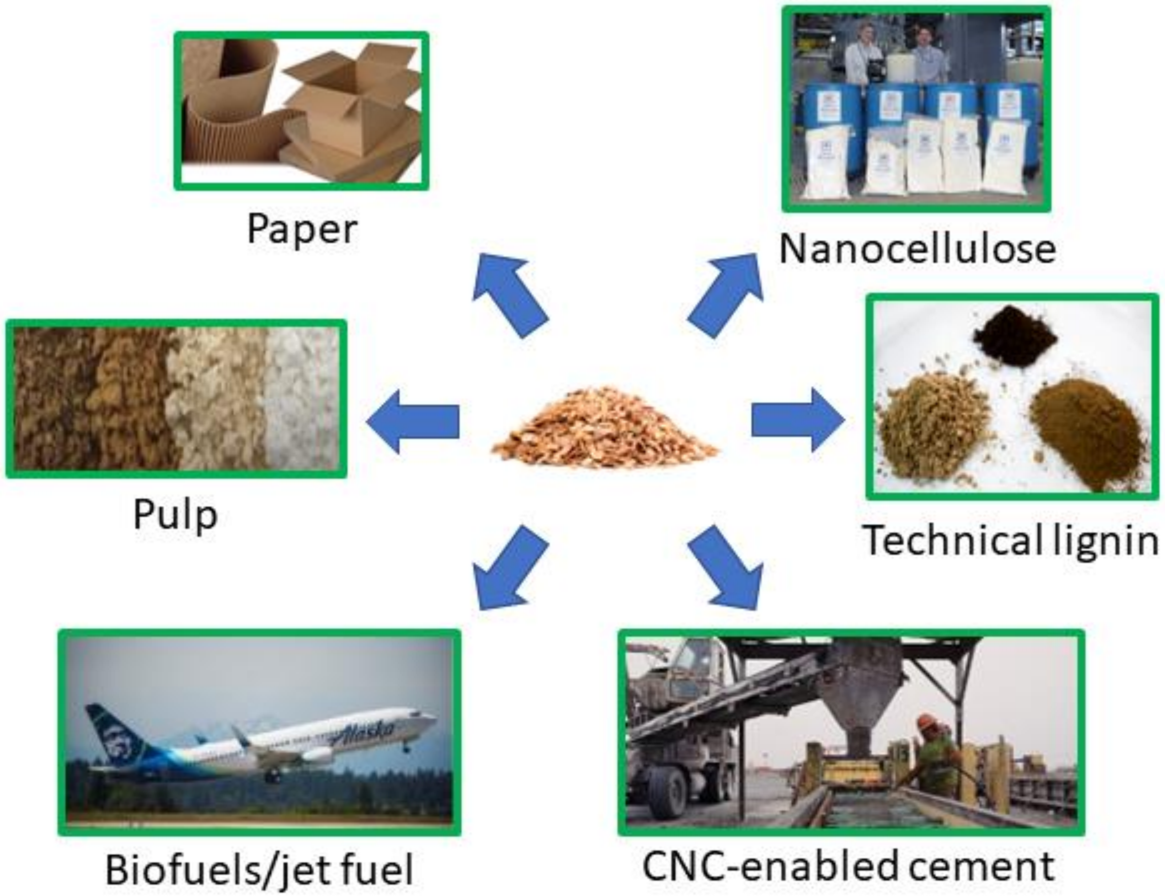
Forest Service
U.S. DEPARTMENT OF AGRICULTURE

