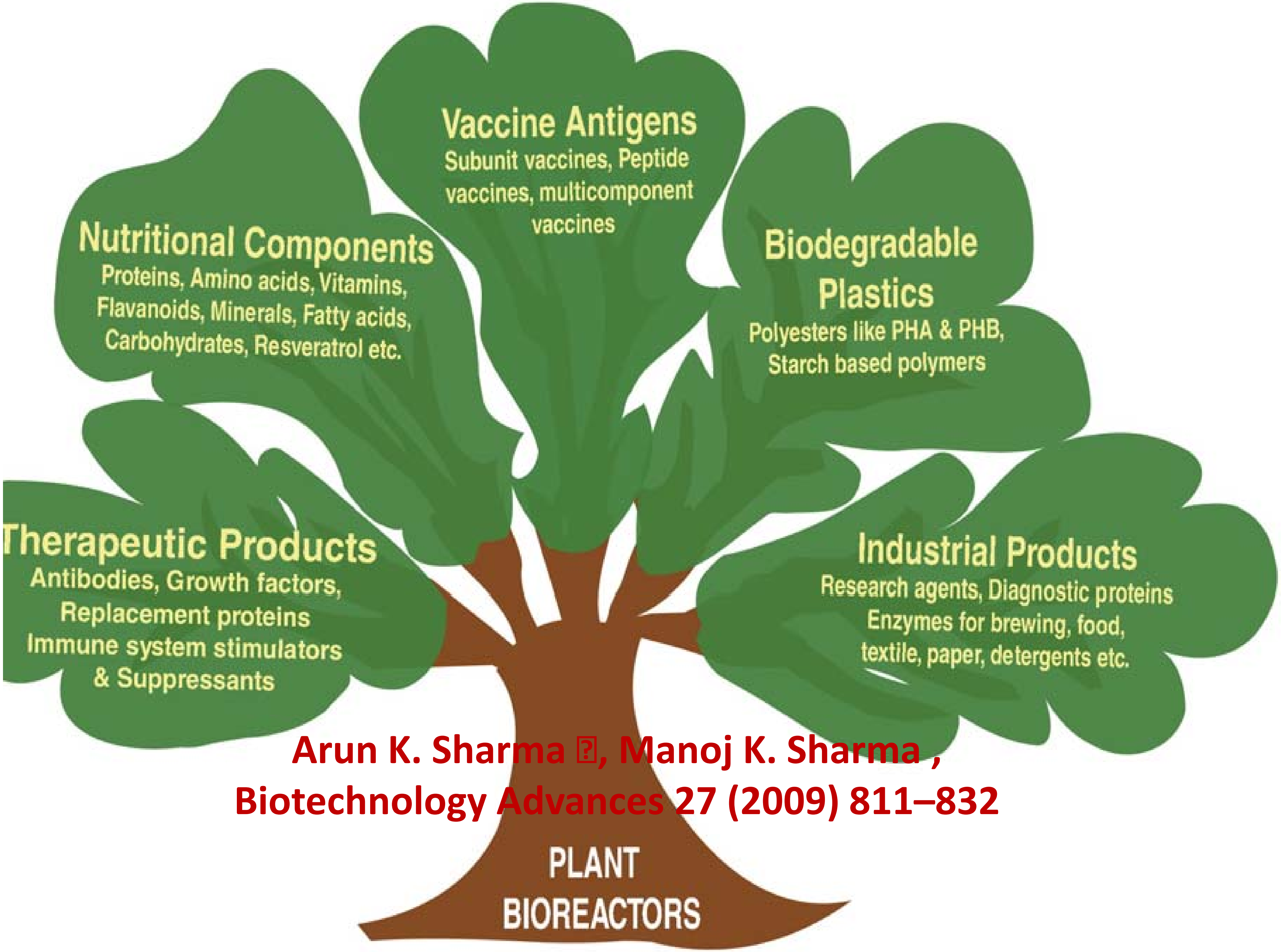

Arun K. Sharma, Manoj K. Sharma ,
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3rd International Workshop Advances in Cleaner Production

PRELIMINARY STUDIES ON THE PRODUCTION OF NANOFIBRILS OF CELLULOSE FROM NEVER DRIED COTTON,USING ECO-FRIENDLY ENZYMATIC HYDROLISIS AND HIGH ENERGY SONICATION

PATENTE DEPOSITADA

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Those who are inspired by a model other than Nature, a mistress above all masters, are laboring in vain. - Leonardo Da Vinci

An ecologically friendly method, to obtain cellulose nanofibrils, starting from Never Dried Cotton (NDC) is described, where cotton bowls are opened and maintained in water. NDC cotton exhibits a highly accessible structure and porosity, thus allowing a more efficient enzyme action and chemical treatments and derivatization. In this work, the conditions utilized to synthesize nano-fibrils from NDC were also tested on once dried cotton; the latter failed to produce nano-fibrils when submitted to the experimental conditions applied

WHY NEVER-DRIED?

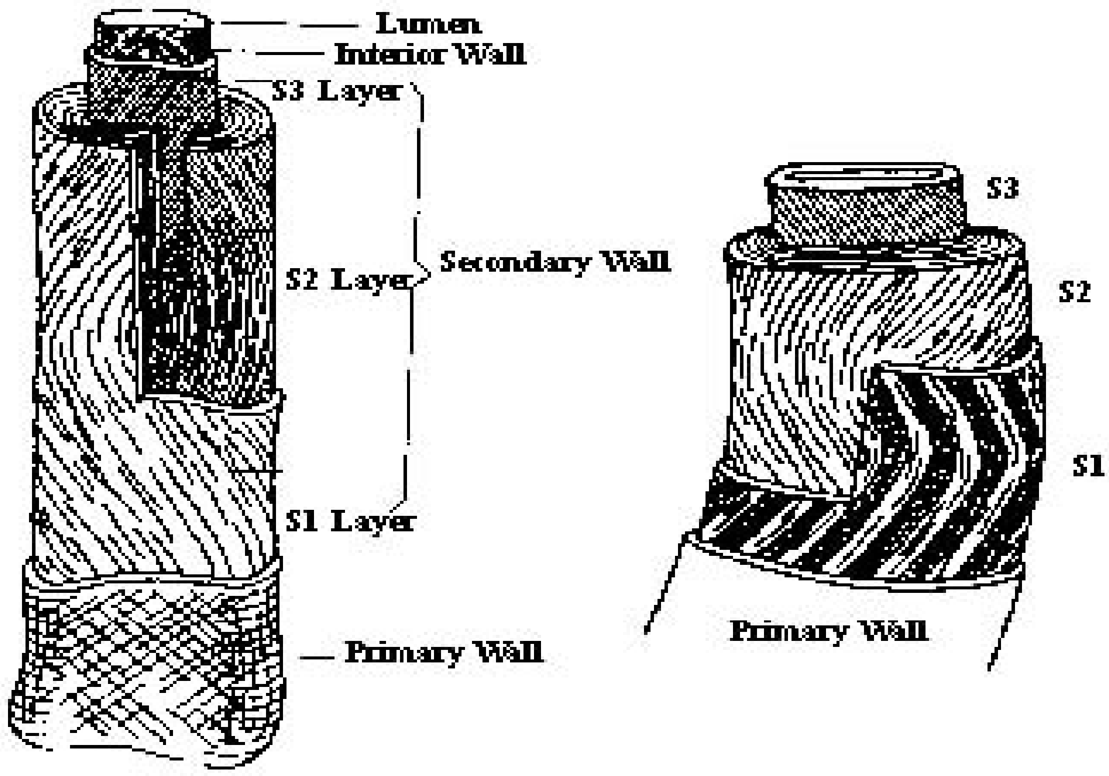
A first-drying of cotton fibers results in a structure characterized by a collapse of the tube-like NDC fiber structure , which change from a circular cross section to its typical "bean- like" cross section, with reduced accessibility and porosity, and lower water sorption capacity. Those changes are of the same nature as the well known *hornification* described in pulp and paper science studies, associated with irreversible reduced accessibility, which affects paper properties, and in general, the utilization of cellulose for utilization as materials or fuel (i.e. alcohol)

