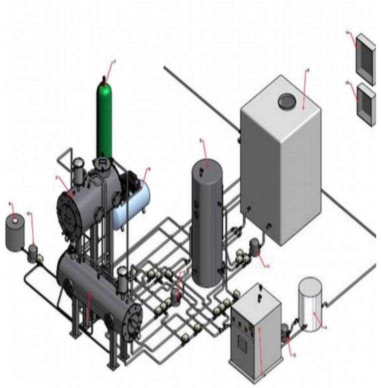
Conclusion

In the time interval of 3-5h of pretreatment, the delignification efficiency reached its maximum and remained statistically constant the rest 90h.

SCALE-UP

Scaling-up - Experimental procedure





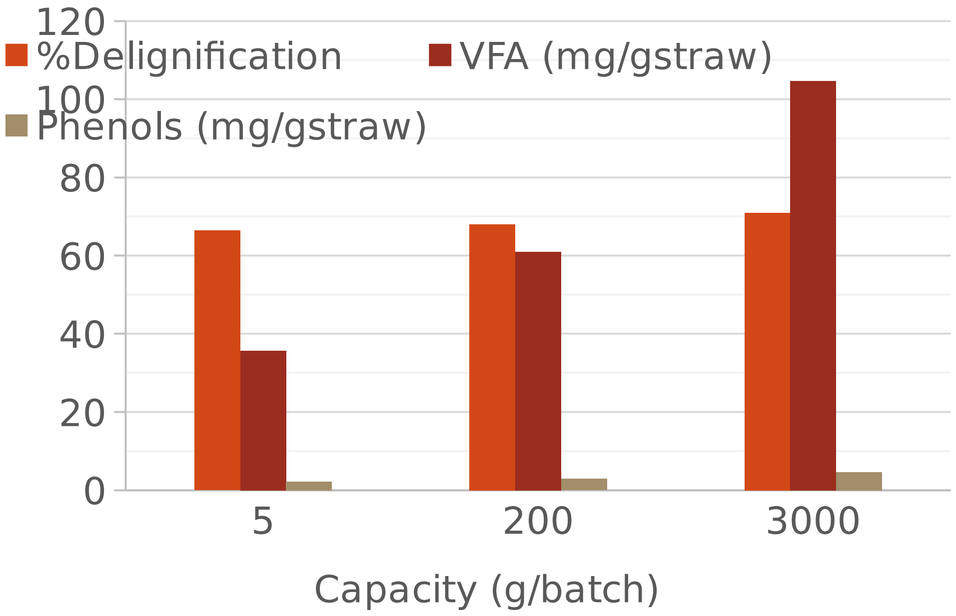
5g/batch
$V_{reactor} = 250mL$

200g/batch
$V_{reactor} = 4L$

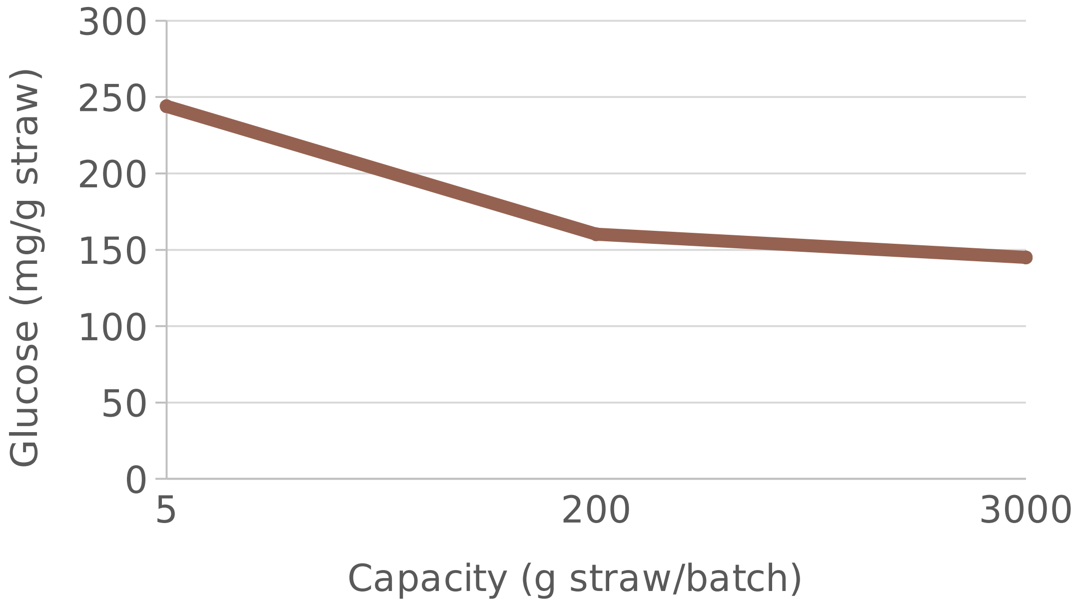
3000g/batch
