

CELULOZĂ ȘI HÂRTIE

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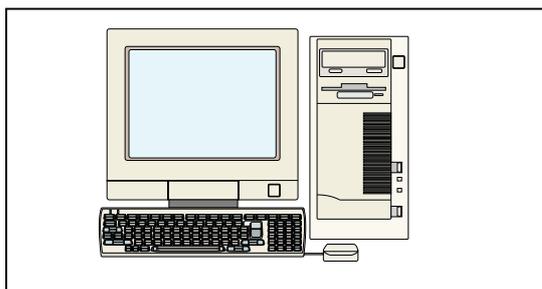
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PLANTELE NELEMNOASE ȘI PRODUCȚIA DE CELULOZĂ

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Rezumat

Lucrarea prezintă o trecere în revistă a stadiului utilizării plantelor nelemnoase pentru obținerea fibrelor celulozice destinate industriei hârtiei, pe plan global și în România. Se prezintă principalele categorii de plante anuale, precum și sortimentele de hârtie care se pot obține. Se discută avantajele și dezavantajele folosirii plantelor anuale ca materie primă pentru fabricarea hârtiei. Se argumentează faptul că paie de grâu constituie o alternativă realistă la lemn pentru industria celulozei și hârtiei din România.

Cuvinte cheie: Plante anuale, Fibre celulozice nelemnoase, Paie de grâu, Hârtie

Abstract

This paper presents an overview on nonwood plants utilization as raw material for cellulosic fibers used in paper industry, worldwide and in Romania. The main categories of annual plants and paper grades which can be obtained are presented. The advantages and disadvantages of using annual plants as a fibrous source for papermaking are also discussed. It is argued why wheat straw represents a realistic alternative for Romanian pulp and paper industry.

Keywords: Annual plants, Nonwood fibers, Wheat straw, Paper

I. INTRODUCERE

Fibrele nelemnoase provenite din plante anuale au o lungă istorie ca materie primă pentru fabricarea hârtiei. Demnitarul chinez Țai-Lun, “părintele hârtiei” a inventat hârtia în varianta ei modernă în jurul anului 105, când a creat pentru împăratul Hă-di prima foaie de hârtie, materialele de bază fiind coaja de dud, cânepa, cârpele și plasele vechi pescărești [1].

Cânepa, ramia, bumbacul și cârpele de bumbac au fost folosite exclusiv timp de aproape 2000 de ani la fabricarea fibrelor celulozice, iar lemnul a început să le înlocuiască numai de aproximativ 200 de ani, datorită creșterii cererii de produse papetare, ce a atras după sine creșterea masivă a necesarului de materii prime [2].

Dintre speciile lemnoase o largă utilizare au speciile de rășinoase - molidul, pinul, bradul și foioasele - plopul, fagul, mestecănușul. În prezent,

resursele de lemn nu mai fac față consumului cerut de dezvoltarea industriei de celuloză în majoritatea regiunilor lumii din cauza ciclului prea lung de reînnoire a materialului vegetal și a defrișărilor [3].

După lemn, plantele nelemnoase reprezintă a doua sursă majoră de materie primă pentru fabricarea celulozei și a altor paste fibroase. Ca materii prime se întrebuințează paie de graminee (grâul, secara, orzul, orezul), bagasa (tulpină de trestie de zahăr), bambusul, bumbacul, stuful, sisalul, iuta, cânepa, abaca, kenaful, inul [4].

Producția de fibre celulozice din plante nelemnoase se bazează în principal pe produsele secundare provenite din exploatarea agricolă: materialul vegetal rezultat la recoltarea gramineelor (paie cerealiere) și cel de la prelucrarea culturilor agricole (trestie de zahăr și bambus), iar într-o măsură mai mică pe culturile

de plante pentru industrializare (bumbac, stuf, cânepa).

Factorul primordial care determină utilizarea plantelor anuale și a deșeurilor vegetale în industria celulozei este economisirea lemnului, pentru o utilizare rațională și economică în alte ramuri industriale [5]. Pe de altă parte, tehnologiile actuale din industria hârtiei, acceptă cantități crescute de fibră scurtă, fiind astfel posibilă extinderea bazei de materie primă prin valorificarea plantelor anuale [6].

II. DATE STATISTICE

În prezent, lemnul intervine cu cca. 47% în producția de materiale fibroase pe plan mondial, hârtia recuperată cu 45%, iar plantele anuale cu 8%, după cum se prezintă în figura 1 [7].

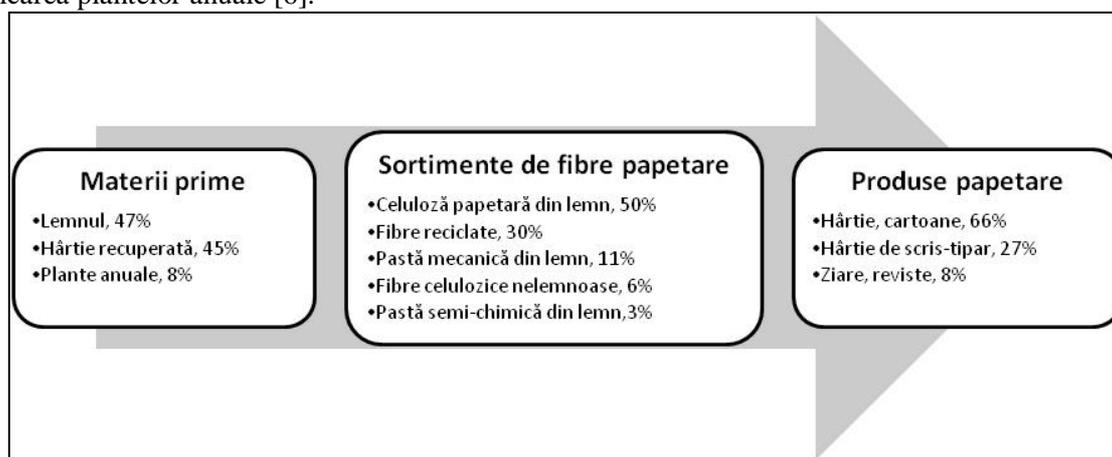


Fig. 1 Ponderea materiilor prime folosite pentru fabricarea celulozei și hârtiei pe plan mondial în 2012

Dinamica producției mondiale de materiale fibroase pentru fabricarea hârtiei din ultimii ani (tabelul 1) indică menținerea constantă a producției de celuloză din lemn, creșterea contribuției fibrelor secundare și scăderea producției de celuloză din plante nelemnoase. Orientarea către folosirea maculaturii este evidentă și reprezintă soluția pentru satisfacerea

necesarului de material fibros în creștere și în perioada următoare. Reducerea producției de celuloză din plante anuale în ultimii 2-3 ani se explică tot prin creșterea consumului de maculatură în țări precum China, în care s-au închis multe unități mici producătoare de celuloză din plante anuale.