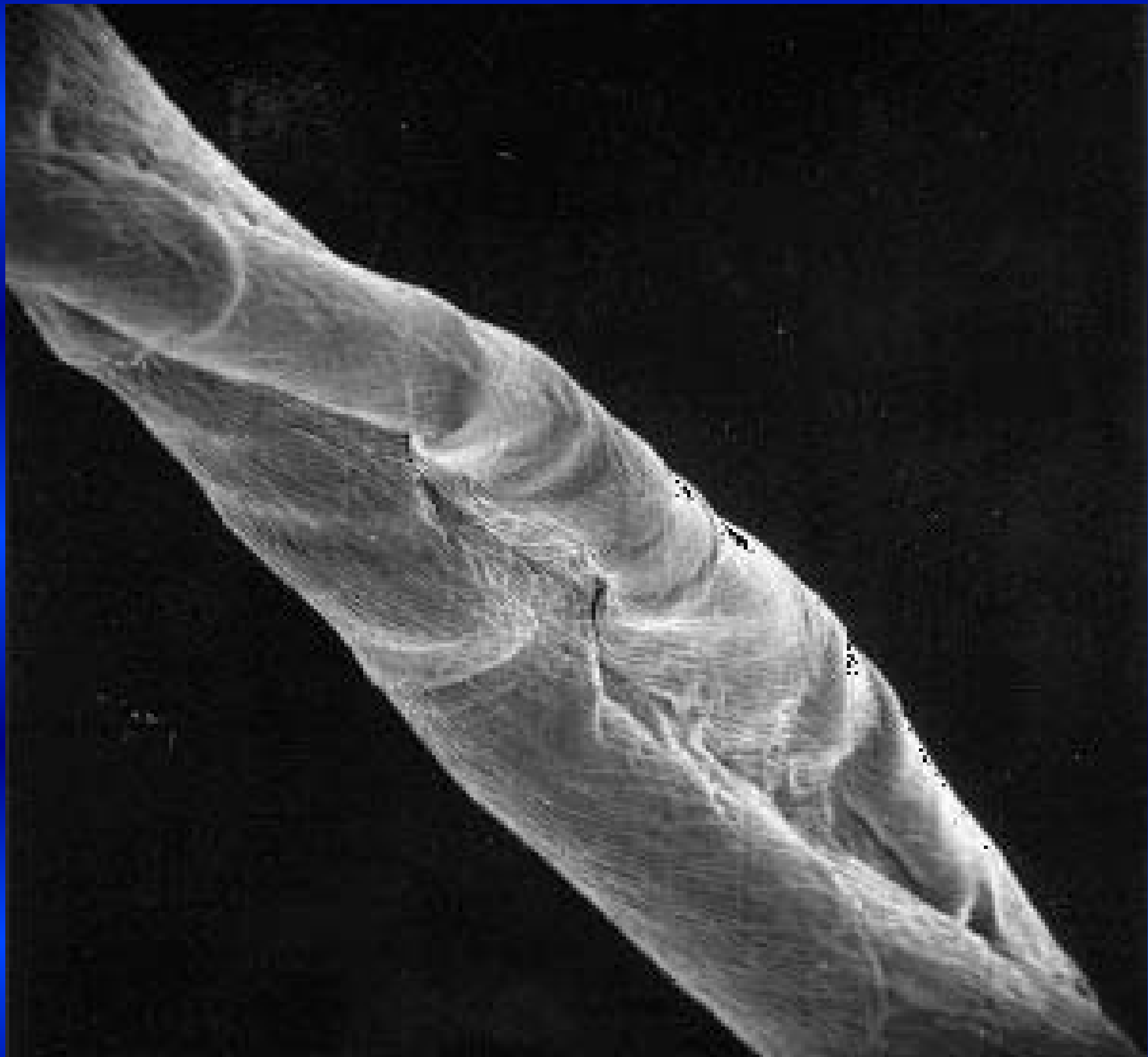
--Keeping cellulose materials in the never-dried state has important advantages: vapor saturated wood chips, for instance, require half the time of impregnation with sodium hydroxide solution compared to the once dried material

--Energy is required to dry pulps, but the drying process stiffens fibers, in a way that refining restores only a portion of the fiber original conformability.

