

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

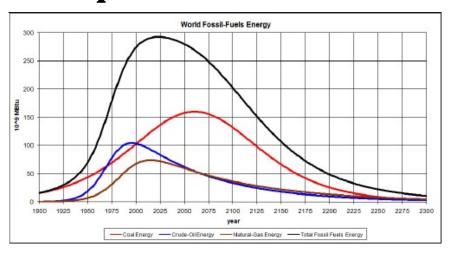
Effect of alkaline pretreatments on the enzymatic hydrolysis of wheat straw

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



World Energy

Depletion of fossil fuel



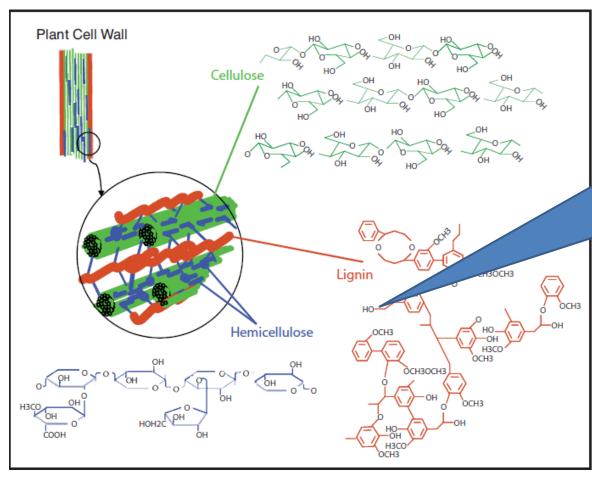
http://www.roperld.com/science/energyfuture.htm

Biofuels

- 1st generation:
 - grain or food sources
- 2nd generation:
- lignocellulosic sources and algae biomass



Agricultural waste -Lignocellulosic material



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

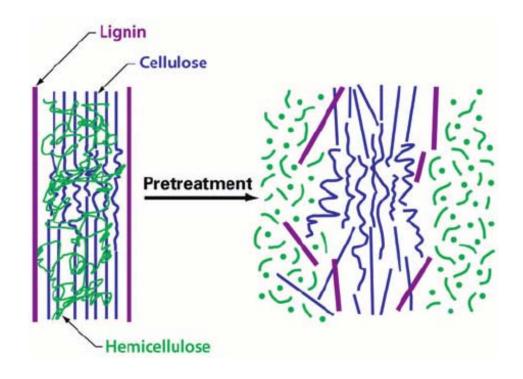
The major barrier to the enzymatic hydrolysis of carbohydrates towards the production of fermentable sugars



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



Lignocellulosic material- Pretreatments



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



Aim

Comparison of the effects of ten alkaline pretreatment methods vis-à-vis improving enzymatic hydrolysis of wheat straw



Materials and Methods



Raw material - Wheat straw

Origin: from Aspropyrgos province. Greece

Preparation:

1. Milled (FRITSCH Cutting mill Pulverisette 15) to 1 mm

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				



Pretreatment techniques of wheat straw

- (i) alkaline peroxide 5%
- (ii) alkaline peroxide 10%
- (iii) dilute NaOH 0.5M
- (iv) dilute NaOH 0.5M autoclaving
- (v) methylamine 25 %w/w
- (vi) methylamine 25 %w/w autoclaving
- (vii) Na₂CO₃ o.5M
- (viii) Na₂CO₃ o.5M autoclaving
- (ix) ammonia 25 %w/w
- (x) ammonia 25 %w/w autoclaving



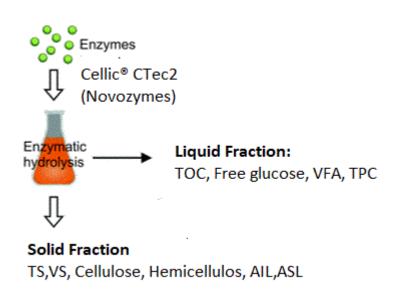
Pretreatment techniques of wheat straw

A/A	Reagent	T	Solid :Liquid (w/w)	Time
i	H ₂ O ₂ (5%) NaOH (pH=11,5)	50°C	1:20	1h
ii	H ₂ O ₂ (10%) NaOH (pH=11,5)	50°C	1:20	1h
iii	NaOH o.5M	50°C	1:10	96 h
iv	NaOH o.5M	121°C	1:10	1h
v	CH ₅ N 25 %w/w	50°C	1:10	96 h
vi	CH ₅ N 25 %w/w	121°C	1:10	1h
vii	Na ₂ CO ₃ o.5M	50°C	1:10	96 h
viii	Na ₂ CO ₃ o.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



