NRC·CNRC

Biomass valorization for a sustainable bio-economy – biobased products innovation at NRC

Dr. Anthony Anyia

July 24, 2018

The National Research Council of Canada

Mandates:

- Federal policy mandates
- Advancing knowledge
- Business innovation

Resources:

- 3,700 personnel
- $1.1B (CDN) in annual expenditure
- 178 buildings in 72 locations



Support for research

102 YEAR HISTORY



MULTI-DISCIPLINARY RESEARCH FACILITIES AND STAFF









NRC works through collaboration

Last year we worked with:

7,500 small firms (IRAP)

1,000 clients (research)

152 hospitals

72 colleges and universities

36 countries



Areas of Research and Development (R&D)

NRC Division	Research Centre
Life Sciences	Aquatic and Crop Resource Development
	Human Health Therapeutics
	Medical Devices
Emerging Technologies	Digital Technologies
	Component Technologies
	Security and Disruptive Technologies
	Herzberg Astronomy and Astrophysics
	Metrology
	Nanotechnology

NRC Division	Research Centre
Transportation and Manufacturing	Aerospace
	Automotive and Surface Transportation
Engineering	Construction
	Energy, Mining and Environment
	Ocean, Coastal and River Engineering

Aquatic and Crop Resource Development

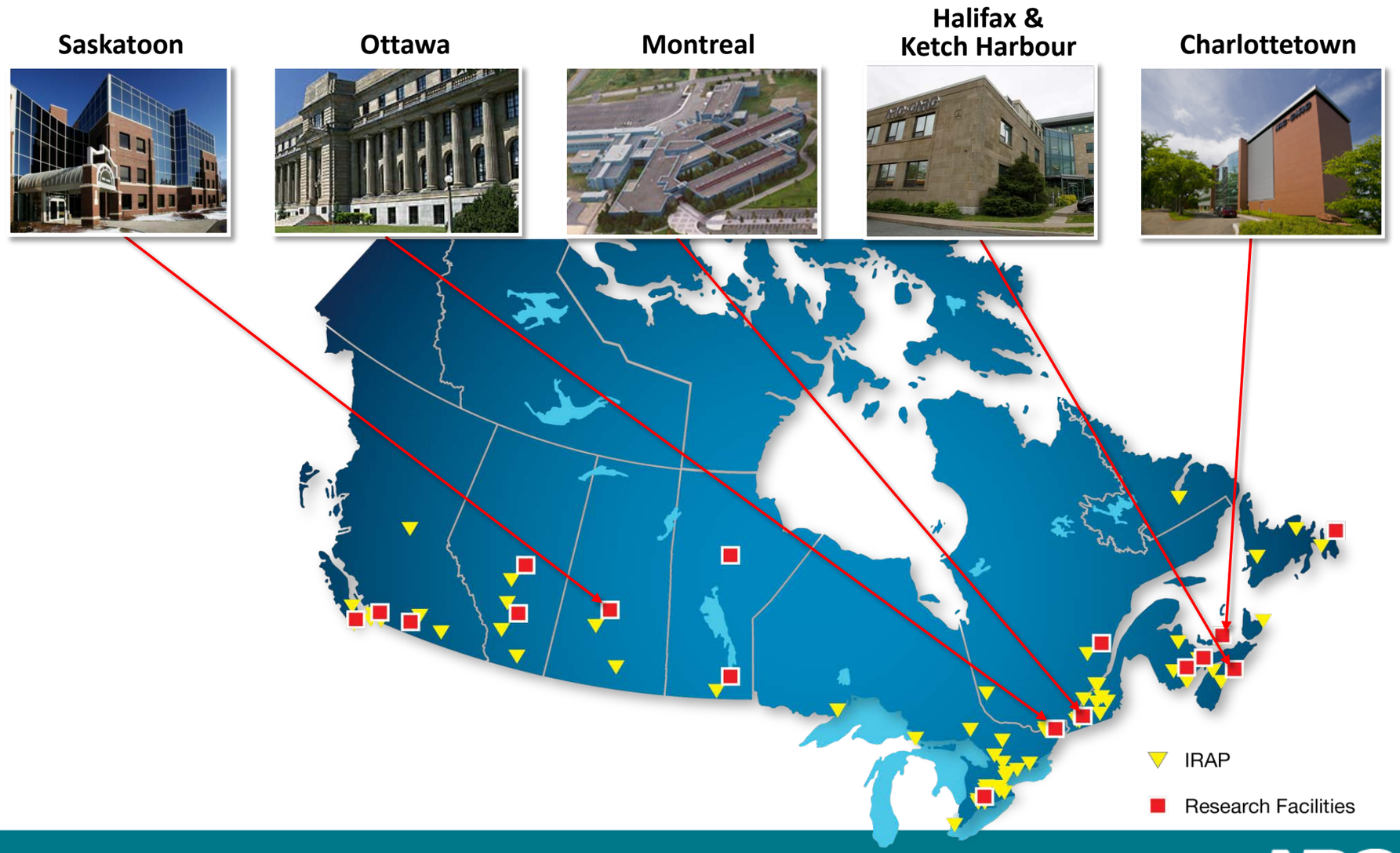
To make Canada a world leader in the sustainable transformation of bio-based resources into economic value