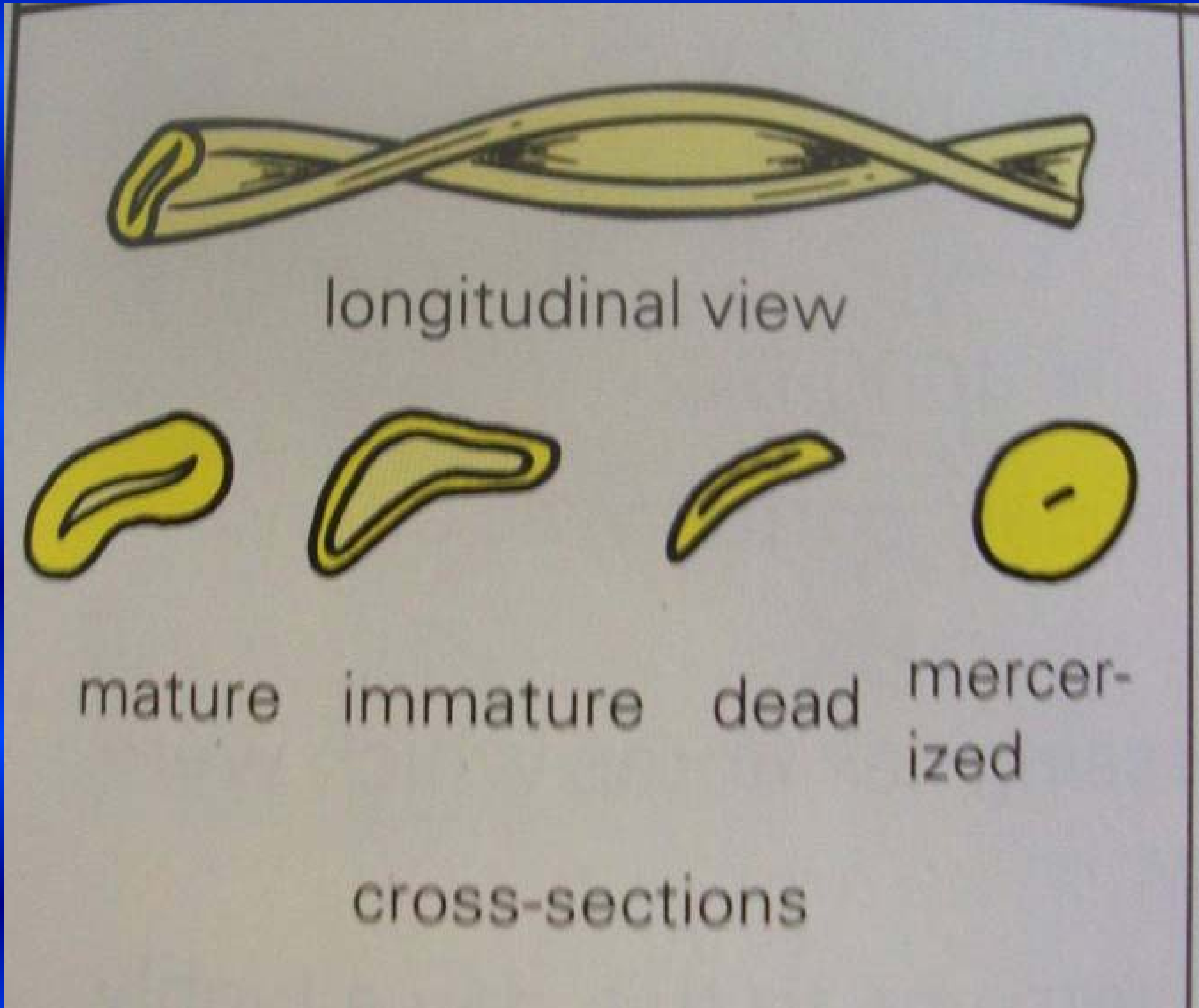
--Pulps should only be dried if storage, transport, or use of wet pulps is uneconomical or impractical. Drying is a critical process affecting the properties of cellulosic materials, and consequently affects negatively the efficiency of processes intended to modify and utilize lignocellulosic yield of biomass products, due to the reduced accessibility

ESTRUTURA DA FIBRA DE ALGODÃO -ANTES DE UMA PRIMEIRA SECAGEM





ONCE DRIED CROSS-
SECTION 70%
CRYSTALINITY


longitudinal view
mature
immature
dead
mercer-
ized
cross-sections

BIOFUELS AND MICROFIBRILS

ACESSIBILITY

The root causes of biomass recalcitrance to hydrolysis have been attributed to several factors: low substrate accessibility to enzymes, high crystallinity of cellulose, presence of hemicellulose, lignin, and other components, and high degree polymerization of cellulose chains.

Highly ordered hydrogen bonds and van der Waals forces among sugar chains in crystalline fibers result in high crystallinity index

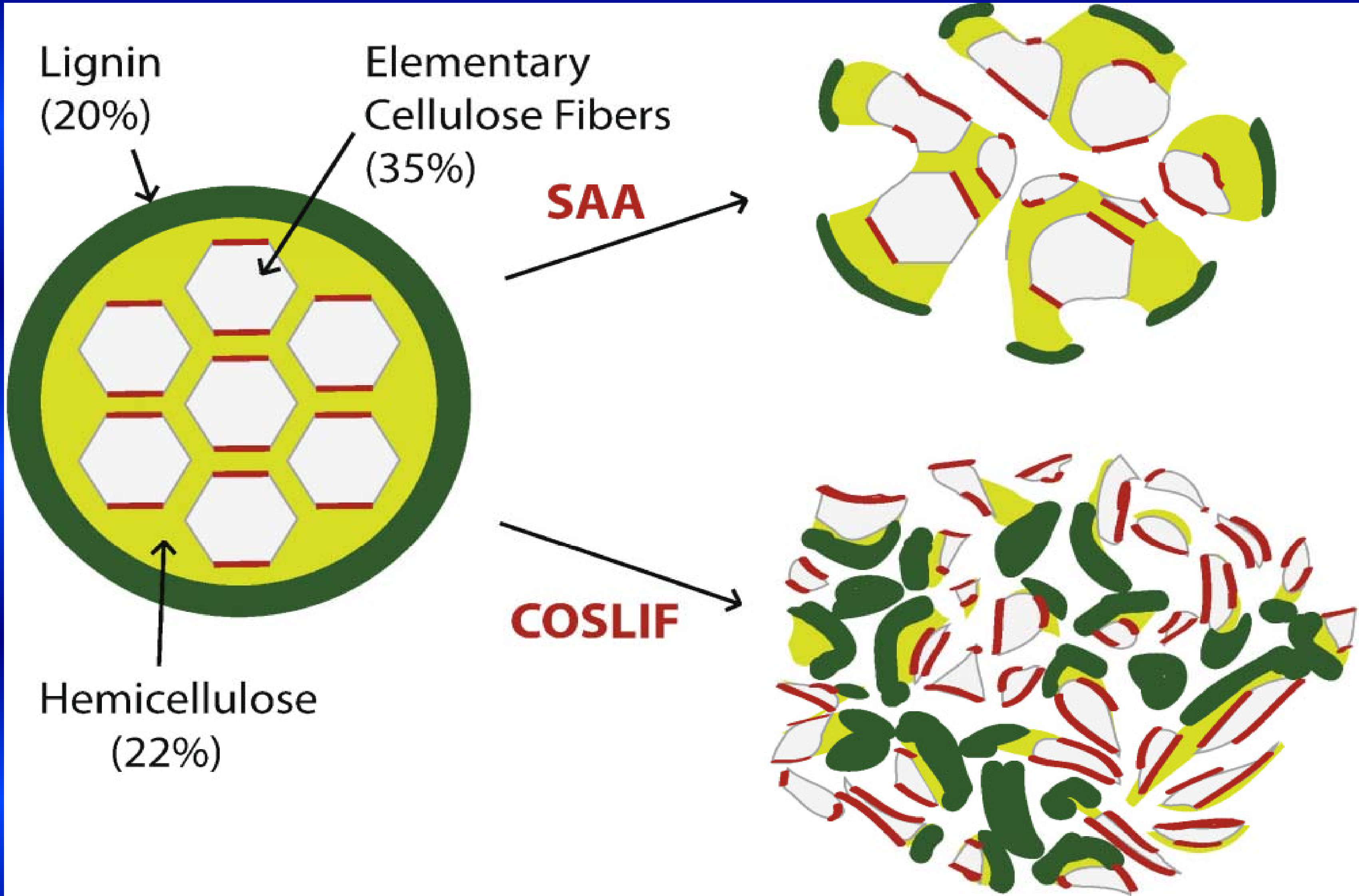
Cellulose Solvent-Based Biomass Pretreatment Breaks Highly Ordered Hydrogen Bonds in Cellulose Fibers of Switchgrass, Noppadon et al., Biotechnology and Bioengineering, Vol. 108, No. 3, March, 2011