Richard Reiner
Chemical Engineer

RWU 4709 Fiber and Chemical Sciences Research



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- John Considine, Res Mat Eng
- Roland Gleisner, Eng Tech
- Carl Houtman, Res Chem Eng
- Clayton Mickles, Chemist
- Roderquita Moore, Res Chemist
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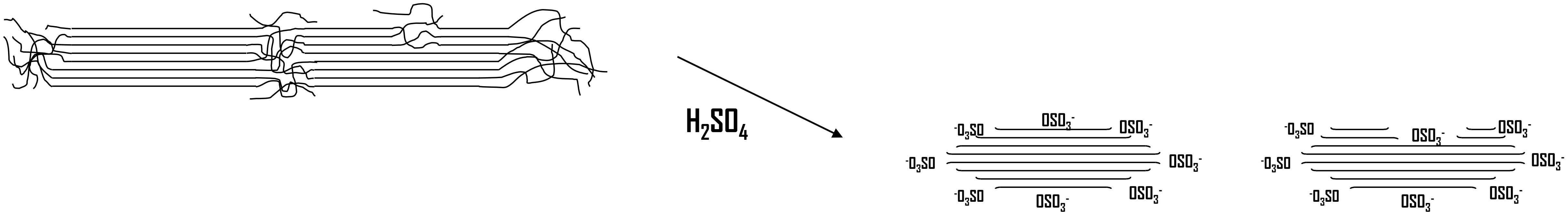
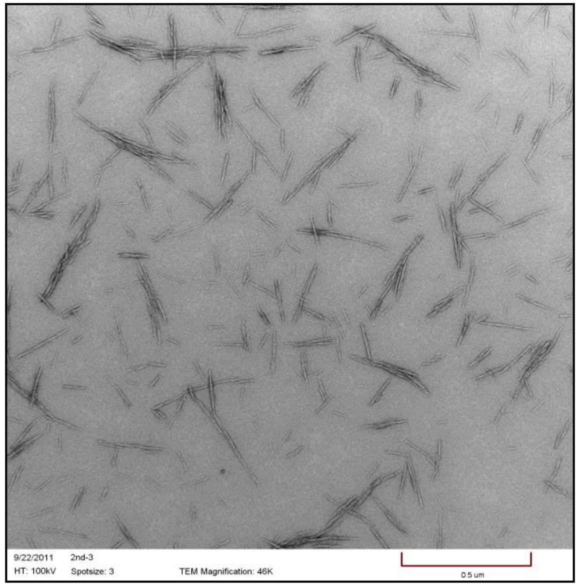
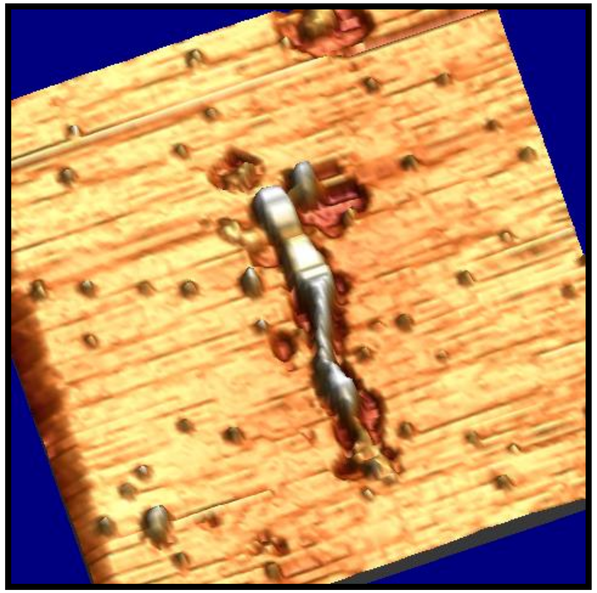
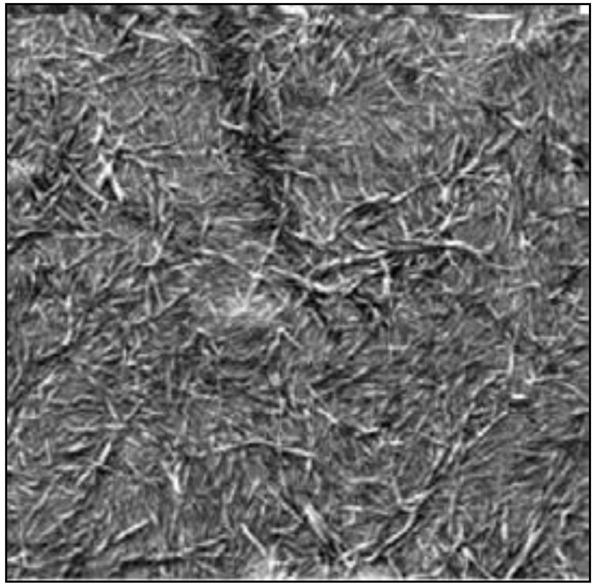
Cellulose Nanocrystals