Enzymatic hydrolysis

- Raw material and pretreated solids
- > 10% w/w dry solid
- > 15μL g⁻¹ dry solid (CellicCTec2)
- > 50°C and 300 rpm for 96 h





Results and Discussion



Degradation of solid fractions after pretreatments

	0/ TC b	ميال	lvaia	%cellulose			%.		% <i>F</i>		%hemicellulose				
	%TS hy	orysis	degradation			degra	tion	degra	tion	degradation					
i	11.68	±	0.02	11.06	±	0.96	31.63	±	0.06	0.76	±	2.87	5.22	±	0.49
ii	28.05	±	0.20	1.88	±	1.37	89.6	±	0.68	43.99	±	0.9	17.69	±	2.21
iii	30.07	±	0.36	4.45	±	1.11	75.06	±	5.03	36.48	±	4.66	30.66	±	8.26
iv	36.47	±	2.78	33.52	±	3.44	84.86	±	0.45	49.86	±	5.72	9.29	±	7.89
v	29.84	±	0.03	22.3	±	5.63	76.38	±	1.06	99.22	±	0.09	8.66	±	9.46
vi	26.09	±	4.73	24.8	±	2.33	70.78	±	4.23	99.03	±	0.19	3.84	±	2.61
vii	11.59	±	0.37	4.87	±	1.76	38.51	±	6.92	16.99	±	2.16	1.31	±	1.72
viii	11.05	±	8.65	3.71	±	1.10	59.81	±	4.15	38.93	±	6.63	0.50	±	3.75
ix	26.75	±	1.49	44.41	±	7.35	57.31	±	2.53	99.21	±	0.01	0.90	±	1.10
x	25.00	±	2.16	17.11	±	1.17	44.83	±	7.55	99.24	±	0.04	24.41	±	2.71

(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) Na₂CO₃ 0.5M, (viii) Na₂CO₃ 0.5M autoclaving, (ix) ammonia 25 %w/w, (x) ammonia 25 %w/w autoclaving.



Components of liquid fractions after pretreatments

		uco a si		(mg /s	FA		TPC (mg/g straw)				
i	0.88	±	0.04	18.10	<u>±</u>	0.28	0.27	<u>±</u>	0.01		
ii	0.15	±	0.03	34.50	±	0.57	0.68	±	0.02		
iii	0.02	±	0.03	33.55	±	1.63	2.13	±	0.04		
iv	0.62	62 ± 0.06		98.30	±	14.99	5.60	±	0.14		
v	1.50	±	0.14	64.10	±	39.46	5.56	±	0.37		
vi	2.10	±	1.27	28.10	±	4.95	4.60	±	0.76		
vii	n.d.	d. ± 0.00		28.20	±	3.39	1.07	±	0.07		
viii	0.70	±	0.94	80.85	±	4.45	2.91	±	0.16		
ix	0.90	±	0.14	38.30	±	9.76	3.63	±	0.44		

(i) alkaline peroxide 5%, (ii) alkaline peroxide 50%, (iii) NaOH 3:9M, (iv) NaOH 0.5M autoclaving,

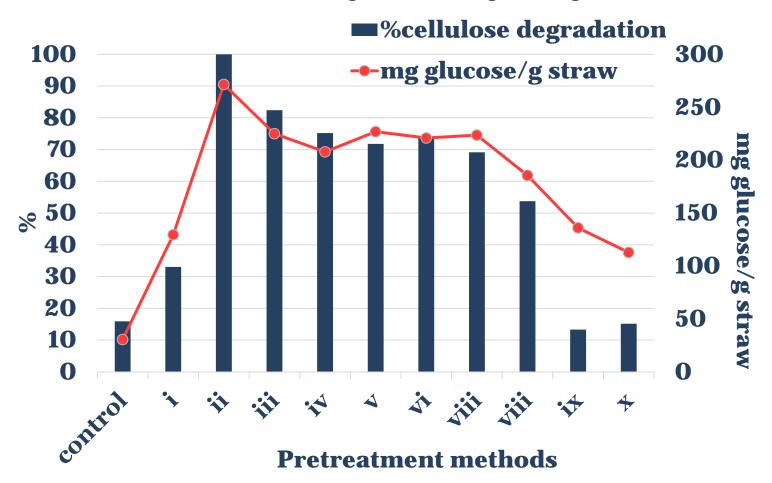
(v) methylamine 25 %w/w, (vi) methylamine 25 %w/w autoclaving, (vii) Na₂CO₃ 0.5M, (viii) Na₂CO₃ 0.5M autoclaving, (ix) ammonia 25 %w/w, (x) ammonia 25 %w/w autoclaving.