Biofuels; biomass pretreatment; cellulose solvent- and organic solvent-based lignocellulose fractionation (COSLIF)

"While many pretreatments attempt to improve the enzymatic digestibility of biomass by removing lignin, this study shows that improving the surface area accessible to cellulase is a more important factor for achieving a high sugar yield. "

Rollin, J. A. et al., (2011), Increasing Cellulose Accessibility Is More Important Than Removing Lignin.. Biotechnology and Bioengineering, Vol. 108, No. 1, January 1, pp. 22-30

The largest obstacle to economical production of cellulosic biofuels (and microfibrils) is cost-effectively releasing sugars from recalcitrant lignocellulose.



CELLULOSE SOLVENT- AND ORGANIC SOLVENT-BASED LIGNOCELLULOSE FRACTIONATION (COSLIF)

DECREASING PROCESSING COSTS CAN BE ACCOMPLISHED BY

(1) IMPROVING PRETREATMENT

(2) ENHANCING CELLULASE PERFORMANCE

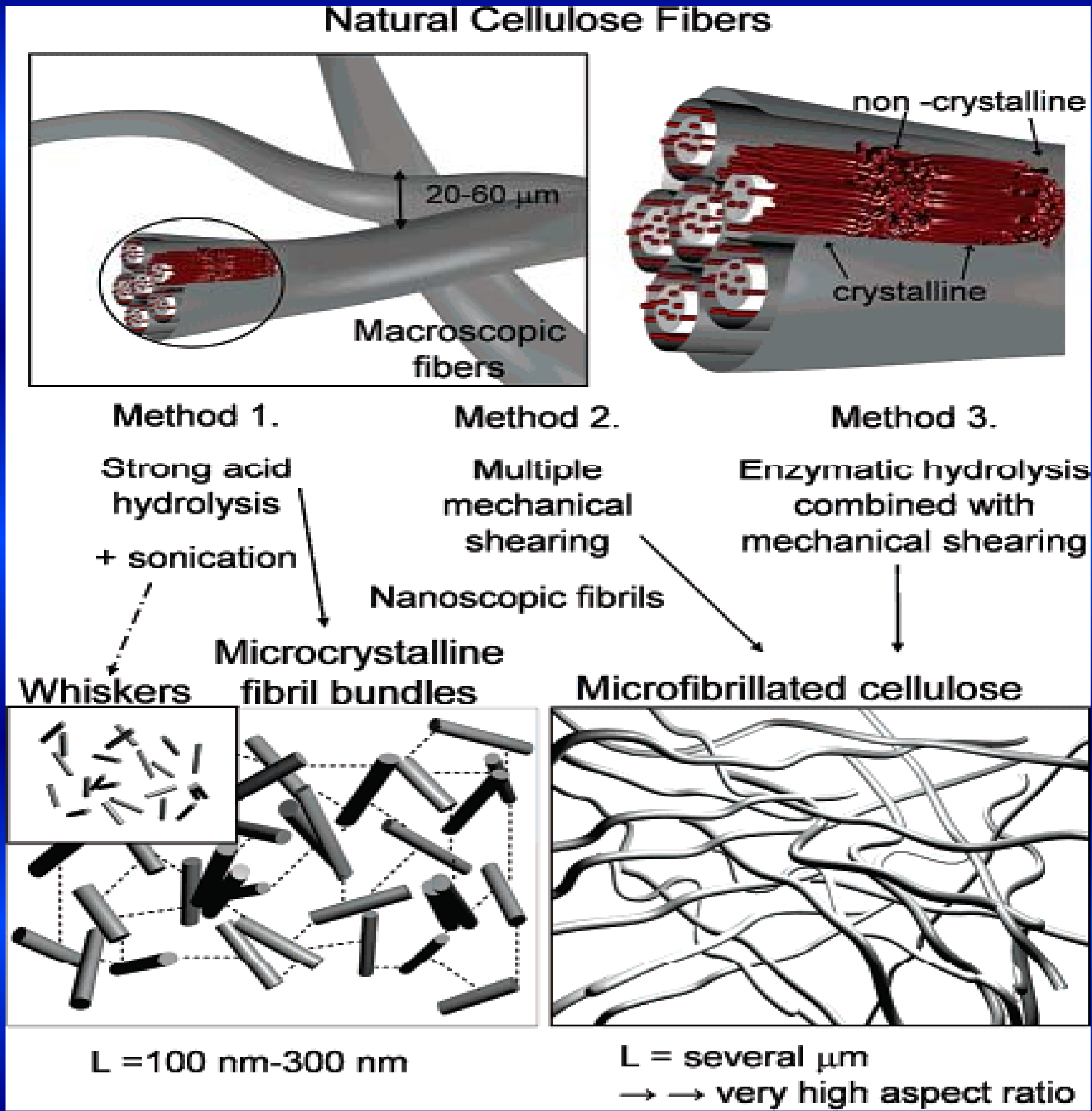
(3) RECYCLING CELLULASE

(4) DECREASING ENZYME PRODUCTION COSTS

(5) PRODUCING LESS RECALCITRANT BIOENERGY PLANTS
(SOME TRANSGENICS YIELD NEARLY TWICE AS MUCH SUGAR FROM CELL WALLS AS WILD-TYPE PLANTS)