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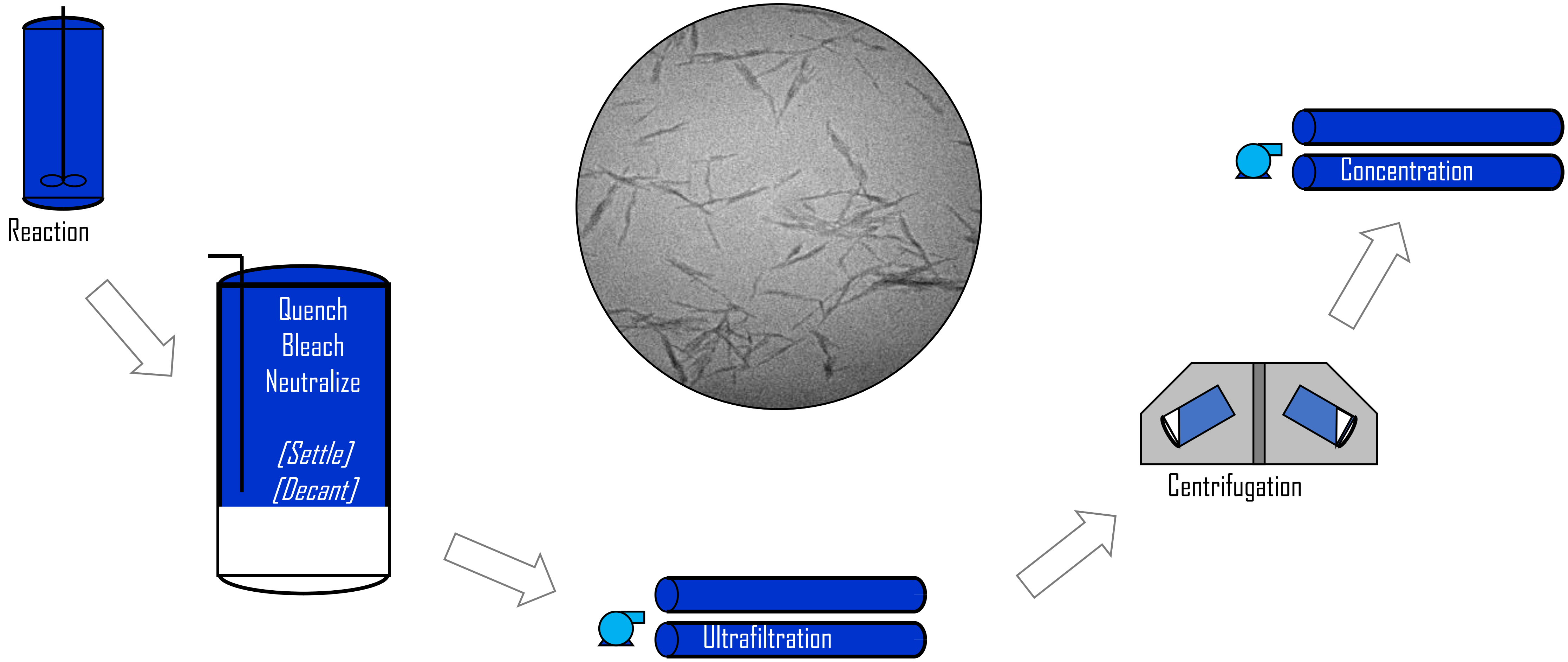
Preparation of Cellulose Nanocrystals (CNCs)



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CNCs: Reaction

- Feedstock
  - Dissolving pulp drylap
  - Combination strip-cut (20%) and cross-cut (80%)
  - 50 kg per batch feed, 25kg per batch product
- Sulfuric Acid
  - 64% H_2SO_4 (PC-grade)
  - Preheated to 48°C
  - 300 L
- Reaction Conditions
  - 45°C for 2 hours
  - Nitrogen/vacuum
  - Glass-lined steel reactors - 400L, water jacket