$V_{reactor} = 200L$

Scaling-up

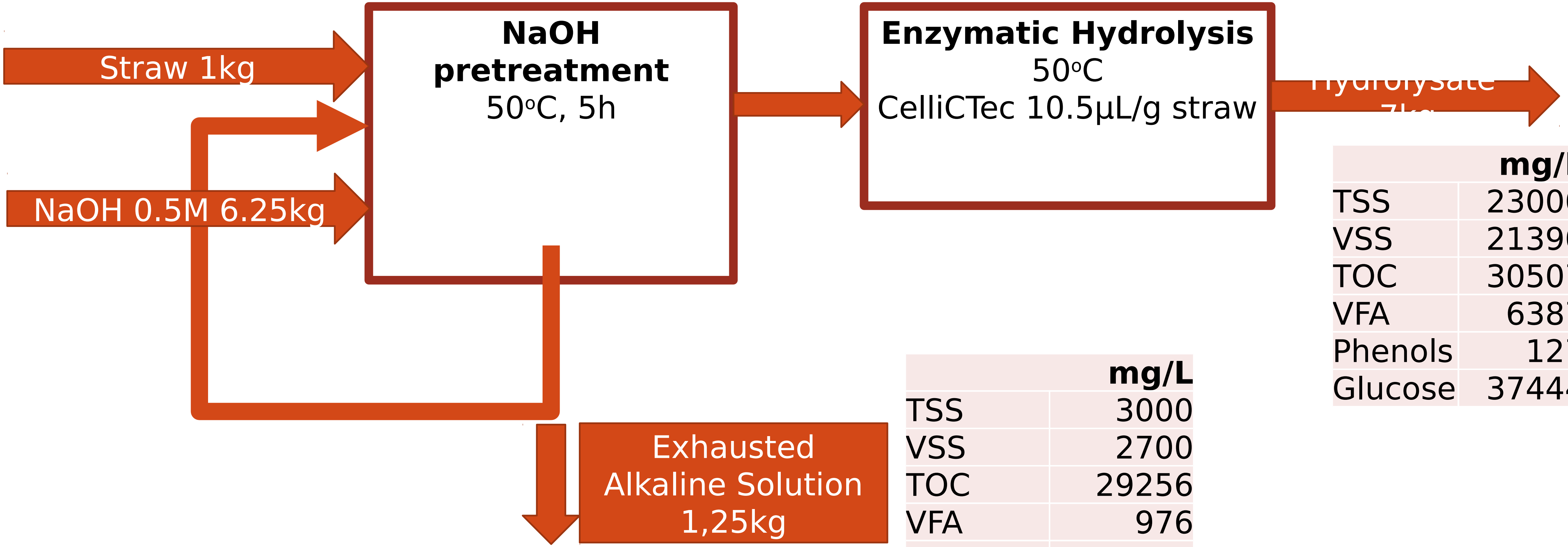
NaOH pretreatment step



Saccharification step



CONCLUSIONS



	mg/L
TSS	23000
VSS	21390
TOC	30507
VFA	6387
Phenols	127
Glucose	37444

	mg/L
TSS	3000
VSS	2700
TOC	29256
VFA	976
Phenols	125

Acknowledgements

The authors acknowledge funding through European Horizon 2020 NoAW (No Agro Waste, Grant no. 688338) project for supporting this work.