IN-DEPTH UNDERSTANDING OF SUBSTRATE CHARACTERISTICS AFTER BIOMASS PRETREATMENT AND THEIR RELATIONSHIP WITH ENZYMATIC CELLULOSE HYDROLYSIS IS VITAL FOR DECREASING COSTS ASSOCIATED WITH BIOMASS SACCHARIFICATION

NON-WOOD LIGNO-CELLULOSIC FIBERS



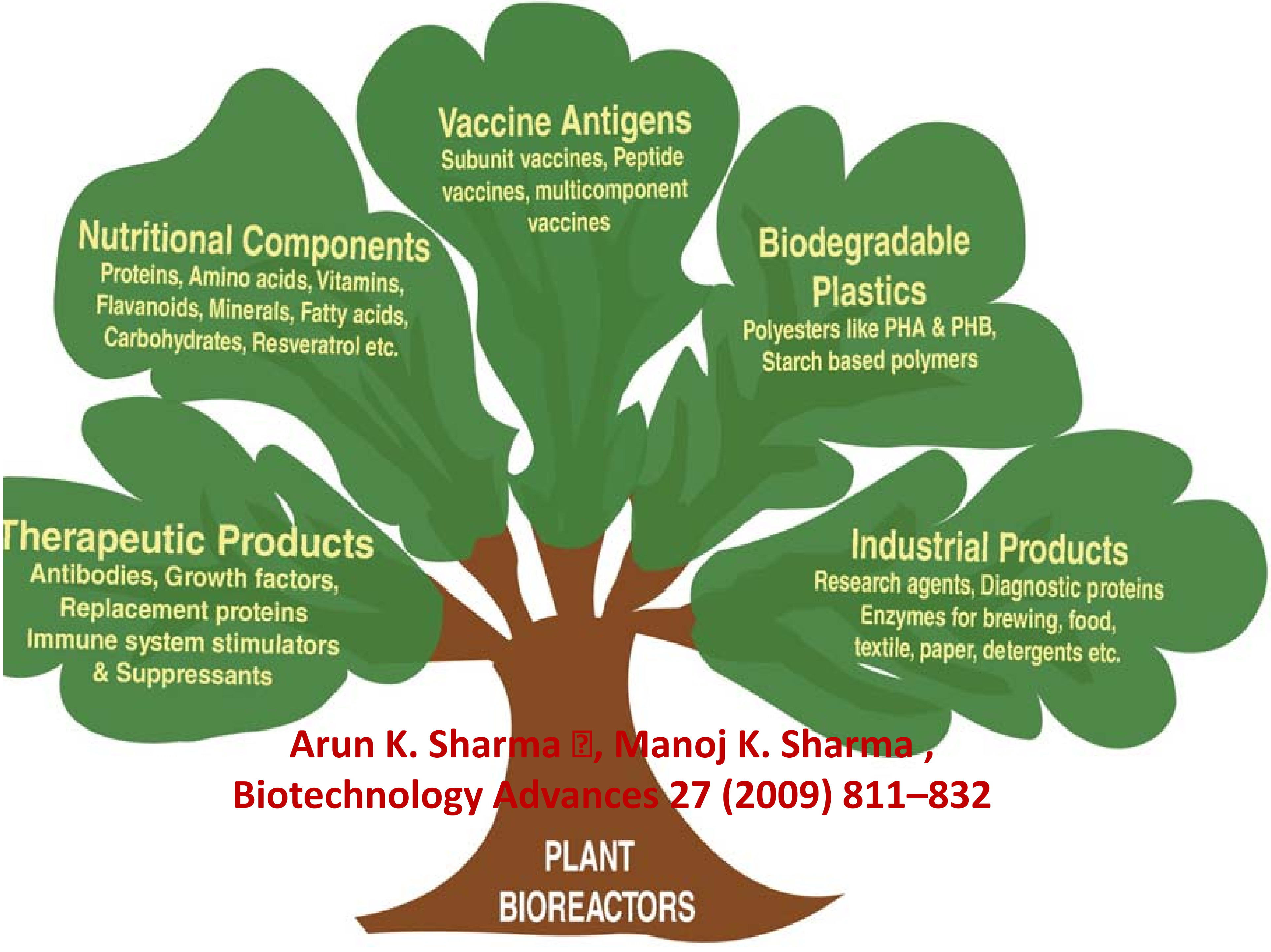
Paako et al, Enzymatic Hydrolysis Combined with Mechanical Shearing Biomacromolecules 2007, 8, ***1934-1941***

Table 1
Chemical composition (wt%) of vegetable fibers

	Cellulose	Lignin	Hemicellulose
Bast fibers			
Flax[a]	71	2	19
Hemp[a]	75	4	18
Jute[a]	72	13	13
Leaf fibers			
Abaca[a]	70	6	22
Sisal[a]	73	11	13
Seed-hair fibers			
Cotton[a]	93	—	3
Wheat straw[a]	51	16	26
Lignocellulose fillers			
LF	58	31	8

[a] Sources: Le Digabel, 2004; Young, 2004.

ENGENHARIA GENÉTICA PROCURA AUMENTAR % CELULOSE



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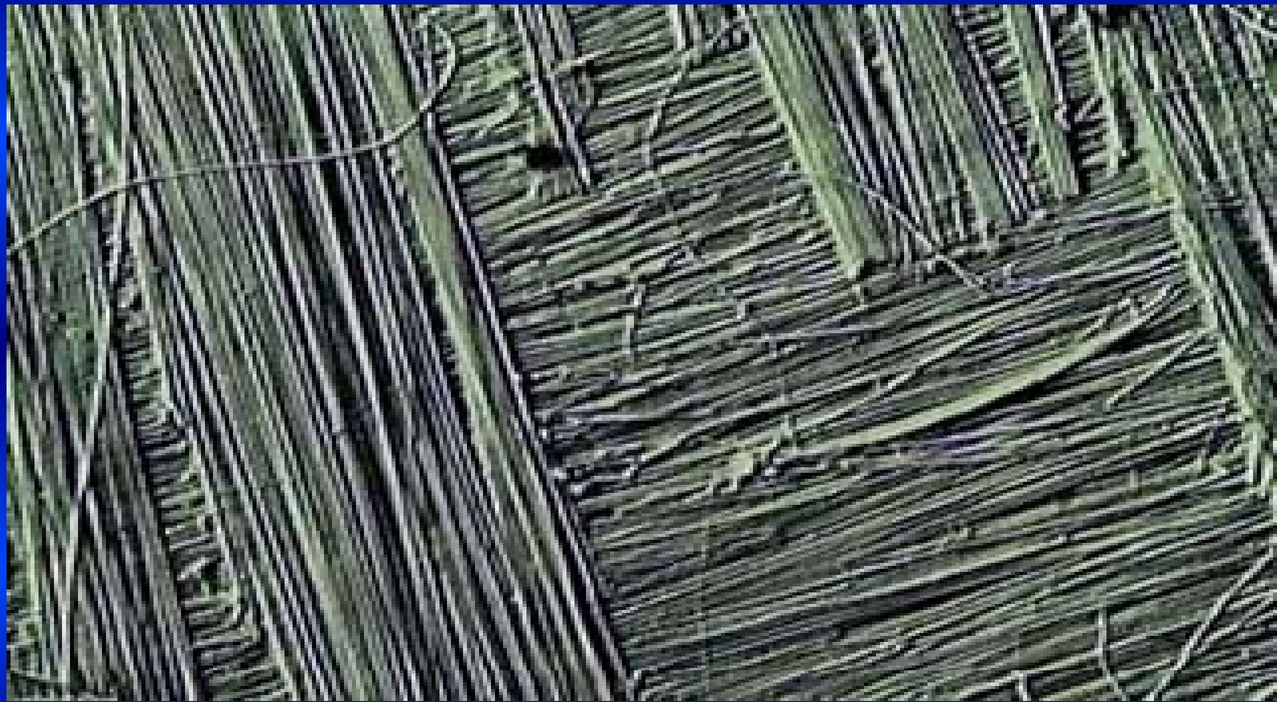
NANOCELLULOSE DIMENSIONS (SAMIR ET AL. 2005; TANEM ET AL. 2006; HUBBE ET AL. 2008)