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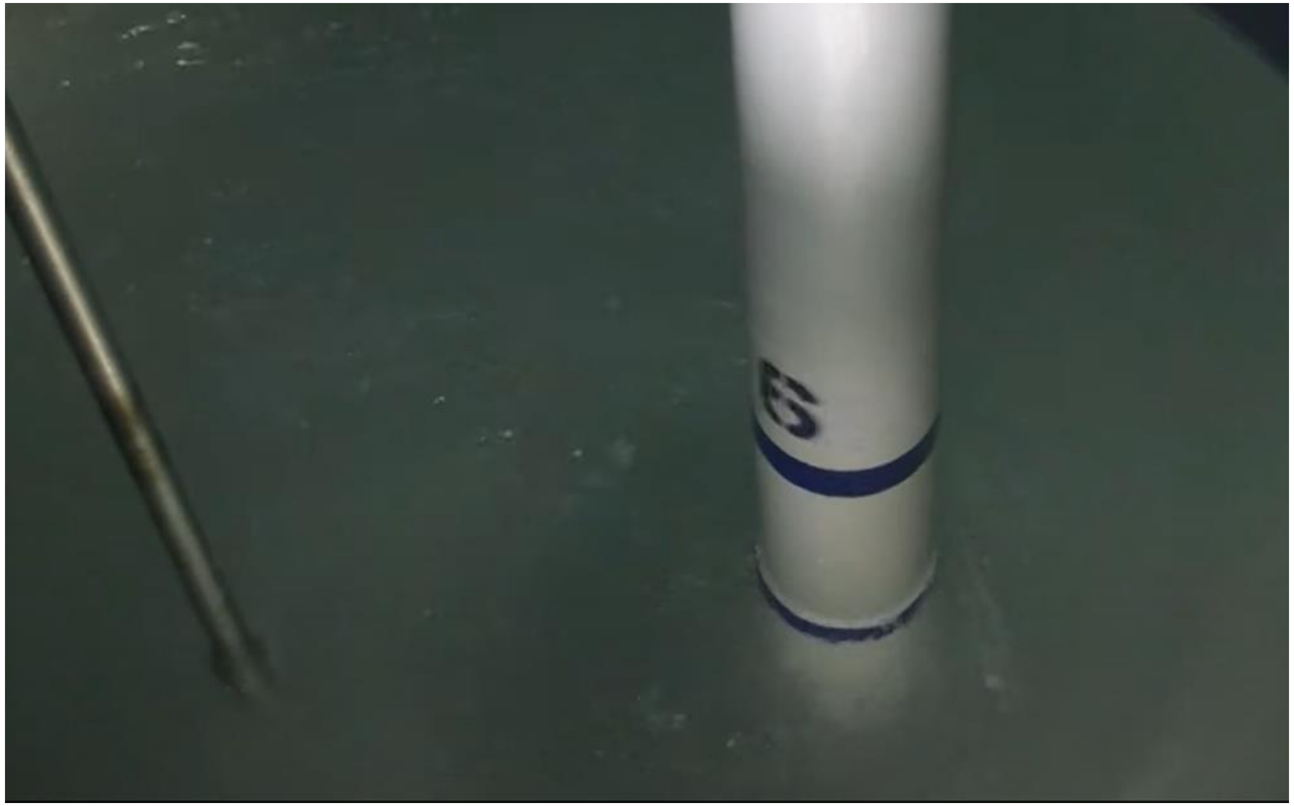
CNCs: Quench, Bleach & Neutralize



- Quench
  - Dilute into approx. 1200L
  - Additional rinse water, approx. 300L
- Bleach
  - While acidic, add 1 kg $NaClO_2$
  - Stir 30-60 minutes
- Neutralize
  - Add 8-10 wt% NaOH to neutral pH

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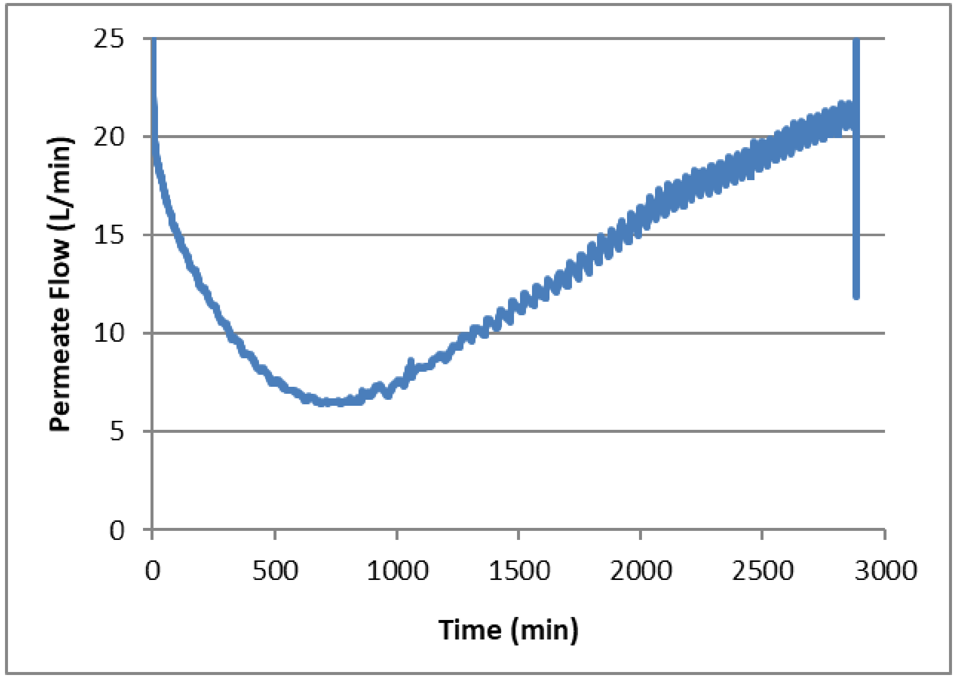
CNCs: Ultrafiltration for Purification