National Research Council Canada
ACRD Research Facilities



Quick Facts about ACRD

- 200+ dedicated, scientific resources
- Innovative tools and expertise to work with partners and clients in bio-based industries
- 300-400 agreements signed each year with third parties
  - Includes CDA, MTAs, Technical/Research Service Agreements and Collaboration agreements
  - Work with SMEs, MNEs, academia and other government departments





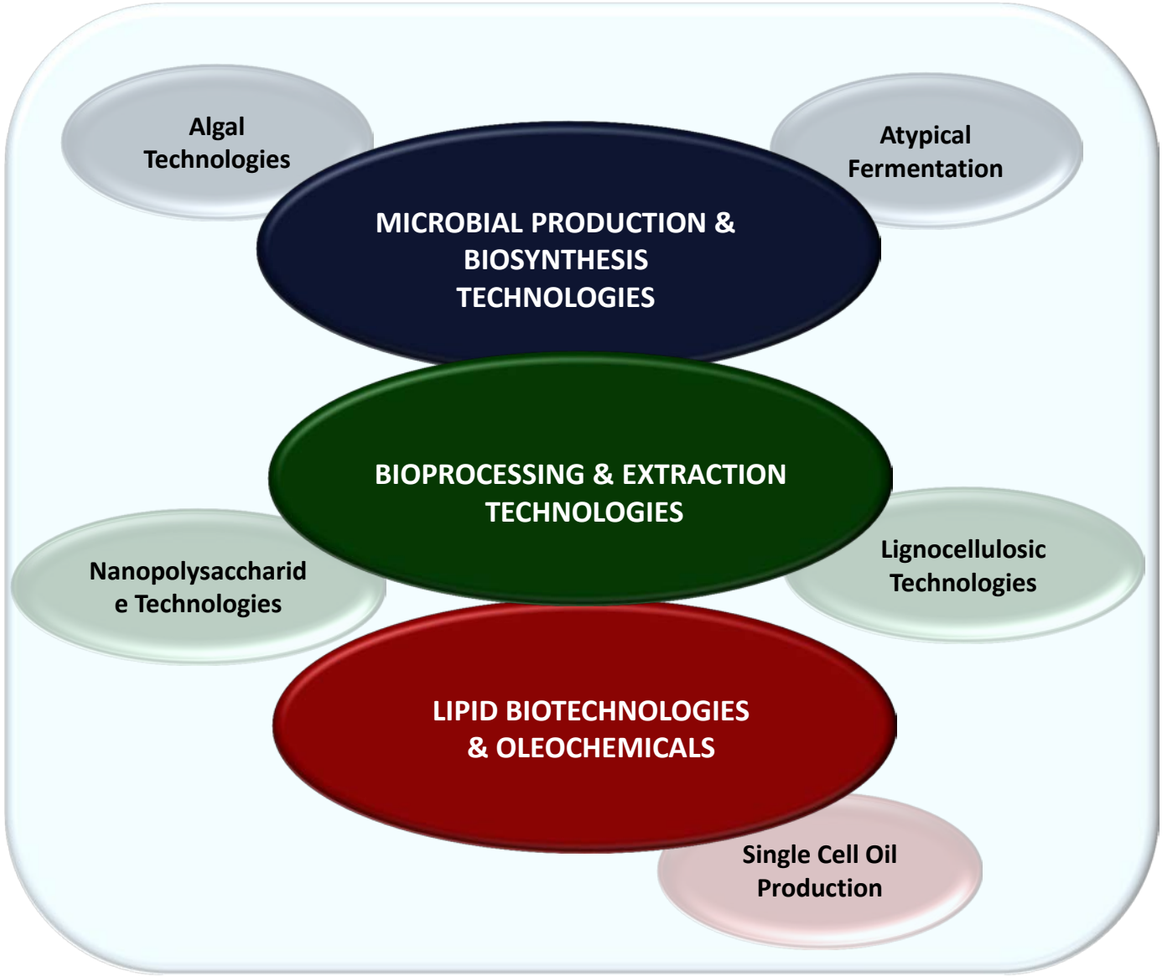


Industrial Biotechnology Program (IBP)

Building on the success of the Bio-based Specialty Chemicals Program

Target Outcomes

- Accelerate the commercial readiness of Canadian bio-based firms:
  - Reducing the costs of technologies
  - Diversifying market applications
  - Market acceptance of products
- Technology advancement
  - Biological systems to **convert** renewable feedstocks to high value products
  - Biological and chemical processes to **obtain** high value products from biomass
  - Terrestrial and marine biomass