Effect of pretreatments on saccharification

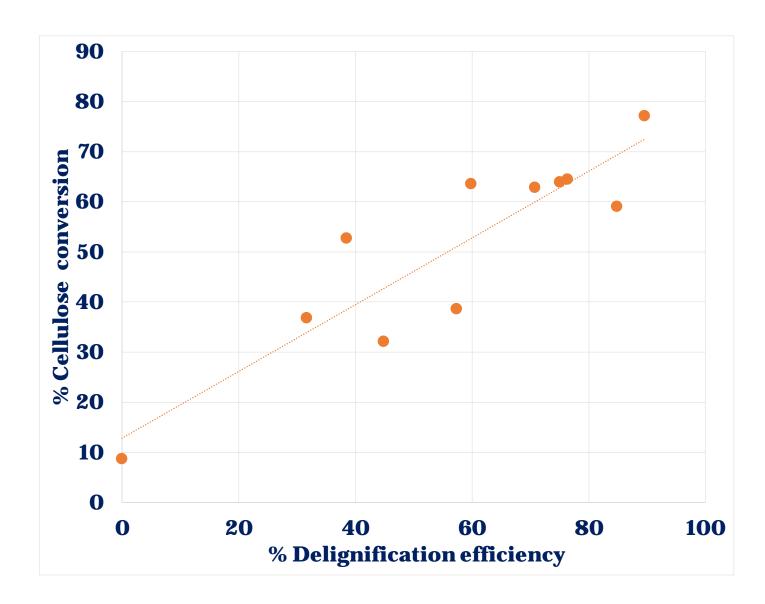
		%TS			%TS %cellulose			%AIL			%A	S	L	%hemicellulose			
		hydrolysis			degradation			degradation			degradation			degradation			
	-	23.61	±	0.62	15.89	±	1.21	13.42	±	0.15	33.61	±	2.16	37.43	±	8.12	
	i	31.18	±	0.12	33.03	±	1.08	20.18	±	0.08	53.74	±	1.87	46.56	±	0.99	
	ii	95.82	±	0.25	100.0	±	2.02	100.0	±	0.78	100.0	±	0.87	100.00	±	3.11	
	iii	77.39	±	0.39	82.40	±	8.92	18.40	±	4.13	78.72	±	5.68	82.43	±	6.15	
	iv	80.72	±	3.18	75.20	±	7.58	9.94	±	0.63	80.67	±	8.65	91.81	±	10.12	
	v	74.08	±	1.13	71.79	±	6.98	3.12	±	0.95	74.08	±	2.17	85.68	±	9.26	
	vi	69.58	±	2.53	74.03	±	9.21	13.93	±	1.11	65.38	±	3.84	77.59	±	7.68	
	vii	10.36	±	2.42	53.73	±	5.36	10.25	±	1.18	44.49	±	2.02	37.29	±	7.98	
	viii	65.61	±	6.85	69.13	±	9.13	1.15	±	2.21	62.62	±	6.21	63.88	±	5.68	
	ix	40.50	±	1.87	13.29	±	5.45	2.16	±	1.23	45.47	±	1.65	66.23	±	6.21	
1	x	36.17	±	1.68	15.12	±	1.27	5.73	±	1.35	46.17	±	1.74	61.16	±	2.68	

After enzymatic hydrolysis



(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) Na₂CO₃ 0.5M, (viii) Na₂CO₃ 0.5M autoclaving, (ix) ammonia 25 %w/w, (x) ammonia 25 %w/w autoclaving.







Conclusions



Conclusions

- 1. Alkaline pretreatments tested proved to promote delignification reactions.
- 2. $\hat{1}$ the delignification efficiency at the pretreatment $\rightarrow \hat{1}$ the glucose recovery at the enzymatic hydrolysis
- 3. Alkaline treatment with:

hydrogen peroxide 10% w/w \rightarrow 73% glucose yield NaOH 0.5M \rightarrow 60%

These pretreatments are efficient for enhancing the enzymatic digestibility of lignocellulosic crop residues to levels approaching the theoretical maximum.



Acknowledgements

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THANK YOU FOR YOUR ATTENTION

