Optimization of Alpha Cellulose and N-Cellulose Solubility in Sodium Hydroxide

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Problem Statement

Cellulose use has been limited in industrial processes because of its low solubility. It does not dissolve in water, and when it has been used, ionic liquids are common solvents. While ionic liquids are "green" for their use in the lab, are very expensive and do not have sustainable end-of-life solutions, as they are made of organic compounds with high toxicity and low biodegradability.

Purpose

Sodium hydroxide is a good alternative to ionic liquids because it fully dissociates in solution, forming ions. This allows it to better disrupt the hydrogen bonds present in cellulose.

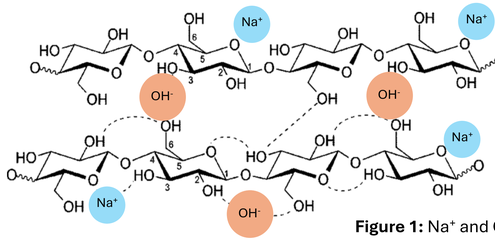
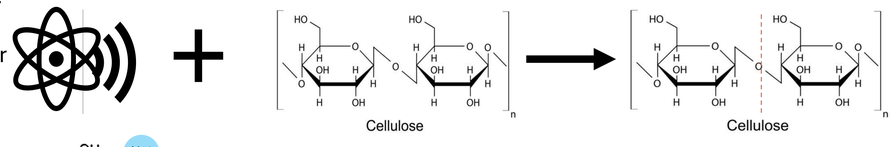


Figure 1: Na^+ and OH^- ions interfering with the hydrogen bonds in cellulose.

Figure 2: The main mechanism of gamma radiation on cellulose is the breakage of the 1-4 glycosidic bond, which breaks the natural polymer into smaller pieces.



Exposing cellulose to gamma radiation prior to dissolving in NaOH degrades the cellulose, which should improve the solubility of the irradiated cellulose by breaking the large fibers into smaller pieces, exposing more surface area and hydrogen bonds normally hidden within the molecule.

Methods

Irradiation of samples:

- Cellulose samples were exposed to gamma radiation at 0, 100, 250, 500, 750, and 1000 kGy on dry cellulose at 14.36 kGy per hour

Percent solubility sample preparation:

- Oven dried at 102°C for 24 hours
- Stirred in 10 wt% NaOH for 3 hours
- Filtered or centrifuged to remove insoluble cellulose
  - Filtrate was reserved for analysis
  - Insoluble cellulose was oven dried, weighed, then stirred in either 18 wt%, 22 wt% or 25 wt% NaOH for 3 hours
    - Filtrate was reserved for analysis

100% solubility sample preparation:

- Oven dried at 102°C for 24 hours
- Stirred in 25 wt% NaOH until dissolved*
  - Filtrate was reserved for analysis

Sample analysis (adapted from TAPPI T-235):

- $K_2Cr_2O_7$ and H_2SO_4 digestion
- $Fe(NH_4)_2(SO_4)_2$* $6H_2O$ titration with ferroin indicator
- % solubility determined by calculation
  - $** S\% = \frac{(V_2 - V_1)\ \mathrm{X}\ N\ \mathrm{X}\ 6.85\ \mathrm{X}\ 10}{A\ \mathrm{X}\ W}$

Figure 4: Analyte color change from green to turquoise to purple indicates oxidation of potassium dichromate with purple being the endpoint

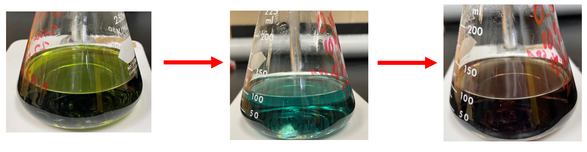


*__Figure 3:__ Example of cellulose completely dissolved in 25% NaOH

Oxidation Reactions for Cellulose Analysis

$(C_6H_{10}O_5)_n + 4\ K_2Cr_2O_7 + 16\ H_2SO_4 \rightarrow 6\ CO_2 + 4\ K_2SO_4 + 4\ Cr_2(SO_4)_3 + 21\ H_2O$

Cellulose is assumed to oxidize completely to carbon dioxide and water

$10Fe(NH_4)_2(SO_4)_2 * 6\ H_2O + K_2Cr_2O_7 + 7\ H_2SO_4 \rightarrow 5\ Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 10\ (NH_4)_2SO_4 + 67\ H_2O$

Chromium is reduced from 6+ to 3+, which promotes the color change

**S% equation only works for non-irradiated cellulose samples.

Results

Graph 1: Solubility of Cellulose in 25 wt% NaOH

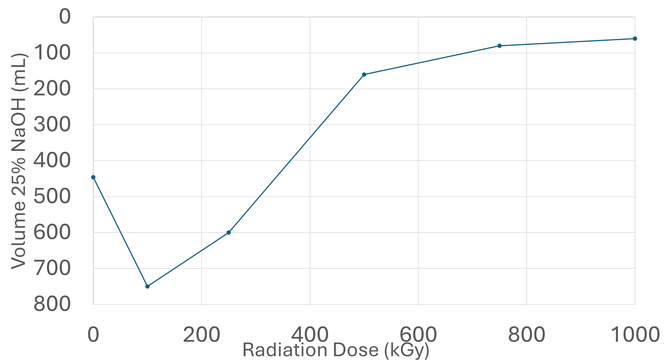


Figure 5: 0, 100, 250, and 500 kGy cellulose did not dissolve completely

Table 2: Percent Solubility Data for Non-Irradiated Cellulose

Type of cellulose	wt% NaOH	Mass cellulose (g)	Volume filtrate (mL)	% Solubility
Alpha	10	0.75	5	19.01
N	10	0.75	5	34.62
Alpha	18	0.75	20	19.31
N	18	0.75	10	39.77
Alpha	22	0.75	20	17.20
N	22	0.75	10	33.43
Alpha	25	0.75	20	10.46
N	25	0.75	10	31.44

S% equation gave over 100% for irradiated samples

Conclusion

The solubility of cellulose increased as the radiation dose increased. This is seen because of the lower volume of sodium hydroxide needed to dissolve higher radiation dosed cellulose and the inability to completely dissolve the lower radiation dosed cellulose.

Future Work

Future work will further examine how radiation affects solubility at lower doses. Additionally, how radiation dose affects the structure and crystallinity of regenerated, soluble cellulose. This can be examined via the Scanning Electron Microscope (SEM), Gel Permeation Chromatography (GPC), X-Ray Diffraction, and Nuclear Magnetic Resonance (NMR).

Acknowledgements

I would like to thank NIST for irradiating my cellulose samples. This project would not have been possible with out them. I would also like to thank Dr.'s List and Driscoll for being sounding boards and helping brainstorm. Additionally, I would like to thank Henry DeVasher, a Junior at ESF for helping with all the titrations I had to complete for this experiment.