Algae Research





- Cultivation of marine and fresh water microalgae, seaweeds, and other marine organisms.
- A range of photobioreactors, fermentation bioreactors, and bioprocessing facilities
- Processing and analytical laboratories
- Extensive natural product chemistry, analytical chemistry
- Bioactive characterization and assay capabilities adapted to marine biomass
- Feed formulation from microalgae
- Food, NHP ingredients from micro and macro algae
- Industrial products from algae; bio plastics, fuel, etc



NRC’s Current Algae Biorefinery

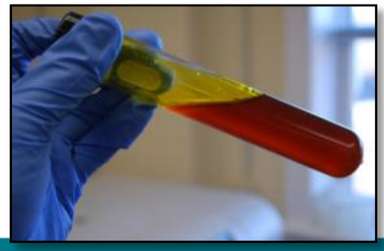




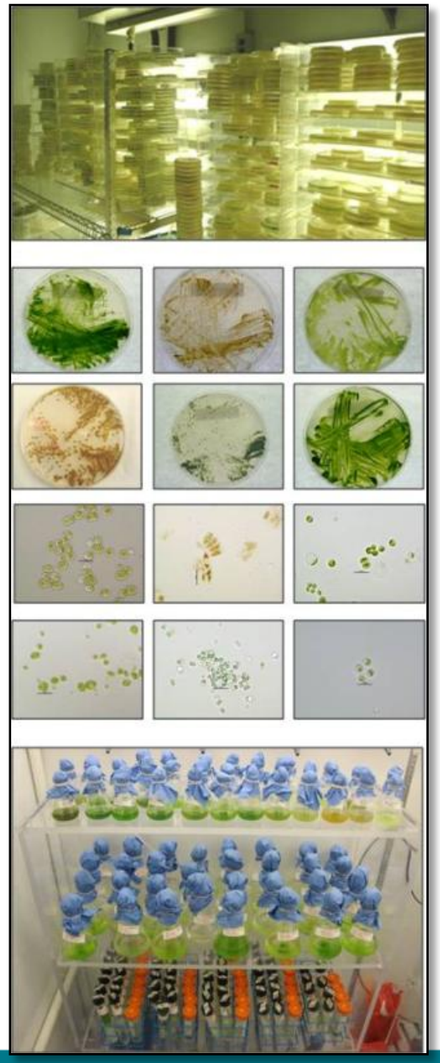








NRC’s Algal Strain Library



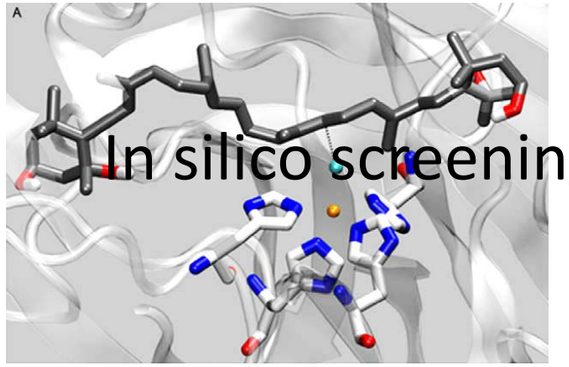






Biocatalysis & Enzyme-mediated Processing

- Ready-to-use enzyme library
  - More than 20 proprietary enzymes for plant cell wall degradation, fibre treatment, value-added bioproducts such as lactones, antioxidants, lactic acid, biopolymers etc.
- Protein engineering and directed evolution to improve:
  - Enantioselectivity and substrate selectivity, catalytic activity, thermostability, organic solvent stability, pH tolerance, etc..
- Validation of engineered protein products
  - In vitro testing, structural analysis
- Non-aqueous enzymology
- Hydrolase-catalysed condensations
- Natural fibers retting and characterization



In silico screening

Natural Fibres – Enzyme-mediated Processing

Flax



- Production varies from annually from 400,000 to 800,000 hectares Canadian Prairies.
- Production is limited by straw management issues – slow decomposition
- Straw is often burned or baled for processing
- Common uses - animal bedding, mulch, cigarette papers, bio-fuel, composites and textiles.

Industrial Hemp



- ~ 55,000 hectares licenced production in Canada (2017)
- Long-fibre used for textiles, geotextiles, paper products, bio-composites, etc.
- Short fibres used for Hemcrete®
- industrial absorbents, insulation,
- animal bedding, mulch, biofuels
- Chemicals, etc.