Cellulose structure	diameter	Length (nm)	Aspect ratio L/D
Microfibril	2–10	10,000	1,000
Microfibrillated cellulose (MFC)	0–40	1,000	100–150
Cellulose whisker	2–20	100–600	10–100
Microcrystalline cellulose (MCC)	1,000	,000	1

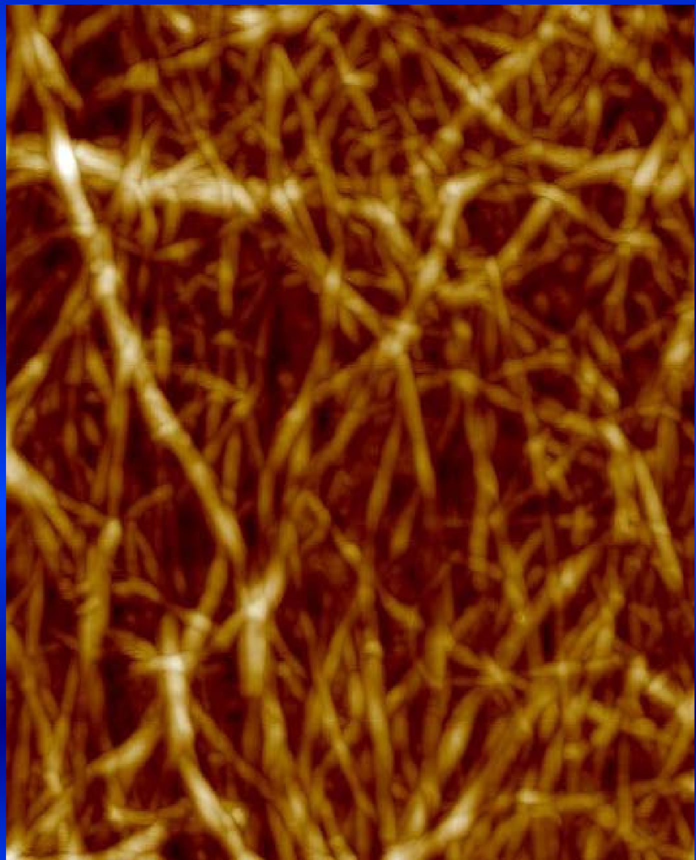


CELLULOSE

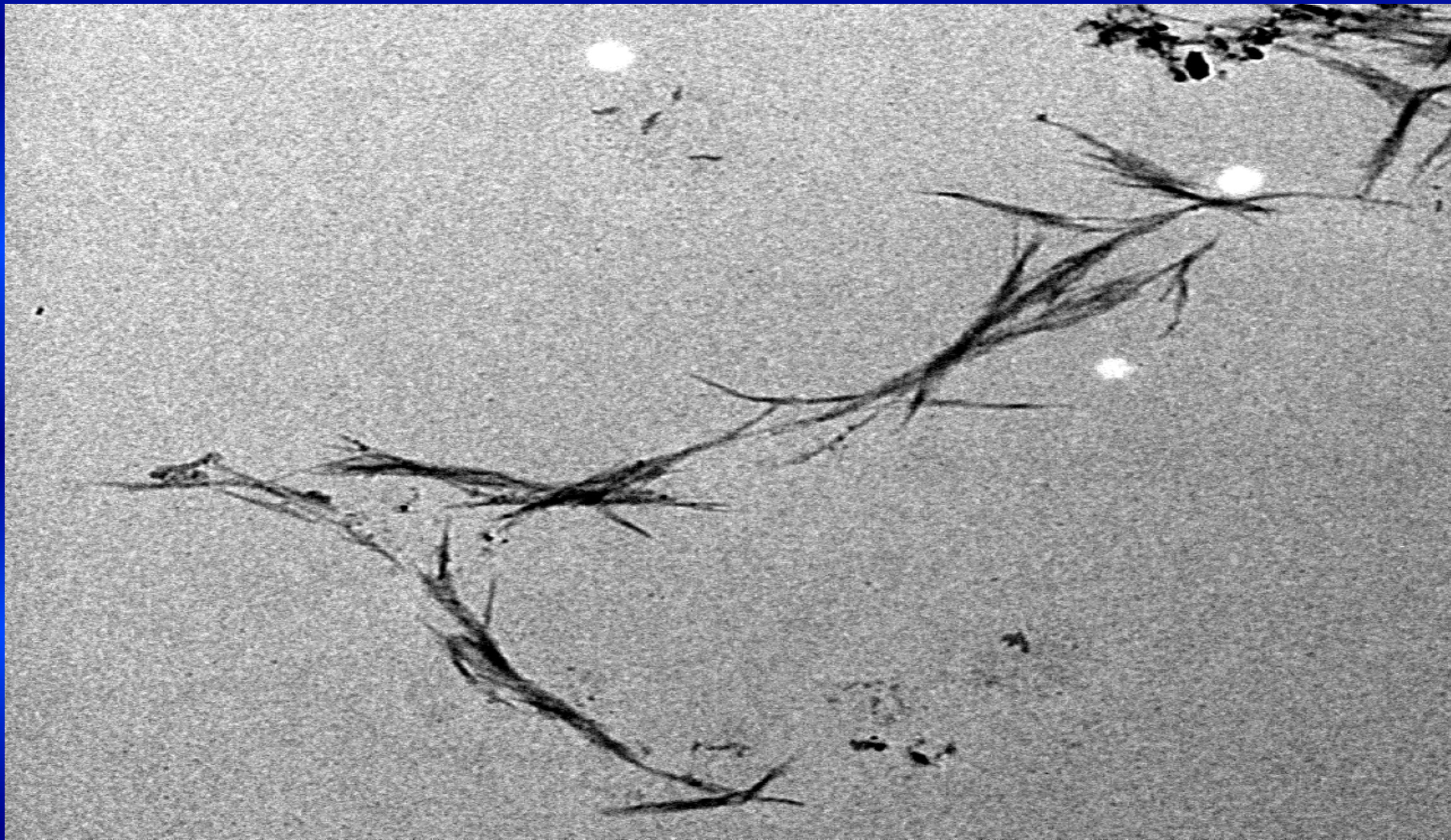
- makes up 50% of the plant cell wall
- each molecule is a chain of approximately 10 000 beta-glucose, unbranched
- OH-groups form H-bonds with neighbouring chains to create a lattice