Tabelul 1 Producția mondială de materiale prime fibroase, milioane tone [7]

Material fibros	2008	2009	2010	2011	2012	2013
Celuloză papetară din lemn	131,63	119,62	127,61	131,17	130,72	131,04
Fibre secundare (maculatură)	155,17	142,50	150,05	169,18	175,56	178,04
Pastă mecanică din lemn	33,39	28,98	30,73	29,49	28,06	27,77
Celuloză din plante nelemnoase	18,41	17,08	18,28	17,72	16,02	13,57
Pastă semi-chimică din lemn	8,91	8,32	8,43	8,64	8,83	8,81
Total	347,51	316,50	335,10	356,20	359,19	359,23

În figura 2 se prezintă evoluția producției de celuloză din plante anuale, precum și ponderea acestora în producția mondială de celuloză. Producția de celuloză din plante anuale a crescut continuu, atingând maximul în anul 1995, cu un

total de aproximativ 25 mil. tone, care reprezenta 14% din producția mondială de celuloză. Ulterior, producția a scăzut, situându-se astăzi la aproximativ 14 mil. tone, respectiv 8% din producția mondială de celuloză.

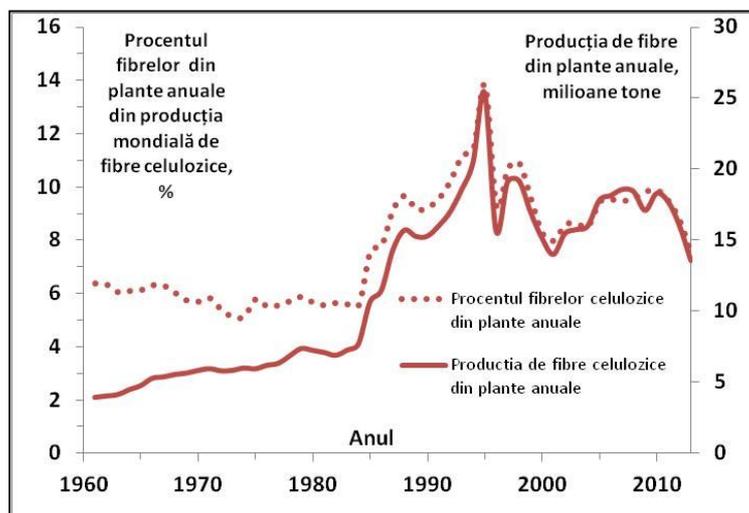


Fig. 2 Dinamica producției mondiale de fibre celulozice din plante anuale în perioada 1961-2013 [7]

Continental asiatic este lider absolut, producând în anul 2012 aproximativ 86% din totalul cantității de celuloză din plante nelemnoase, după cum se observă din figura 3. Explicația este legată de existența resurselor mari de materii prime de tipul paielor cerealiere și altor plante nelemnoase, în țări precum China, India,

Pakistan, Vietnam, Tailanda. Producția se realizează în numeroase fabrici cu capacitate redusă, dotate cu instalații simple. În cele mai multe cazuri, soluțiile reziduale nu sunt prelucrate în fabrică, fiind evacuate în diferiți emisari, în condițiile legislației permissive de protecție a mediului.

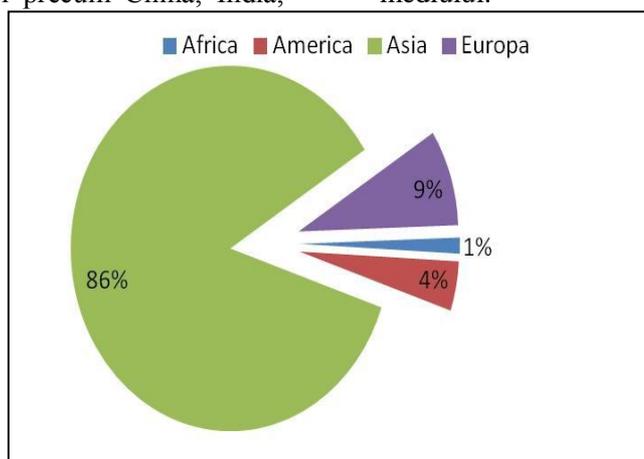


Fig. 3 Producția de fibre celulozice din plante anuale pe continente în %, 2012 [7]

În ultimii ani, producția de celuloză din plante anuale a continentului asiatic s-a redus, pe seama scăderilor înregistrate în China, unde

producătorii de hârtie au început să înlocuiască celuloza din paie cu maculatura.

Tabelul 2. Producția anuală de fibre celulozice din plante anuale pe continente, milioane tone [7]

Continentul	2008	2009	2010	2011	2012	2013
Africa	0,272	0,22	0,23	0,23	0,23	0,22
America	0,811	0,80	0,81	0,70	0,70	0,71
Asia	16,00	14,74	15,96	15,42	13,73	11,26
Europa	1,32	1,33	1,28	1,368	1,367	1,372
Total	18,41	17,08	18,28	17,72	16,02	13,56

China și India sunt cele mai mari producătoare de fibre celulozice din plante anuale, producția lor însumând aproximativ 80% din totalul mondial, vezi tabelul 3. Din restul țărilor producătoare, doar Spania (5%), Pakistan (2%), USA și Italia dețin o pondere ce depășește 1% din producția globală de celuloză din plante anuale.

În China, celuloza din plante anuale reprezintă aproximativ 65% din totalul producției de fibre celulozice, în timp ce în India procentul este de 45%. Spania, cel mai important producător european de fibre celulozice din plante anuale, are 31% din producția internă realizată din materii prime nelemnoase [7].

Tabelul 3. Producția anuală de fibre celulozice din plante anuale – țări producătoare, mii tone [7]

Țara	2008	2009	2010	2011	2012	2013
China	12970	11748	12970	12400	10738	8285
India	1995	1995	1995	1995	1995	1995
Spania	900	900	900	900	900	900
Pakistan	370	370	370	370	370	370
USA	245	245	245	245	245	245
Italia	176	213	176	203	203	203
Columbia	174	167	160	160	183	178
Argentina	139	216	236	133	135	135
Tailanda	131	131	126	131	133	133
Egipt	120	120	120	120	120	120

III. UTILIZAREA CELULOZEI DIN PLANTE NELEMNOASE LA FABRICAREA HÂRTIEI

Chiar dacă utilizarea plantelor anuale pentru producția de celuloză este avantajoasă din multe puncte de vedere, fabricarea celulozei din plante anuale este totuși problematică. Principalele dezavantaje sunt dificultățile de colectare, transport și depozitare a materiei prime. Plantele anuale sunt voluminoase ceea ce implică costuri ridicate de transport și suprafețe mari de depozitare [8]. De asemenea, tehnologiile de obținere a celulozei din plante anuale cele mai utilizate, și anume procedeele alcaline (natron și sulfat), implică probleme de poluare a mediului. În timpul procesului de delignificare, siliciul prezent în materia primă se dizolvă în leșia de fierbere, iar silicații produc dificultăți la regenerarea chimicalelor și formează depuneri pe circuite.