Natural Fibre - processing and characterization



Agri-Fibres Production

Cultivation
Harvesting
Field retting

Retting Protocol

Primary transformation
Decortication
Fibre opening

*Refining **bio** treatment*
(NRC technology)

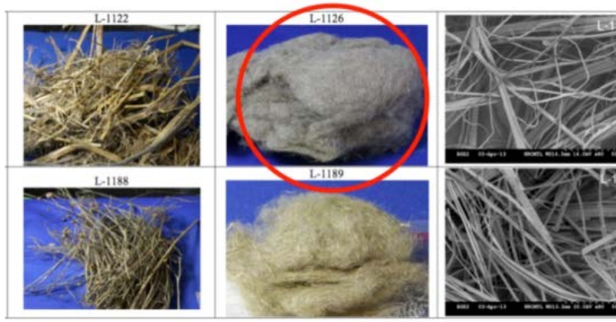
Secondary transformation
Mats & yarn/fabrics

Biocomposites

Characterization
(properties, attributes)
NIR, macro/micro-photography
SEM, FTIR, Color, Diameter, …
Strength, Elongation

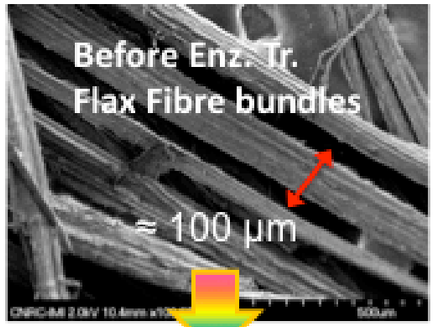
Data bank
(1500+ samples)

Fiber Datasheets



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Production of Enzyme-treated fibres *via* NRC-Linase

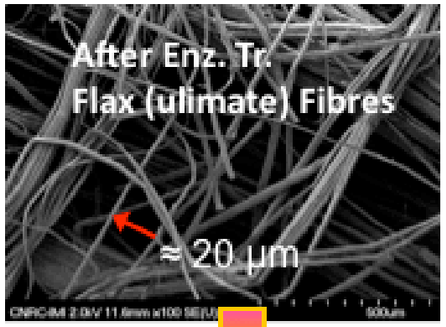


NIR Cellulose = 60 %

Fibre diameter 100 – 120 µm (≈ 80%)

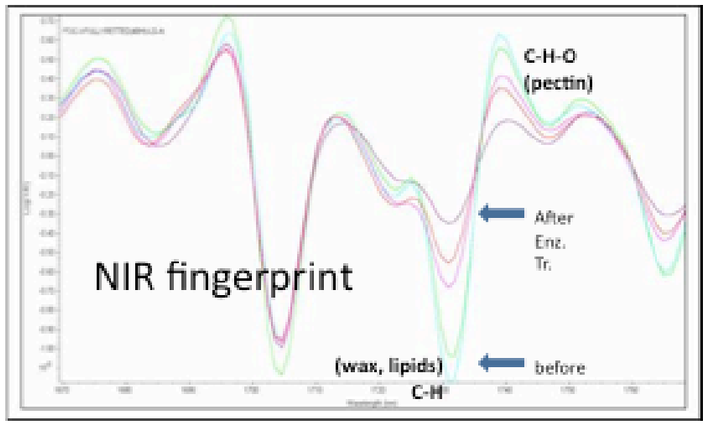
NIR Cellulose = 78 %

Fibre diameter 15 – 30 µm (≈ 75%)

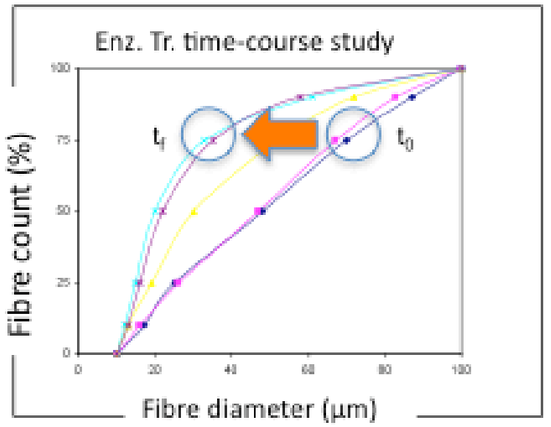


Mechanically decorticated **unretted** fibres (from oilseed flax). Numerous fibre bundles… Coarse fibres (80% of the fibres show an average diameter of 100 to 120 µm), as determined using the image analysis software FibreShape; and the cellulose content of these fibres is 60%, as determined by NIR.

Fully enzyme-retted fibres.
Fibres are significantly different from original material; numerous unitary fibres can be observed; and their surface is very clean and smooth. These fibres show a silver-like color.



Ready for Biocomposite applications



Enzyme-Assisted Fibre Cottonization Process



(12) **United States Patent**
Sung et al.

(10) **Patent No.: US 8,603,802 B2**
(45) **Date of Patent: Dec. 10, 2013**

(54) **ENZYMATIC PREPARATION OF PLANT FIBERS**

(75) Inventors: **Wing L. Sung**, Ottawa (CA); **Mark Wood**, Ottawa (CA); **Fang Huang**, Ottawa (CA)

(73) Assignee: **National Research Council of Canada**, Ottawa, Ontario (CA)