- Three A19 modules: 3.66 m, 12 mm tubes
  - 7.5 m^2 filtration area
  - 200 kDa MWCO
- Retentate circulation: 675 L/min
- Approximately 1 wt% CNCs in suspension
- Terminate at permeate conductivity 100 uS/cm

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CNCs: Clarification and Concentration

- Removing less than 1% as rejects
- 3850 G
- 20 L/min, approximately 4 min retention time

- Product concentration to 10 wt% CNCs
- Permeate flow drops dramatically with concentration of CNCs (<1 L/min)
- Use circulation pump as viscometer
  - Terminate at retentate flow 325 L/min
  - "Flush-on-the-fly" rinse

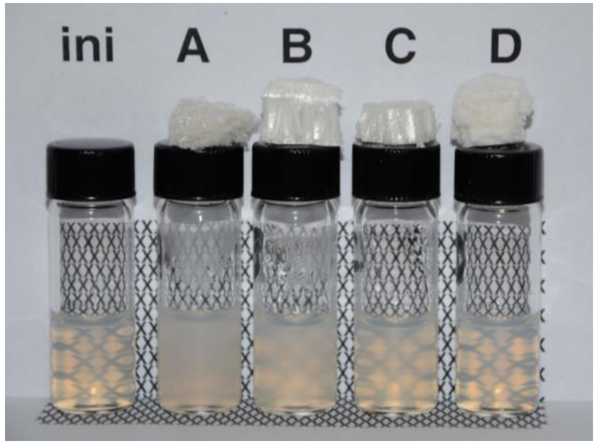
CNCs: Acid Recovery

- Decant approximately 8% H2SO4 from CNC production run
- Use membranes to separate to pass acid while retaining sugars
- Distill 8% acid to 64 wt % acid under vacuum
  80C at 6.5 kPa

- Recovered 64 wt% H_2SO_4
- Recovered 64 wt% H_2SO_4 boiled at 150°C (atm) for 4 hrs
- Reaction acid concentrated on rotavap: 50°C, water aspirator
- Boiled 64 wt% H_2SO_4 reaction acid (with sugars ~1%).