În ansamblu, utilizarea plantelor nelemnoase prezintă următoarele avantaje și dezavantaje [9]:

- plantele anuale ajung la maturitate mult mai repede decât resursele lemnoase;
- fibrele au conținutul de lignină mai scăzut decât foioasele și rășinoasele iar lignina este mai accesibilă la chimicalele de dezincrustare și este mai reactivă; necesarul de chimicale și de energie la dezincrustare este mai mic și timpul de staționare în fierbător mai scurt decât la fierberea lemnului;

- conținutul ridicat de substanțe anorganice și în special de dioxid de siliciu provoacă dificultăți la prelucrarea soluțiilor reziduale;
- asigurarea cu materie primă pe toată durata anului este mai dificilă comparativ cu lemnul.

Există două direcții principale de valorificare a plantelor nelemnoase: obținerea de celuloze înălbite și fabricarea pastelor de mare randament. Pentru primul caz se pretează îndeosebi paie cerealiere și stuful, din care se pot obține celuloze cu grad de alb și caracteristici de rezistență apropiate de celuloza din foioase. A doua direcție presupune utilizarea de procedee chimico-mecanice pentru obținerea de semiceluloze (randament între 65-75%) sau de paste cu randamente mai mari, peste 80%.

Materialele fibroase din plante anuale se pot folosi fie singure, fie în amestec cu celulozele din lemn pentru fabricarea unor sortimente de hârtii și cartoane: hârtii de scris-tipar, hârtii pentru cartonul ondulat sau cartonul obișnuit, hârtii igienico-sanitare, hârtii speciale, după cum rezultă din tabelul 4 [2, 10]. În mod normal, celulozele din plante nelemnoase sunt produse în fabrici integrate, iar celulozele sulfat înălbite din lemn sunt adăugate în pastă pentru a îmbunătăți funcționarea mașinii și proprietățile de rezistență cerute sortimentului de hârtie. Procentul de celuloze nelemnoase variază între 50-90% și poate ajunge la chiar 100% în funcție de sortimentele și cerințele de calitate ale hârtiei.

Hârțile speciale (bancnote, țigarete) sunt fabricate fie în proporție de 100% din fibre celulozice din plante nelemnoase (bumbac, in), fie

în diferite proporții ale acestora cu alte materii prime [11].

Tabelul 4. Utilizarea celulozei din plante nelemnoase în fabricarea hârtiilor și cartoanelor [2, 10]

Plante anuale	Sortimentul de hârtie/carton	Adaosul (%)	Alte celuloze utilizate
Paiele cerealiere (grâu, orz, orez)	Hârtii miez pentru carton ondulat	60 - 90	Fibre secundare
	Cartoane duplex și triplex	40 - 80	Celuloză înălbită
	Hârtii de scris fără pastă mecanică	20 - 90	Celuloză înălbită
Bagasa	Hârtii capac pentru carton ondulat	60 - 100	Celuloză înălbită
	Hârtie de ziar	70 - 90	Celuloză sulfat
	Hârtii de scris fără pastă mecanică	20 - 100	Celuloză înălbită
	Hârtii sanitare	60 - 90	Celuloză înălbită
Bambusul	Hârtii capac pentru carton ondulat	50 - 100	Celuloză din paie
	Hârtie de ziar	50 - 70	Pastă mecanică
	Hârtii de scris fără pastă mecanică	70 - 100	Celuloză din paie
	Hârtii de ambalaje	80 - 100	Celuloză sulfat
Inul	Hârtii de țigarete	20 - 100	Celuloză din bumbac
	Hârtie de bancnote	50 - 80	Celuloză din in
	Hârtii de scris cu gramaj redus	50 - 100	Celuloză din bumbac
	Hârtii securizate	50 - 80	Celuloză din bumbac
Kenaful	Hârtii capac pentru carton ondulat	40 - 50	Fibre secundare
	Hârtie de ziar	80 - 90	Celuloză înălbită
	Hârtii de scris fără pastă mecanică	20 - 80	Celuloză înălbită
	Hârtii sanitare	50 - 60	Celuloză înălbită
Stuful	Hârtii miez pentru carton ondulat	60 - 90	Fibre secundare
	Hârtii de scris fără pastă mecanică	20 - 90	Celuloză înălbită

Alte argumente în favoarea utilizării plantelor anuale sunt legate de protecția mediului și sunt de natură socio-economică, prin ocuparea și stabilizarea forței de muncă în zonele de cultivare a plantelor cu valorificare papetară. În același scop pot fi valorificate și terenurile necultivate și cele degradate. Un argument important în favoarea plantelor anuale ca materie primă pentru celuloză este și acela că se realizează o importantă economie de lemn.

IV. SITUAȚIA DIN ROMÂNIA

În România, una din ramurile în plină dezvoltare după al II-lea Război Mondial a fost industria de celuloză și hârtie, o importanță deosebită acordându-se creșterii producției prin valorificarea lemnului și a plantelor nelemnoase. Pe lângă lemnul de celuloză din rășinoase, folosit tradițional, s-au utilizat și foioasele tari (fagul și carpenul), precum și specii de lemn repede crescătoare (plopul și salcia). Plantele anuale au fost reprezentate de stuf și paiele de cereale.

În perioada 1950-1970 au fost efectuate cercetări sistematice privind caracterizarea anatomică, compoziția chimică, precum și pentru stabilirea potențialului papetar al plantelor anuale, ca materie primă pentru fabricarea celulozei. Cercetările au fost concentrate la institutul departamental de profil de la București, la Institutul de Chimie Macromoleculară „Petru Poni” din Iași și la Catedra de Celuloză, Hârtie și Fibre Artificiale de la Institutul Politehnic din Iași. Studiile au fost concretizate prin editarea de cărți și monografii, publicarea de lucrări de specialitate și teze de doctorat, prin realizarea de tehnologii privind fabricarea celulozei din plante anuale.

Potențialul oferit de plantele anuale pentru industria celulozei a constituit subiectul unor cărți și monografii care au evidențiat valoarea deosebită a acestor materii prime [12,13]. O lucrare de referință este „Chimia stufului”, [14], care conține abordări în premieră mondială ale structurii și proprietăților componentelor chimici principali (celuloză, lignină și hemiceluloze) ai stufului

dunărean, *Phragmites communis*. S-au derulat și cercetări privind dezincrustarea stufului prin procedeul sulfat, studiindu-se în detaliu cinetica fierberii, factorii care influențează procesul, precum și valoarea papetară a celulozei din stuf [15]. Atenția specialiștilor s-a concentrat și asupra valorificării pe cale chimică a paielor de grâu, studiile vizând implicațiile tehnologice și economice ale folosirii paielor la fabricarea celulozei [16, 17].

Rezultatul principal al activității de cercetare s-a concretizat în investiții în linii de producție, România devenind în scurt timp un important producător de celuloză din plante anuale:

- fabrica de celuloză din stuf pentru fibre artificiale (celofibră) de la C.C.H. Brăila;
- fabrica de celuloză papetară din stuf de la C.C.H. Brăila;
- fabrica de celuloză din paie „Palas” Constanța;
- fabrica de celuloză din paie de la C.C.H. Călărași.