(57) **ABSTRACT**

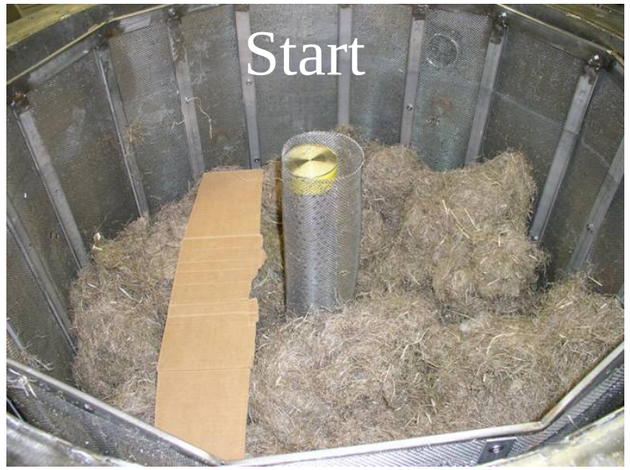
A method of extracting fibers from decorticated plant bast skin involves pre-treating decorticated plant bast skin of a fiber plant with an aqueous solution containing trisodium citrate having a pH in a range of about 8-14 at a temperature of about 90° C. or less; and subsequently treating recovered fibers with a protease at alkaline pH.

Enzyme-Assisted Fibre Cottonization Process

The process consists of a mild chemical pre-treatment followed by an enzymatic treatment and then a natural bleaching step. The process takes between eight and ten hours to complete. After drying, the fibers are ready for carding and spinning into yarn.



Enzyme-Assisted Fibre Cottonization Process at a Glance













Enzyme-Assisted Fibre Cottonization - process scale-up



These are tanks capable of holding 10000 liters of solution and 200 kilos of fiber.



Enzyme-Assisted Fibre Cottonization

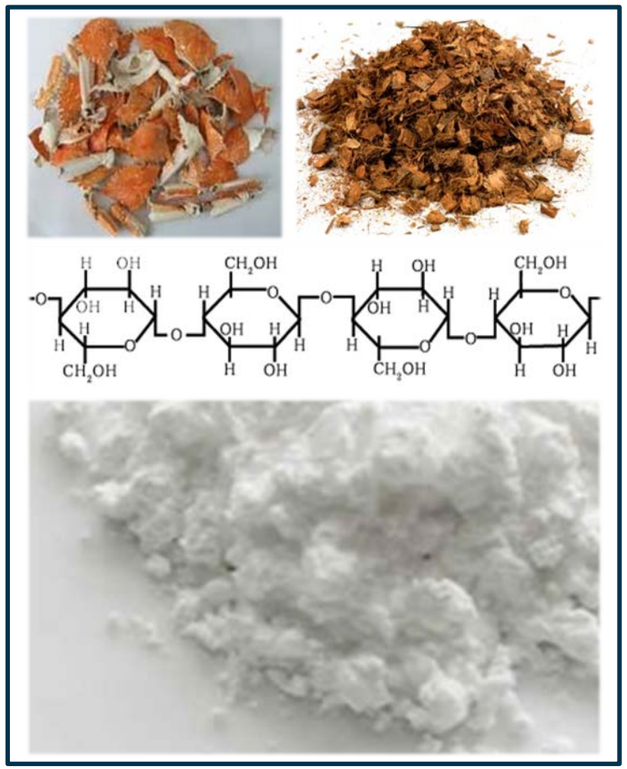
Areas of applications:

Advanced products: hemp garments, curtains, carpet and upholstery, automobile panels, paper, windmill blade, reinforcement belt in tires...



Polysaccharide Nanotechnologies

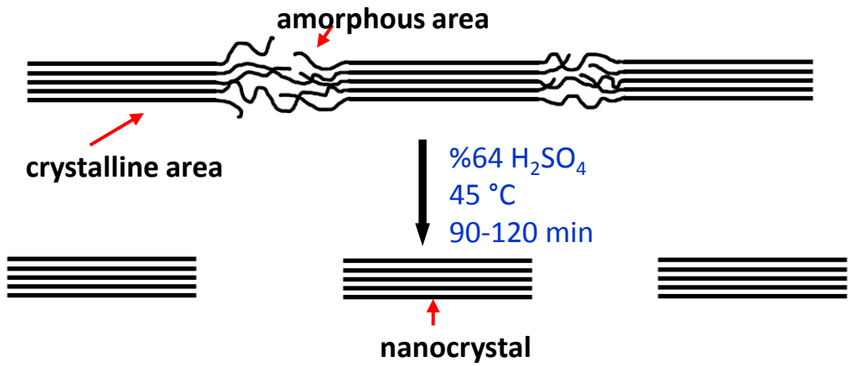
Production, characterization and commercial application of polysaccharide (e.g. chitin, cellulose) nanoparticles from diverse agricultural, forestry and marine biomasses