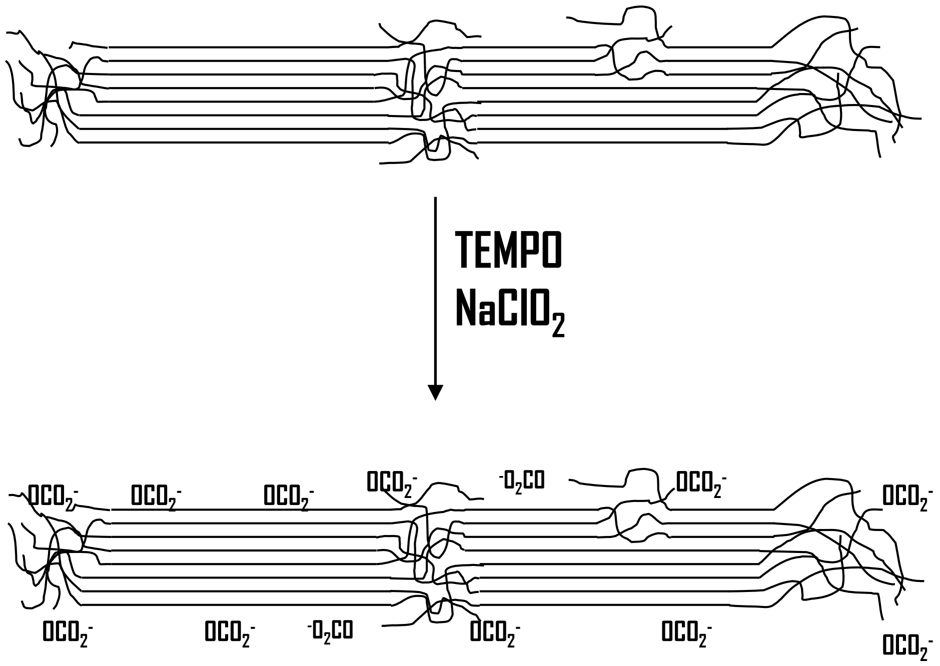
CNCs: Freeze Drying

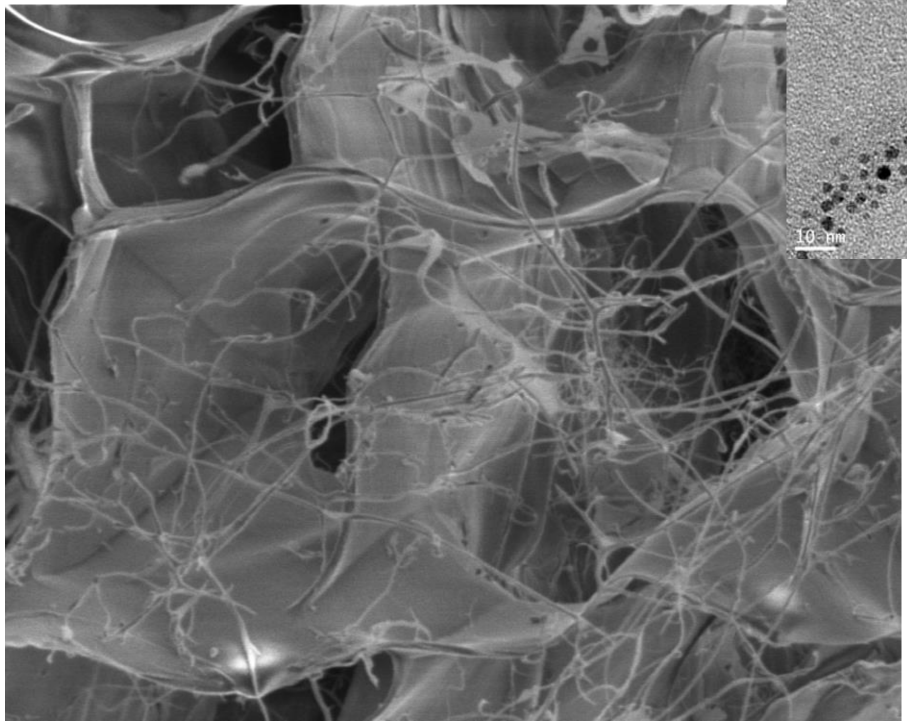
- Freeze drying is admittedly slow and expensing
  - 100L nanocellulose suspension in 2-3 weeks
- Manner with which the suspension is frozen is important
  - Nanocellulose concentrates between ice crystals
- Freeze to "soft-serve" using an ice cream machine with addition of 8 vol% tert-butyl alcohol
- t-BuOH recovered with distillation, azeotrope ~85 vol%

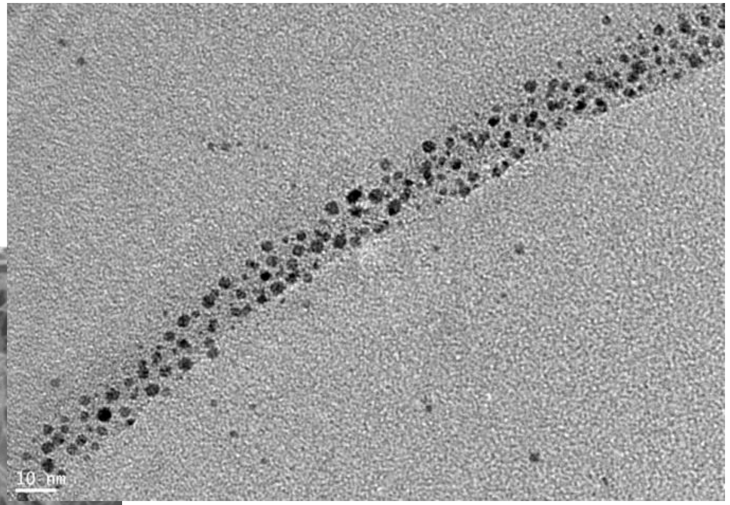


- Never-dried CNC suspension
- Slow freeze
- Liquid Nitrogen freeze
- Ice cream freeze without t-BuOH, no mixing
- Ice cream freeze with t-BuOH and mixing