În anul 1965, capacitatea instalată a fabricilor de celuloză din plante anuale era de 162 000 t/an, România devenind un important producător la nivel european. Celulozele înălbite din stuf și din paie s-au dovedit a fi materii prime valoroase pentru fabricarea hârtiilor de scris-tipar și hârtiei suport cretare. După un număr important de ani de funcționare, fabricile de celuloză din stuf și din paie au fost trecute pe lemn, deoarece s-a interzis recoltarea industrială a stufului din Delta Dunării și nu s-au mai asigurat ritmic cantitățile de paie necesare. Se poate afirma că în România s-a investit mult capital uman și financiar pentru valorificarea plantelor anuale în industria de celuloză și hârtie, dobândindu-se o bogată experiență, recunoscută și pe plan internațional.

În prezent, în România, producția de hârtie și carton este dominată de sortimentele pentru fabricarea cartonului ondulat și de hârtiile igienico-sanitare. Materia primă este asigurată în proporție de peste 70% din maculatură, consumul de maculatură depășind 300 000 t/an. Utilizarea celulozei este limitată la fabricarea sortimentelor superioare de hârtie igienico-sanitară, iar celuloza necesară se aprovizionează în totalitate din import. Patronatul Industriei de Celuloză și Hârtie (ROMPAP) estimează că în anul 2014 s-au importat în România aproximativ 105 000 tone

celuloză înălbită și estimează că în anul 2015 importul de celuloză va crește semnificativ prin intrarea în funcțiune de noi capacități de fabricare a hârtiilor igienico-sanitare [18].

România prezintă în continuare un potențial important de fabricare a celulozei, atât din lemn cât și din plante anuale, deoarece dispune de materia primă necesară și de expertiza în domeniu. O fabrică modernă de celuloză înălbită din lemn are pragul de rentabilitate 1000 tone celuloză/zi și consumă între 4500 și 5500 m³ lemn/zi, funcție de specie (foioase sau rășinoase) și de caracteristicile celulozei. Se apreciază că acest volum de lemn poate fi aprovizionat ritmic, fabrica urmând să funcționeze cu lemn de rășinoase și cu lemn de foioase, alternativ. Plantele anuale, mai ales paietele de grâu, reprezintă o alternativă realistă la lemn, România fiind un important producător de grâu. În anul 2104, în România s-au obținut 7,3 mil. tone grâu, iar cantitatea de paie a fost estimată la aproximativ 10 mil. tone.

Celuloza din paie este considerată un material fibros valoros pentru fabricarea hârtiei. Proprietățile papetare recomandă celuloza din paie pentru fabricarea unei game largi de hârtie. Celuloza înălbită din paie se folosește, alături de celuloza înălbită din rășinoase în compoziția hârtiilor de scris-tipar deoarece le conferă caracteristici de imprimare superioare. Pastele de mare randament din paie se utilizează la fabricarea hârtiei strat ondulă pentru cartonul ondulat, împreună cu alte tipuri de materiale fibroase, îndeosebi maculatură. Prețul celulozei înălbite din paie este inferior prețului celulozei înălbite din lemn.

Utilizarea paielor la obținerea pastelor fibroase prezintă implicațiile sociale și de mediu. Paietele reprezintă o sursă valoroasă cu multiple întrebuințări în agricultură. Deasemenea, paietele pot fi folosite pentru obținerea combustibililor, direct, sub formă de peleți, sau constituie materia primă pentru obținerea bioetanolului. Prin urmare, paietele sunt disputate între mai multe sectoare de activitate, între care există o stare concurențială legată de aprovizionarea cu această materie primă. Un argument solid al folosirii paielor la fabricarea celulozei este efectul benefic asupra mediului deoarece reduce necesarul de lemn care trebuie recoltat. Decizia de a utiliza paietele ca materie primă pentru fabricarea celulozei (pastelor fibroase)

trebuie luată pe baza unor criterii care, în esență, se referă la:

- existența surselor de paie la distanțe convenabile pentru transportul acestora;
- nivelul cererii de celuloză din paie;
- tipul de celuloză (pastă fibroasă) care se fabrică;
- procedeele de dezincrustare care pot fi aplicate;
- implicațiile sociale și de mediu ale fabricării celulozei din paie.

Utilizarea paielor de grâu pentru obținerea celulozei ridică o serie de probleme legate de sursa de aprovizionare și de caracterul sezonier al recoltării. Pentru o tonă de celuloză se consumă între 2,5-2,8 t paie a.u., cantitate care se obține aproximativ de pe un hectar de teren agricol [19]. În condițiile României, dacă s-ar utiliza doar 10% din cantitatea de paie recoltată anual (cca. 1 milion de tone) s-ar obține cel puțin 350 000 tone celuloză, cantitate importantă care acoperă necesarul intern și creează disponibilități și pentru export. Este cunoscut că în România cantitățile de lemn sunt limitate și sunt intens disputate între diferite ramuri industriale, situație în care paiele reprezintă o opțiune realistă pentru producerea materialelor fibroase necesare industriei hârtiei.

V. CONCLUZII

Pe fondul scăderii resurselor de lemn, trebuie lărgită gama de materii prime pentru fabricarea celulozelor și altor pastelor fibroase. Dintre plantele anuale, paiele de grâu se remarcă prin disponibilitate, compoziția chimică convenabilă și prețul competitiv, fiind recomandate și prelucrării pe cale chimică. Analiza literaturii de specialitate arată două direcții principale de valorificare a paielor: obținerea de celuloze înălbite și fabricarea de paste fibroase de mare randament.

Avantajele folosirii paielor se referă la faptul că ele conțin mai puțină lignină decât lemnul iar lignina este mai reactivă și de aceea paiele sunt mai ușor de dezincrustat. Lungimea medie a fibrelor este comparabilă cu cea din lemnul de foioase, iar potențialul papetar al celulozei din paie este comparabil cu al celulozei din foioase. Celuloza din paie rezultă cu grad de măcinare ridicat și nu mai necesită măcinare pentru fabricarea multor sortimente de hârtie. Totuși, celuloza din paie conține o

cantitate mare de material fin care îi reduce substanțial capacitatea de deshidratare.

Dezavantajele paielor ca materie primă pentru fabricarea celulozei se referă la densitatea scăzută, care mărește costul operațiilor de transport și depozitare. Totuși, paiele se compactizează ușor, fapt care atenuază costurile. Totodată, paiele se utilizează și în agricultură sau la obținerea combustibililor prin peletizare. Principalul dezavantaj tehnologic al paielor la fabricarea celulozei este conținutul ridicat de dioxid de siliciu, care îngreunează prelucrarea soluției reziduale.

Procedeele pentru obținerea celulozei din paie au fost preluate de la dezincrustarea lemnului și adaptate noii materii prime. Cele mai utilizate sunt procedeele alcaline: sulfat, natron, natron cu antrachinonă, sulfat alcalin. Pe scară mai mică se utilizează procedee cu hidroxid de potasiu și amoniu și cu var. Cu ajutorul procedeele alcaline se obțin celuloze cu conținut redus de lignină care se înălbesc ușor, cu reactivi nepoluanti de tipul peroxidilor, ozonului, oxigenului.