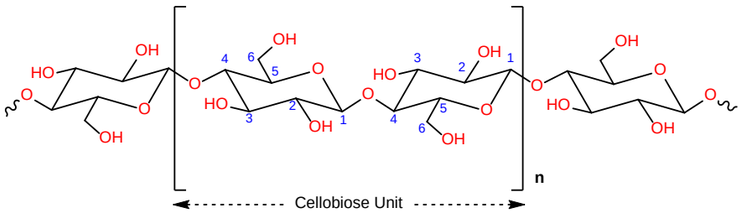


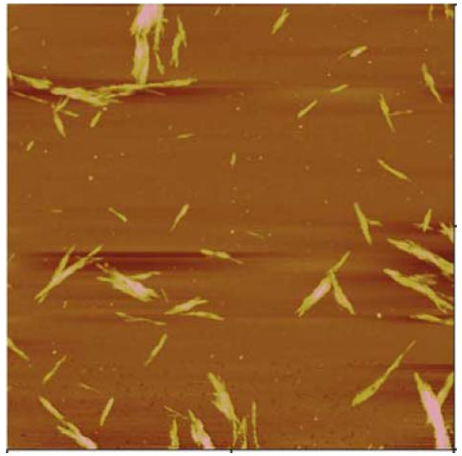
- Valorization of food processing and lignocellulosic biomass into higher value material with applications in
  - ✓ Encapsulation of agricultural products: soil amendments, pesticides, fertilizers, seed coatings
  - ✓ Food and feed additives: thickeners, preservatives, antimicrobial agents
  - ✓ Smart and innovative packaging solutions
  - ✓ Water remediation: wastewater flocculation, metal ion chelation, protein recovery

Polysaccharide Nanotechnologies - Cellulose nanocrystals (CNCs)

- CNC are elongated, rigid and rod-like or whisker-shaped particles with a rectangular cross-section.
- CNCs are typically made from bleached wood pulp through the H_2SO_4 process
- CNC has unique properties;
  - High aspect ratio
  - High tensile strength
  - Superior thermal & mechanical properties
  - Optical properties
  - Biodegradable
  - Amenable to physical & chemical modification







NRC has developed and patented an alternative process for making CNCs



(12) **United States Patent**
Leung et al.

(10) **Patent No.: US 8,900,706 B2**
(45) **Date of Patent: Dec. 2, 2014**

(54) **CELLULOSE NANOCRYSTALS FROM RENEWABLE BIOMASS**

(75) Inventors: **Chi Woon Leung**, Westmount (CA); **John H. T. Luong**, Mount Royal (CA); **Sabahudin Hrapovic**, Laval (CA); **Edmond Lam**, Westmount (CA); **Yali Liu**, Pointe Claire (CA); **Keith B. Male**, Kirkland (CA); **Khaled Mahmoud**, St-Laurent (CA); **Denis Rho**, Montreal (CA)

(73) Assignee: **National Research Council of Canada**, Ottawa, Ontario (CA)

(57) **ABSTRACT**

A process for producing cellulose nanocrystals (CNCs) involves providing a cellulosic material, contacting the cellulosic material with an inorganic persulfate at an elevated temperature to produce CNCs, and recovering the CNCs. The process permits one-step production of CNCs from vegetative biomasses such as flax and hemp. Cellulose nanocrystals produced by the process with carboxylic groups are more uniform and have higher aspect ratios than CNCs produced by prior art processes.

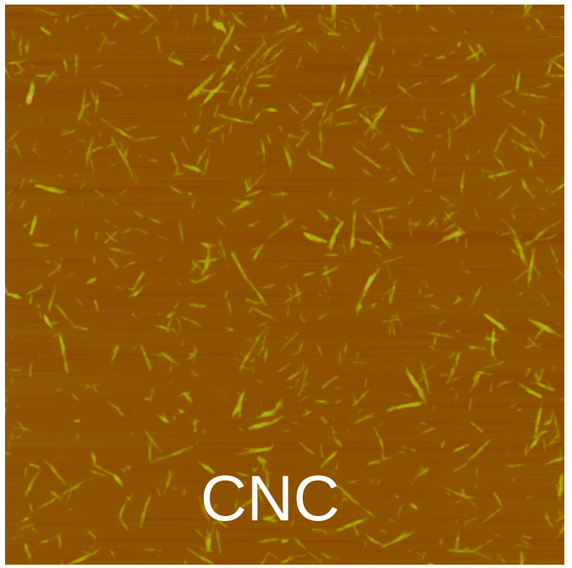
Production of CNC using ammonium persulfate (APS)



plant fibers

1 M APS

60 °C, 16 h





Non-flocculate stable suspension

- Green process – Green process- APS has no long term toxicity, spent APS can be regenerated electrochemically
- APS can be regenerated electrochemically
- No pretreatment necessary
- High yield – 30% from fibers, 35 – 60% from wood pulp
- CNC has surface carboxylate groups, size ≈ 150 × 5 nm

Small **2011**, *7*, 302
US patent granted

Crystallinity Index and Crystal Dimensions

cellulose type	yield (%)	CRI (%) before treatment	CRI (%) after treatment	length (nm)	diameter (nm)
Flax	28	69	75	144 ± 5	3.8 ± 0.1
Flax shives	22	48	64	296 ± 16	5.1 ± 0.1
Hemp	36	56	73	148 ± 4	5.8 ± 0.1
Triticale	31	61	73	134 ± 5	4.2 ± 0.1
MCC	84	79	83	128 ± 5	5.5 ± 0.1
Whatman CF1	81	91	91	121 ± 5	6.7 ± 0.3
Wood Pulp	46	73	81	124 ± 6	6.0 ± 0.2
Bacterial cellulose	14	59	70	88 ± 5	6.5 ± 0.2
Cardboard	67	67	76	185 ± 6	7.0 ± 0.1