Cellulose Nanofibrils







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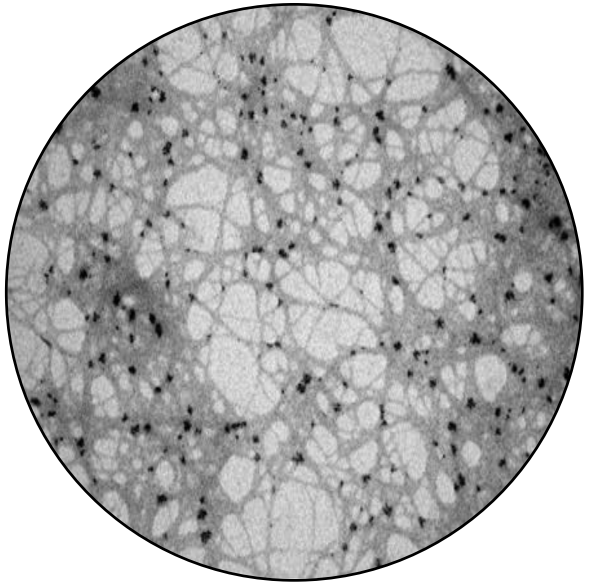
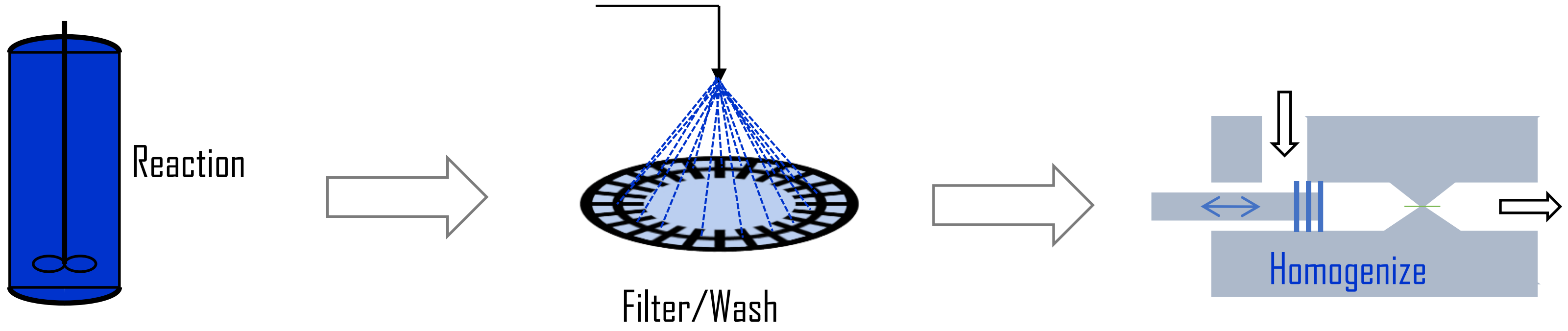
Preparation of Cellulose Nanofibrils (CNFs)





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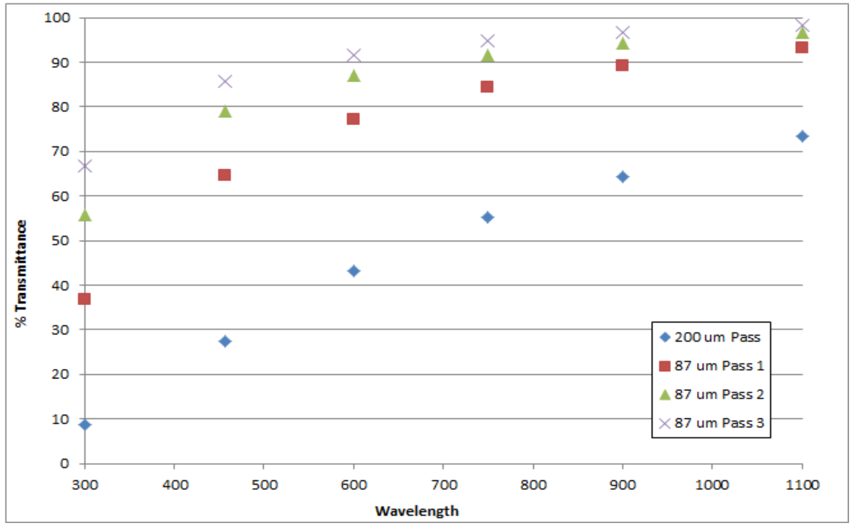
CNFs: Reaction