Din plante anuale se obțin și paste de mare randament prin procedee de rafinare, cu sau fără tratament chimic. Pastele de mare randament diferă semnificativ de celuloze prin compoziția chimică și proprietățile fibrelor. Ele conțin aproape aceeași cantitate de lignină și de hemiceluloze ca în materia primă și din acest motiv, de regulă, nu sunt destinate înălbirii. Datorită conținutului ridicat de lignină, fibrele sunt rigide și de aceea se folosesc la fabricarea hârtiilor pentru cartonul ondulat. Pasta conține o cantitate mare de material fin, existent inițial sau format în timpul tratamentului mecanic. Pastele de mare randament din paie sunt destinate fabricării hârtiilor pentru cartonul ondulat sau intră în compoziția unor sortimente de cartoane.

VI. MULȚUMIRI

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OBTAINING OF NANOCELLULOSE (II)

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Abstract

Nanocelluloses represent new materials with interesting properties being used in different fields of applications. This explains why, at present there are a lot of preoccupations to improve the obtaining procedures to increase the efficiency and to reduce energy consumption. At the same time, the possibilities to find accessible and cheap raw materials, especially residues resulting in different industries, are followed. In this review some examples to use wood and different wastes to obtain nanocelluloses are presented.

Key words: Celluloses, Nanocrystals, Nanofibres, Wood, Agriculture Wastes, Bioresidues

Rezumat

Nanocelulozele reprezintă materiale noi cu proprietăți interesante utilizabile în diferite domenii de aplicații. Această situație explică mulțiplele preocupări pentru îmbunătățirea procedurilor de obținere cu scopul de a crește eficiența tehnologiilor și reduce consumul de energie. În același timp sunt urmărite posibilitățile de a găsi materii prime rezultate ca produse secundare în diferite industrii. În acest articol sunt prezentate câteva exemple privind utilizarea atât a lemnului, cât și a unor deșeuri rezultate din prelucrare pentru obținerea nanocelulozelor.

Cuvinte cheie: Celuloză, Nanocristale, Nanofibre, Lemn, Deșeuri agricole, Bioreziduuri

I. INTRODUCTION

Nanotechnology could transform the forest and agricultural products and some wastes from food industry ranging from production of raw materials to new applications and to new generation of functional nanoscales celluloses [1].

The development of nanocelluloses has attracted significant interest in the last few decades due to the unique characteristics it endows such as surface area-to-volume ratio, high Young's modulus, high tensile strength low coefficient of thermal expansion and optical properties. These amazing physico-chemical properties and wide application prospects have attracted significant interest from both research scientists and industrialists.

Thus, nanocelluloses could be applied as composite materials, nonwovens, adsorbent webs, paper and board, food products, cosmetics and toiletry, filter materials, advanced building products, recyclable structural and interior components for transport (automobile and aircraft), novel plastics, fiber-reinforced composites, switchable optical films, biocomposites for bone-repair, additives for paints, pigments and inks iridescent or magnetic films. The applications in the food industry include as low calorie thickeners, flavor carriers and suspension. They hold promise for use in personal hygiene and absorbent products and are being investigated for use in emulsion, dispersion, oil drilling muds and hydraulic fracturing fluids for oil and gas recovery. There are possible medical,

cosmetic and pharmaceutical uses and a host of other uses have been suggested (e.g. fibers, films, cellulose derivatives, tobacco filter additives, battery separators, loudspeakers, flexible displays, computer components, lightweight body armor etc.).

In order to efficiently isolate cellulose nanomaterials, the removal of lignin and hemicelluloses is essential. During isolation process of nanocellulose, chemical purification such as delignification-bleaching is done with the aim of changing lignocellulosic fibers into individual cellulose fibers through the removal of the lignin from the plant structure. Generally, the raw materials with higher

carbohydrate contents and lower amounts of extractives and lignin are suitable for nanocellulose production. The higher extractives and lignin content reduces nanocellulose isolation yield and increase chemicals and energy consumption during the separation process, which can be easily translated into higher cost.

The nanocellulose can be extracted from natural sources using chemical, enzymatic and mechanical processes, which include high-pressure homogenization, grinding and refining treatments [2].

II. PREPARATION OF NANOCELLULOSES

Nanocelluloses can be obtained from various cellulosic sources. (figure 1).

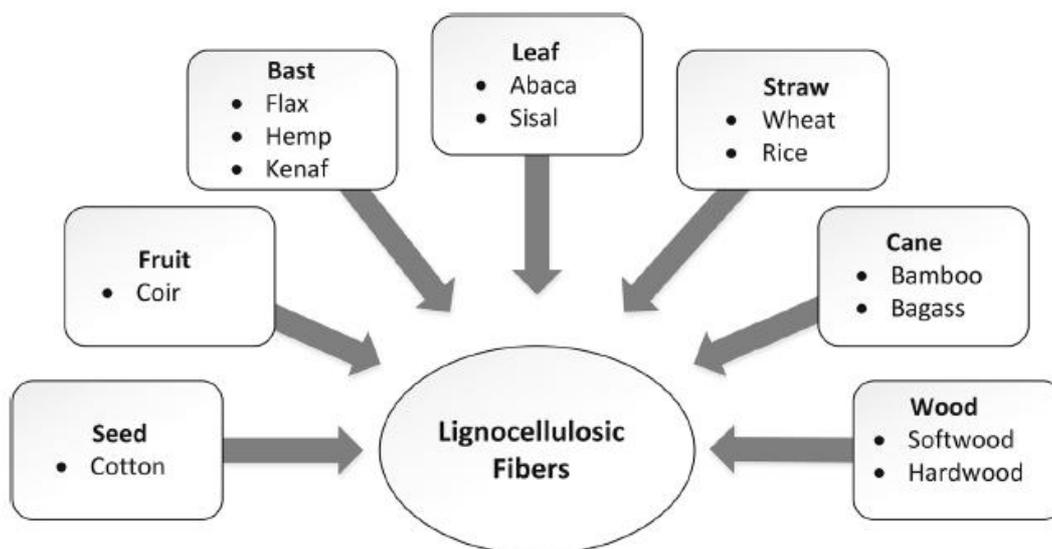


Fig. 1 Classification of lignocellulosics used to obtain nanocellulose

In this review some methods for isolation of nanocelluloses, including nanocrystals and nanofibres (CNCs and CNFs, respectively) are presented.

Regarding the extraction of crystalline cellulosic regions, in the form of CNCs, a simple process mostly based on acid hydrolysis is generally used. Acid hydrolysis is a well-known process to produce CNC.

It is believed that this method leads to isolation of CNCs with a high degree of crystallinity by removing the amorphous part of the raw material.

Acid hydrolysis is usually performed using HCl or H₂SO₄, along with microbial/enzymatic hydrolysis to produce nanocrystals. Effective parameters in this process include the hydrolysis time and temperature, acid concentration and acid/fiber ratio. In case of nanocrystals the effect of the acid/pulp ratio and H₂SO₄ hydrolysis time on the properties of wood nanocrystals suspensions were evaluated. It was found that shorter CNCs with a lower dispersion index can be obtained for a longer time of hydrolysis. By increasing the acid/pulp ratio the dimensions of the nanocrystals decreased. Microbial hydrolysis is ecofriendly and does not need surface modification.