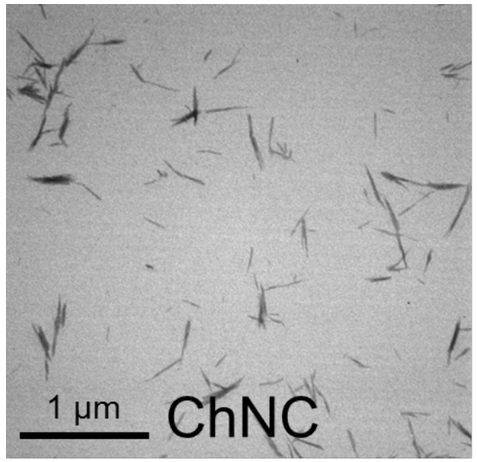
- Crystallinity Index (CRI) increase up to ~20%

Chitin Nanocrystal (ChNC) and Chitosan Nanocrystal (ChsNC)

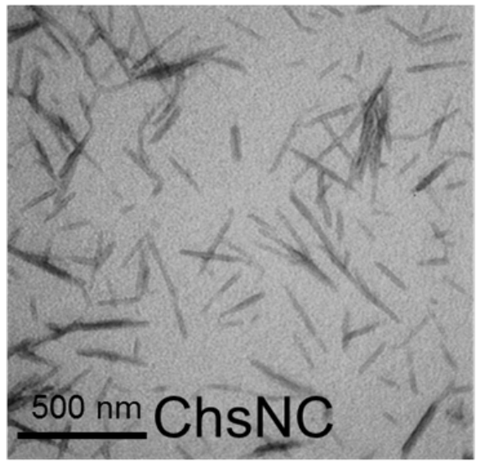


WO/2015/070346

APS



NaOH



- Chitin is a polymer of N-acetylglucosamine – major sources are crustaceans such as shrimps and crabs
- Deacetylation of ChNC with NaOH to yield ChsNC
- ChNC and ChsNC has average dimensions ≈ 130 nm × 4 nm
- Surface carboxylic acid and amino groups

Applications of Chitin and Chitosan

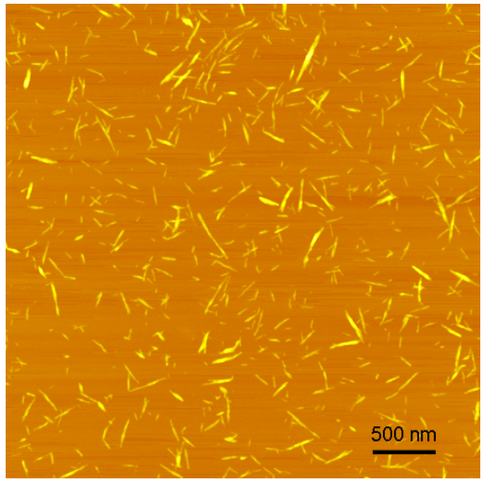
Uses	Compounds
Cationic sludge dewatering and flocculating agents for polluted wastewaters	Chitosan
Recovery of metal ions and proteins in aqueous waste solutions	Chitosan
Agricultural materials (e.g., plant seed coating, fertilizer)	Chitin and chitosan
Food additives	Chitin and chitosan
Feed additives for pets, fishes, and animals	Chitin and chitosan
Food processing (e.g., in sugar refining)	Chitosan
Hypocholesterolemic agents	Chitosan
Dressing materials for the burns and skin lesions of humans and animals and for plant tissue wounds	Chitin and chitosan
Biomedical materials (e.g., absorbable suture)	Chitin, *N*-acylchitosans
Blood anticoagulant materials (e.g., heparinoids)	Sulfated chitin
Blood antithrombogenic materials	*N*-Hexanoyl and *N*-octanoyl derivatives
Hemostatic materials	Chitosan
Cosmetic ingredients for hair and skin cares	Chitosan, CM-chitin, HP-chitin
Textile and woven fabrics	Chitin, chitosan, chitin xanthate
Paints and dyeing and weaving	Chitosan
Natural thickeners	Chitosan
Papers, films, sponge materials	Chitin, chitosan, *N*-acylchitosan
Chromatographic and immobilizing media	Chitin, chitosan, *N*-acylchitosan, *N*-alkylidenechitosan
Analytical reagents (e.g., colloid titration and enzyme substrates)	Chitosan, HP-chitosan, HP-chitin, CM-chitin, CM-chitosan, *N*-acetylchitosan, D-glucosamine, *N*-acetyl-D-glucosamine, chitin and chitosan oligosaccharides

Nanocrystals of chitin and chitosan may have better performance in these applications due to their small size, high surface area and dispersibility!