- Feedstock
  - Eucalyptus bleached kraft pulp from drylap
  - Acid wash and touch-up bleaching
- Reaction Conditions
  - TEMPO, NaBr catalysts
  - Hypochlorite terminal oxidant
  - Maintain pH 10 with alkali (CO_3^{2-}/HCO_3^- buffer)
  - Room temperature for 4 hours
  - Glass-lined steel reactors - 400L
  - Typically 2 kg/batch, literature recipe 4 kg/batch
- Filter and wash
  - Minimize mechanical shear
  - Swells further as salt is washed from pulp

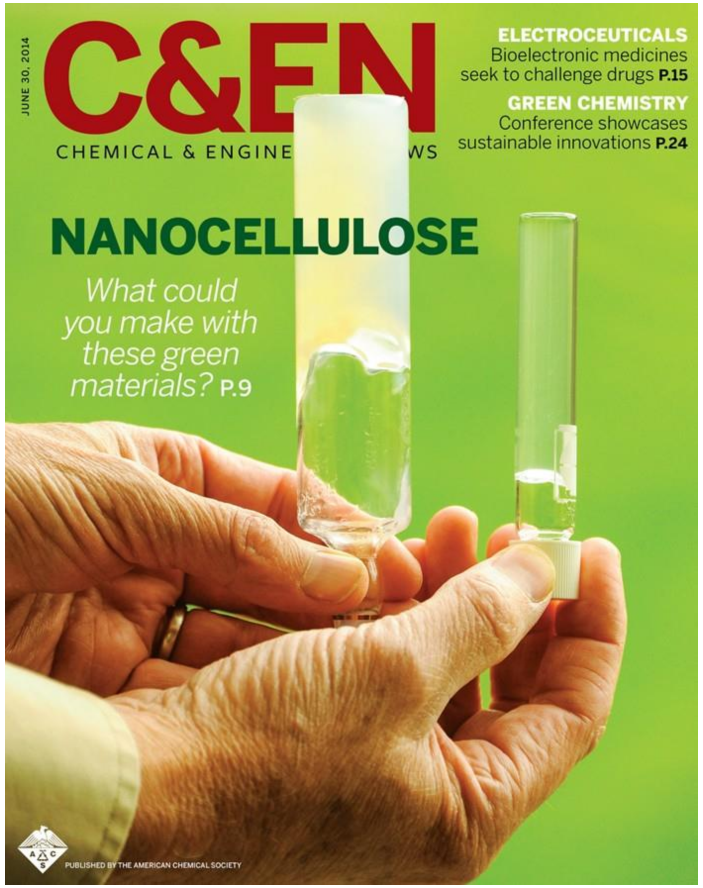
CNFs: Homoginization

- Four passes 800-900 bar, 250L/hour
- 1 wt % CNF suspension
- 5% easy to disperse, add'l material more and more recalcitrant
- Similar results to microfluidizer



How do we improve from here?

- Ultrafiltration bottleneck
  - Leap-frog with centrifuge
    - High shear causes temporary dispersion
    - Soft solids make it difficult to operate decanter
  - Ultrafiltration filter agent
- Drying
  - 25-50 percent solids CNC, 10 percent CNF
  - Integrate by drying with end use products
  - Additives that are compatible with end-use products
  - How much energy to redisperse?
    - Do we need a "perfect" (re)dispersion?
- Preservation in wet storage
  - Additives
  - Pasteurization



FPL – R&D pilot-scale, Boutique Production

- Continue to source material
  - Distribution through University of Maine
  - Supply FPL research
  - Supply pilot demonstrations (US Endowment for Forestry and Communities, Inc.)
- Optimization with end-use products
- Novel sources of material for nanocellulose
  - Wood species variation
  - Other plant (animal) cellulose sources
    - Cotton, Algae, Tunicate, etc.
  - Waste cellulose sources
    - Mill sludge, recycle waste, forest slash, farm crop waste, etc.
- Integral part of forest biorefinery