Wood

The CNFs was extracted by a mechanical disintegration of wood cells and this new type of cellulosic material was named microfibrillated cellulose (MFC). It was obtained using a Gaulin homogenizer and a pressure of 8,000 psi. Cooling was used to maintain a product temperature in the range 70-80°C during homogenization treatment. The majority of cellulosic materials can generally be taken as a source to be used to produce CNF and this can be isolated from wood using a combination of chemo-mechanical treatments. There are several steps involved in mechanical treatments such as crushing in liquid nitrogen, refining and homogenizing [2]. Usually, bleached kraft pulp was used in order to isolate CNFs.

Agriculture and bioresidues

Although wood is a major source for isolation of CNFs, the increasing demands from paper industry, building production and furniture industries have increased the need for low cost raw materials such as agriculture residues and annual plants. These materials are considered as an effective alternative source of cellulose for producing CNFs with acceptable properties. In addition, the industrial bioresidues can also be another by-product which has great potential for use a cheap and suitable source for nanocellulose production.

For this purpose various researchers have suggested using annual plants such as flax, hemp, sisal, kenaf and agricultural crops including those obtained from the empty fruit bunches, rice, sugar cane, pineapple and wheat. If comparing crop residues with wood they possess positive characteristics such as low contents of lignin and hemicelluloses. Another example of non-wood sources that might be used to derive nanocellulose is industrial bioresidues. In fact, industrial bioresidues have an advantage compared to other cellulosic feedstocks by having low or even negative costs. On the other hand, in an ever-increasingly environmentally friendly world, the use of the bioresidues as another usable material can contribute to solving disposal problems for industries.

Numerous studies have focused on the isolation of CNFs from non-wood and bioresidues sources including kenaf bast, kenaf stem, wheat straw and soy hulls, empty fruit bunches, sugar beet pulp, potato pulp, swede root, bagasse, rice straw, algae, stem of cacti, banana rachis and industrial bioresidues. On the other hand kenaf bast, coconut husks, grass, rice straw, pea hull fiber, cotton. Sisal, flax and agriculture by-products are some examples of non-wood sources for preparing CNC.

Purification of cellulose from plant fibers involves chemical treatments consisting of alkali extraction and bleaching. Owing its hierarchical structure (Figure 2) and semicrystalline nature, nanoparticles can be extracted from this naturally occurring polymer using top-down mechanically or chemically deconstructing strategy.

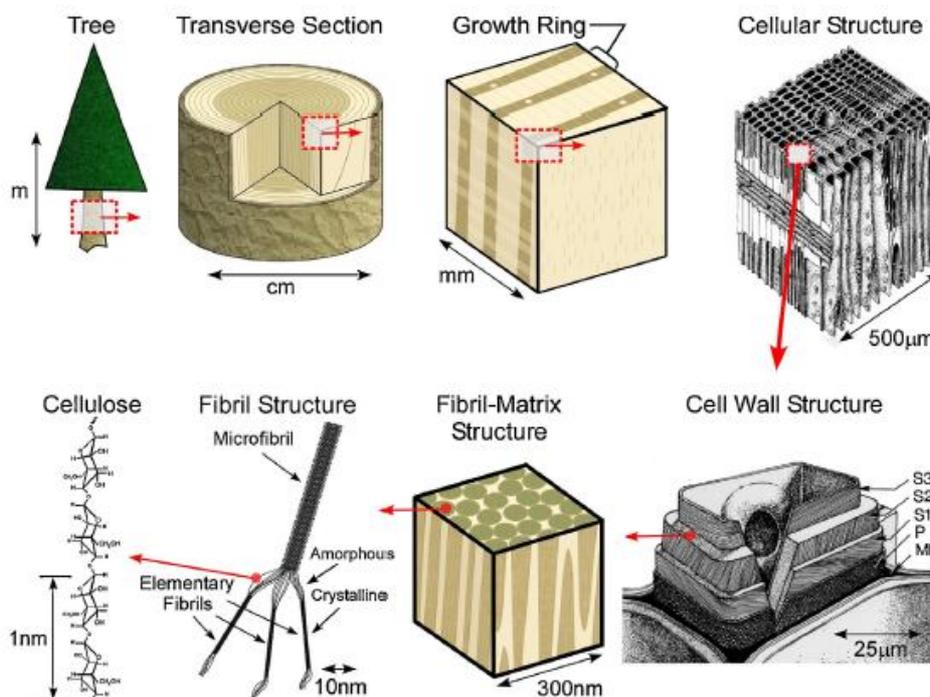


Fig. 2 Wood hierarchical structure: from tree to cellulose [3]

Mechanically induced destructuring strategy

Multiple mechanical shearing actions applied to cellulose fibers release more or fewer individual microfibrils. This material is usually called microfibrillated/nanofibrillated cellulose (MFC)/(NFC/CNF). They mainly consist of high-pressure homogenization and/or grinding. However, this production route is normally associated with high energy consumption for fiber delamination. Therefore, different pretreatments have been proposed to facilitate this process, for example, mechanical cutting, acid hydrolysis, enzymatic pretreatment, and introduction of charged groups through carboxymethylation or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation.

Chemically induced destructuring strategy

A controlled strong acid hydrolysis treatment can be applied to cellulosic fibers allowing dissolution of amorphous domains and therefore longitudinal cutting of the microfibrils. The ensuring nanoparticles are generally called cellulose nanocrystals (CNCs) and are obtained as an aqueous suspension. When observed between crossed-Nicols the CNC dispersion shows the formation of birefringent domains. During the acid hydrolysis process, the hydronium ions penetrate the cellulose chains in the amorphous regions promoting the hydrolytic cleavage of the glycosidic bonds and releasing individual crystallites after mechanical treatment (e.g. sonication). Different strong acids have been shown to successfully degrade fibers but hydrochloric and sulfuric acids have been extensively used. However, phosphoric, hydrobromic and nitric acids have also been reported for the preparation of crystalline cellulosic nanoparticles. One main reason for using sulfuric acid as

hydrolyzing agent is its reaction with the surface hydroxyl groups *via* an esterification process allowing the introduction of anionic sulfate ester groups. The presence of these negatively charged groups induces the formation of a negative electrostatic layer covering the nanocrystals and promotes their dispersion in water. However, it compromises the thermostability of the nanoparticles. To increase the thermal stability of H₂SO₄-prepared nanocrystals, neutralization of nanoparticles by sodium hydroxide can be carried out.

These nanoparticles occur as high aspect ratio rod-like nanocrystals, or whiskers. Their geometrical dimensions depend on the origin of the cellulose substrate and hydrolysis conditions. Each rod can be considered as a cellulose crystal with no apparent defect. CNCs generally present a relatively broad distribution in length because of the diffusion-controlled nature of the acid hydrolysis. The average length is generally of the order of a few hundreds nanometers and the width is of the order of a few nanometers. An important parameter for CNCs is aspect ratio, which is defined as the ratio of the length to the width. It varies between 10 for cotton and 67 for tunicin or capim dourado (golden grass). Acid hydrolysis is classical way of preparing CNCs. However, other processes allowing the release of crystalline domains from cellulosic fibers have more recently been reported, including enzymatic hydrolysis treatment, TEMPO oxidation, hydrolysis with gaseous acid and treatment with ionic liquids [4].