-about 2000 chains mass together to form <u>microfibrils</u>, which are visible under an electron microscope

Cellulosic nanofibers Image has dimensions of 1 µm on each side (photo courtesy of M. Österberg, Helsinki University of Technology) -Hubbe et al



WHISKERS



--The cotton bowls were collected approximately a week before expected opening, and the fibers were manually removed from seeds inside water

--An alkaline and bleaching step was applied to the fibers to remove hemicelluloses, pectin, and wax After washing to pH 7 fibers were submitted to enzymatic hydrolysis

--Once-dried cotton and viscose fibers were submitted to the same treatments as NDC for comparison

--After the enzymatic treatment, the fibers were taken to the sonication procedure.

--TEM (Dr Juan P Hinestrosa , Cornell University) was used to verify the nature of the disaggregation obtained

RESULTS

Figure1 – Transmission electron mycroscopy view of NDC submitted to enzymatic hydrolysis , sonicated for 20 minutes, potency 400 W

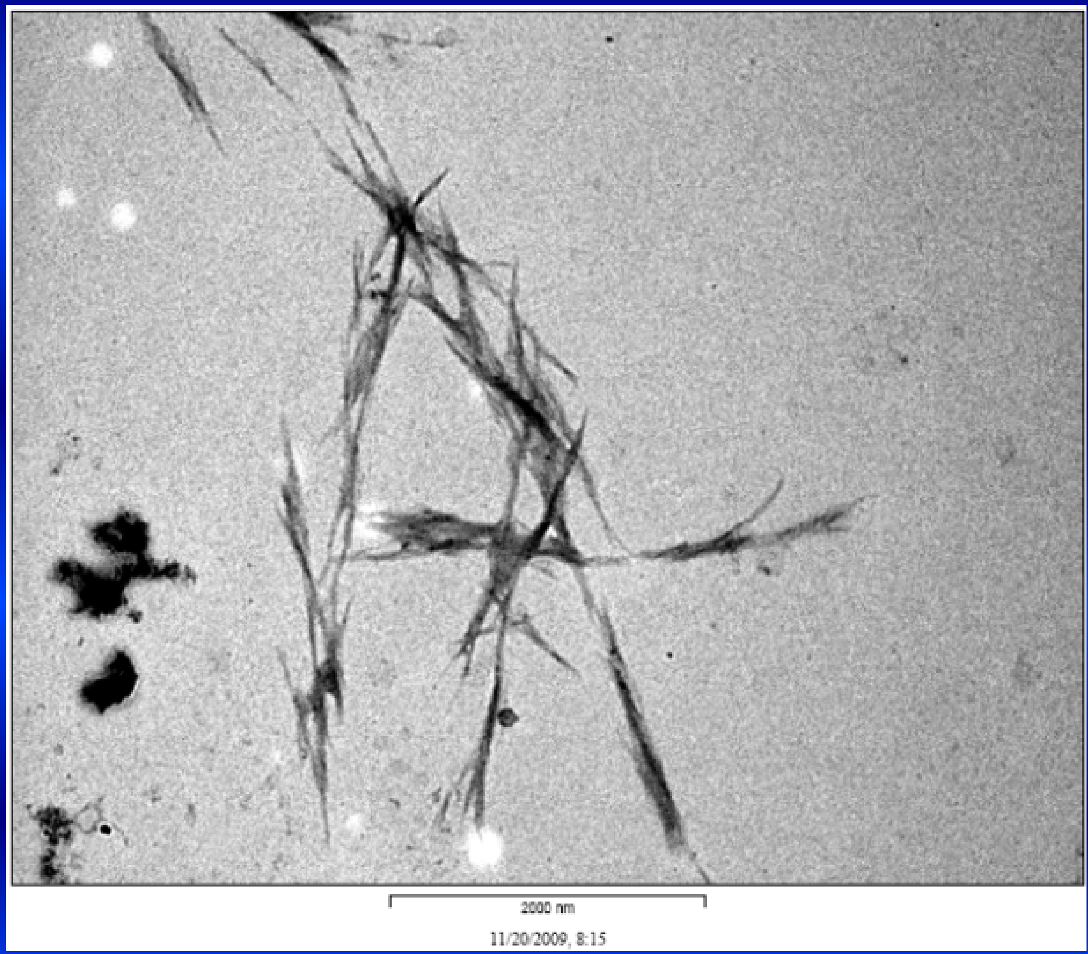


Figure 2 – Transmission electron mycroscopy view of NDC submitted to enzymatic hydrolysis ,sonicated for 50 minutes, potencv 400W