Scale up production







- Pilot scale production lines were set up in-house using 200 L and 1000 L reactors to demonstrate the scalability of the process
- 120 kg of CNC produced

Nano- Polysaccharide *- Application Examples*

- ✓ **Aerogels** (as strength filler – insulation materials)
- ✓ **Packaging** (food and consumer goods)
- ✓ Hydrogels
- ✓ **Paints, varnishes, coatings** (abrasive resistance)
- ✓ Adhesives
- ✓ Films
- ✓ Flexible displays
- ✓ Optical devices

- ✓ **Composites** (reinforcement material in building & automobile apps)
- ✓ Environmental remediation (waste water treatment)
- ✓ Films (birefringence properties)
- ✓ **Antimicrobial coatings** (chitosan nanocrystals)
- ✓ Health and personal care (cosmetics & pharmaceutical)
- ✓ **Encapsulation** (pesticides, drugs, enzymes)

How Do We Work with Collaborators & Clients?

There are many ways to work with NRC:

- ‘One-off’ contracts for technical, testing and consulting services
- Joint technology development projects between a firm and NRC
- Large-scale collaborative R&TD projects with multiple partners (companies, universities, other organizations)
- Licensing deals
- IRAP application for technology assistance (funding)

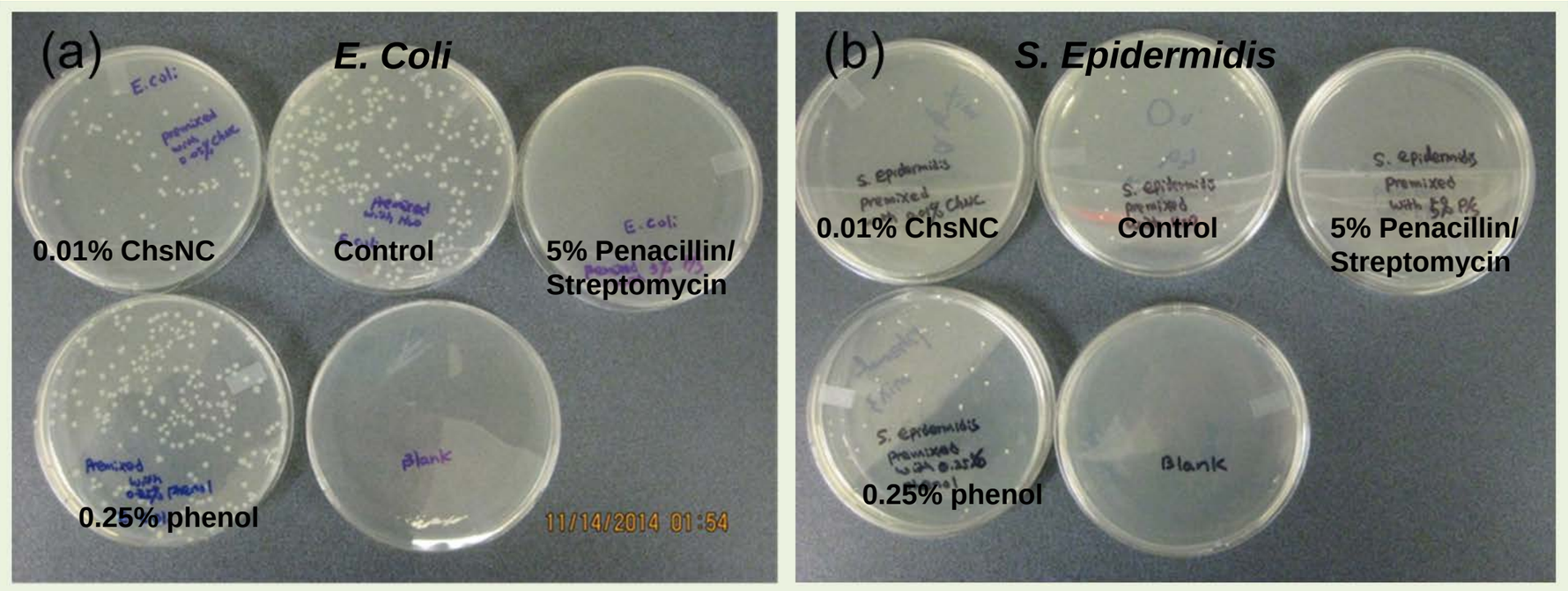
Our Researchers work with Client Relationship Leaders to develop customized solutions that address clients’ specific requirements

NRC·CNRC

Thank you

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Antimicrobial properties of ChsNC



- ChsNC was found to be effective against *E. coli* and *S. epidermidis*
- IC_{50} is 22 mg/L for *E. coli* and 3.7 mg/L for *S. epidermidis*
- Preliminary testing against periodontitis-causing bacteria (*A. actinomycetemcomitans* and *P. gingivalis*). Strong biocide effect observed at 1 mg/ml.