Nanocellulose from wood

Nanocellulose is a novel material that can be produced from wood, non-woody plants and agricultural residues. The morphology and type of wood nanocellulose may vary significantly including cellulose nanocrystals, micro- and nanofibrillated celluloses. Nanofibrillated cellulose has commonly been produced with homogenizers, fluidizers and grinders. Nanofibrillated cellulose materials contain a major

fraction of nanofibrils with typical diameters less 20 nm and length in the micrometer scale.

Pretreatments, which are applied to facilitate the fibrillations of cellulose fibres, involve mechanical, enzymatic and chemical pretreatments. Mechanical and enzymatic pretreatments preserve the surface chemistry of cellulose fibres, i.e. the surface of cellulose nanofibrils is strongly hydrophilic and is covered by hydroxyl groups. Chemical pretreatments yield a homogeneous nanofibril morphology with typical width less than 20 nm.

TEMPO-mediated oxidation leads to a regiospecific introduction of carboxyl groups in the C5 position and small amounts of aldehyde groups. Carboxymethylation modifies the surface chemistry of the nanofibrils, introducing carboxymethyl groups. In addition to the mentioned chemical pretreatments, sodium metaperiodate, followed by an oxidation with sodium chlorite, has been applied to enhance the nanofibrillation of cellulosic fibres and reduce energy consumption during production of nanocellulose. Sodium metaperiodate oxidizes cellulose by selective cleavage between C2 and C3 groups and yields 2,3 -dialdehyde units along the polymer chain.

Never-dried bleached *Pinus radiata* fibres were pretreated before homogenization. The pretreatment comprised three different procedures: (a) carboxymethylation, (b) carboxymethylation and periodate and (c) periodate oxidations. It was expected that carboxymethylation would produce highly nanofibrillated qualities of nanocellulose.

Carboxymethylation (CMNC)

About 110 g of pulp was disintegrated according to ISO standard 5263-1. This was followed by exchange of solvent from water to ethanol. The fibres were impregnated in a solution of 2 % monochloroacetic acid in 500 mL isopropanol for 30 min. This was transferred to a 5 L reaction vessel equipped with reflux and containing a heated solution of 16.2 g NaOH in a mixture of 500 mL methanol and 2 L

isopropanol. The carboxymethylation reaction was allowed to continue for 1 h. The carboxymethylated pulp was washed with 20 L deionized water and 2-1 0.1 M acetic acid followed by additional 10 L deionized water. The carboxyl groups were converted to sodium form by soaking the pulp in a 4 % NaHCO₃ solution for 60 min. The pulp was finally filtered and washed with deionized water until the conductivity was <5μS/cm.

Periodate oxidation (sample PNC)

The reaction was performed in a 4 % suspension of cellulose pulp. About 0.82 g NaIO₄ was added per gram cellulose. The NaIO₄ was dissolved before the cellulose pulp was added. The NaIO₄ solution was protected against light by covering the reaction vessel with an aluminium foil. The reaction was allowed to continue for 2 h at 55° C. The pulp was filtered and washed with deionized water until the conductivity was <5μS/cm.

Carboxymethylation and periodate treatment in combination (sample CMPNC)

The pulp fibres were both carboxymethylated and oxidized using NaIO₄ according to the methods described above. Carboxymethylation was performed prior to NaIO₄ oxidation. The pretreated pulp fibres were then homogenized with a Rannie 15 type 12.56 x homogenizer. The pulp consistency during homogenization was 0.5 %. The nanofibril width distribution of CMNC and CMPNC samples is given in Figure 3 [5].

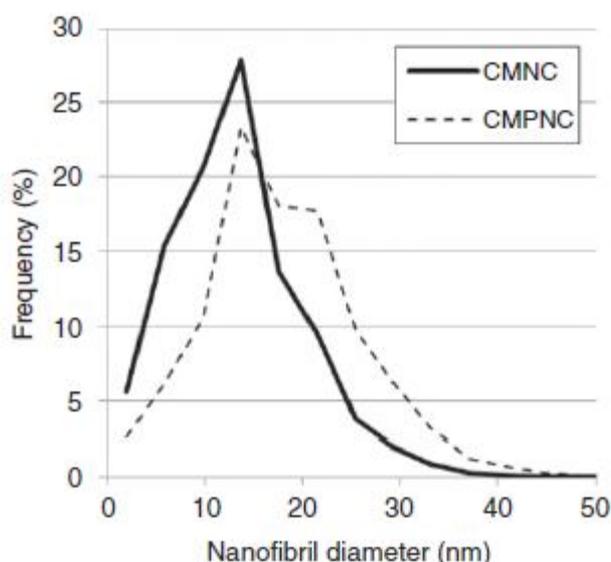


Fig. 3 Nanofibril diameter distribution based on AFM images and automatic image analysis

Nanocellulose from different lignocellulosics

At present the research is focusing on the possible use of forest or agricultural residues as NCC sources for their abundance at low economical and energetic cost, and for simplified waste disposal.

In the different climatic zones worldwide, various local sources are used for attempts of valorization in this sense and, in some cases technologies must be adapted to use certain sources (Figure 4).