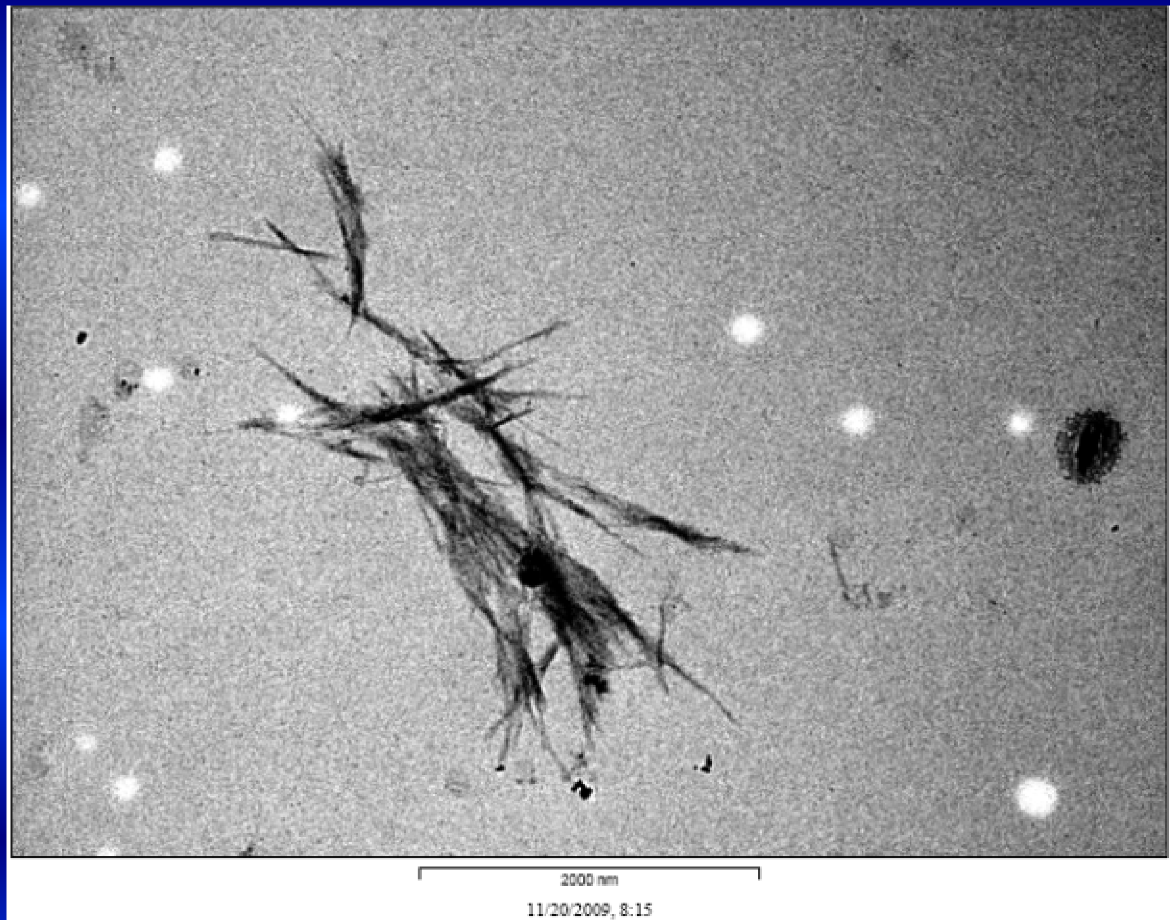
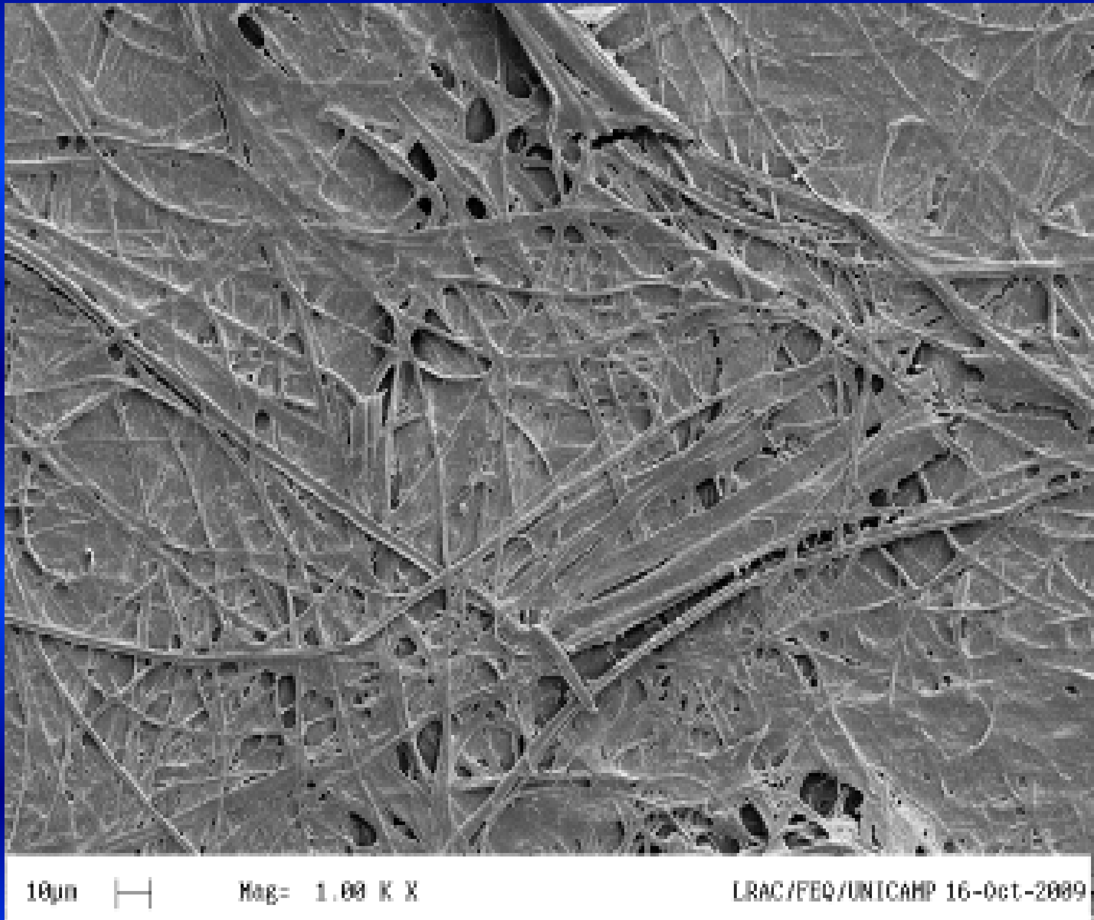


Figure 3. Scanning electron mycroscopy of viscose films after enzymatic hydrolysis sonicated for 20 minutes, potency 400W



CONCLUSION

NDC has been studied since the early 70's. In this work we have synthesized nanofibril structures starting with NDC, under conditions which do not produce the nanofibrils if applied to once dried cotton. Although much work remains to be done, to the best of our knowledge, this is the first time NDC has been studied with respect to the synthesis of nanofibrils. Furthermore, the combination of enzymatic hydrolysis and high-energy sonication, consist of two eco-friendly processes that have gained increasing studies and utilization, including in the more efficient, and cleaner utilization of the biomass

THIS WORK IS INTENDED TO ADD KNOWLEDGE TO THE IRREVERSIBLE MODIFICATIONS THAT OCCUR IN WOOD AND NO-WOOD LIGNOCELLLULOSIC MATERIALS - WHICH MAKES MORE DIFFICULT TO USE THE BIOMASS TO PRODUCE FUEL AND MATERIALS

COTTON CAN BE CONSIDERED LIGNIN FREE