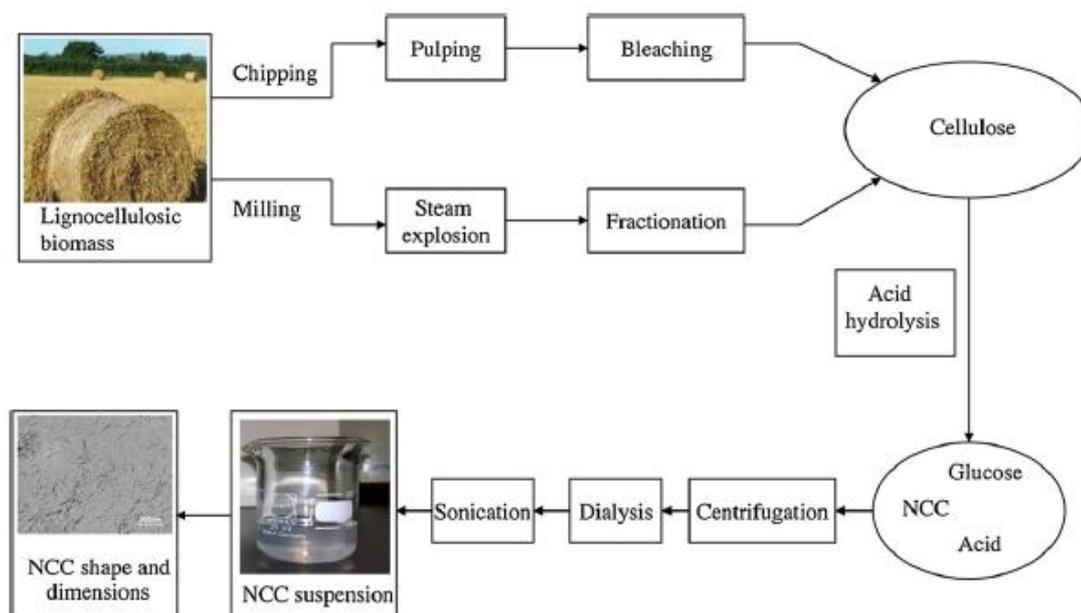


Fig. 4 Scheme of main steps needed to prepare NCC from lignocellulosic biomass

Table 1 Types of nanocelluloses

Type of nanocellulose	Synonyms	Typical source	Average size
Nanocrystalline cellulose, NCC	Cellulose nanocrystals, crystallites, whiskers, rod like cellulose, microcrystals	Wood, cotton, hemp, flax, wheat straw, rice straw, mulberry bark, ramie, MCC, Avicel, tunicin, algae, bacteria	Diameter:5-70 nm Length: 100-250 nm (from plant), 100 nm-several micrometers (from cellulose of tunicates, algae, bacteria)
Microfibrillated cellulose, MFC	Microfibrillated cellulose, nanofibrils, microfibrils, nanofibrillated cellulose	Avicel, tunicin, algae, bacteria, wood, sugar beet, potato tuber, hemp, flax	Diameter: 50-60 nm Length: several micrometers

Typical procedures for the production of NCC (Table 1) consist of the following steps:

1. Strong acid hydrolysis of pure cellulosic material under strictly controlled conditions of temperature, time, agitation, and with control of other conditions such as nature and concentration of the acid and the acid to cellulose ratio;
2. Dilution with water to stop reaction and repeated washing with successive centrifugation;
3. Extensive dialysis against distilled water to fully remove free acid molecules;
4. Mechanical treatment usually sonication, to disperse the nanocrystals as a uniform stable suspension;
5. Eventual concentration and drying of the suspension to yield solid NCC.

Integration of NCC and cellulose biofuels productions

Currently both production of nanocelluloses and cellulose biofuels are not economical, so the inclusion of the production in biorefinery would increase the number of jobs and the profitability of the venture. It was demonstrated a novel concept to integrate these productions: enzymatic fractionation was used to separate glucose stream for biofuel production and recalcitrant cellulosic solid fraction. The last one was used to produce MFC. On the other hand NCC was separated from a bioresidue of bioethanol production from lignocellulosic biomass. The bio-residue used called usually "lignin", resulted to contain high percentage of cellulose (ca. 50 %), and NCC with more than 73 % crystallinity was obtained from it with relatively good yield.

Valorization of waste liquor of acid hydrolysis

In order to decrease the general cost and to face environmental concern of concentrated strong acid solutions,

valorization of the waste liquor stream needs to be addressed. It contains sugars, in monomeric and oligomeric forms and residual sulfuric acid [6], and can be used to obtain ethanol by fermentation.

Isolation of nanocellulose from waste sugarcane bagasse

Delignification of bagasse

The dried and ground bagasse was first bleached with 0.7 % (w/v) sodium chlorite solution (fiber to liquor ratio of 1:50) at pH 4, adjusted by 5 % acetic acid and maintained with buffer solution of pH 4 while the mixture was being boiled for 5 h to remove the lignin [7]. The residue was subsequently washed with distilled water. The neutral residue was then boiled with 250 mL 5 % (w/v) sodium sulfite solution for 5 h, followed by washing with adequate distilled water to remove lignin completely and hemicelluloses partially.

Isolation of cellulose

The holocellulose thus obtained was boiled with 250 mL 17.5 % (w/v) sodium hydroxide solution for 5 h to remove hemicelluloses. At the end of the extraction, the insoluble residue (cellulose) was collected by filtration and washed thoroughly with distilled water until the filtrate was neutral. The resulting cellulosic materials were air dried, and the added to 50 mL dimethylsulfoxide in an 80°C water bath for 3 h. The product thus obtained was the filtrated washed with distilled water and air-dried.

Preparation of nanocellulose

An aqueous suspension of cellulose was prepared as follows. The delignified and hemicelluloses free cellulose as obtained earlier was acid hydrolyzed by refluxing with 60 % w/v sulfuric acid (fiber to liquor of 1:20) for 5 h at 50 °C under strong agitation. The hydrolysis was quenched by adding 5-fold excess water (100 mL) to the reaction mixture. The resulting mixture was cooled to room temperature and centrifuged. The fractions were continuously washed by

addition of distilled water and centrifuged. The centrifugation process was stopped after at least five washings, while the supernatant liquor became turbid, i.e., becoming a colloidal suspension. Under this condition, the pH of the suspension was above 5. The suspension was then sonicated for 5 min in an ice bath to avoid overheating, which can cause desulfation of the sulfate groups on the cellulose. The newly generated suspension was stored in refrigerator at 4°C.

In another variant the nanocellulose from **sugarcane bagasse** was prepared by high pressure homogenization (HPH) coupled with an ionic liquid pretreatment [8]. The HPH process resulted in nanocellulose with a diameter range of 10-20 nm. The dried and ground bagasse was first washed with deionized water, and then bleached with 1 % (w/v) sodium hydroxide solution for 1.5 h at 90° C to remove the lignin and hemicelluloses, respectively. The original cellulose was subsequently washed with acid and distilled water until the solution was neutral, and then air dried.

The dissolution of cellulose was carried out according to the following procedure. Briefly, the 1 % (w/w) bagasse cellulose/BmimCl was mixed in the microwave oven (Qpro-M, Questron Inc., Canada) at 130°C for 2 h under magnetic stirring, until cellulose was completely dissolved to form a clear and viscous solution. Then it was homogenized by high pressure homogenizer (AH100D, ATS Engineering Inc., Canada) at pressure level ranging from 40 to 140 MPa and for up to 50 HPH cycles. After cooling to room temperature, cellulose was precipitated from the IL solution by the addition of water, due to the impairment of the IL solvent properties and the increased hydrogen bond of cellulose. Finally, the regenerated nanocellulose was dried in a vacuum freeze drying equipment until reaching a constant weight.

It was proved that the [Bmim]⁺ cations in ILs can attack the oxygen atoms of H-O-H bonds, and Cl⁻ associate with the hydroxyl proton of H-O-H bonds. These two interactions can destroy the extensive hydrogen bonding network among cellulose chain, resulting in the

dissolution of cellulose. Therefore, it was considered to be an appropriate homogeneous media for cellulose because of its non-volatility, thermal stability and recyclable. Conventionally solubility of cellulose using ILs was carried out by conductive heating with an external heat source for a comparatively long time. To improve the method, cellulose was treated with ILs under microwave (MW) irradiation using MW oven with mechanically stirring. The reaction time was only 2 h, which is much shorter than the time required without microwave treatment (24 h).

Several factors could influence the efficiency of solubilisation, such as the mass ratio of cellulose to ionic liquid, the power of the microwave, the reaction temperature, as well as the dissolution time. Finally, it was found experimentally that the best solubilisation could be achieved in 1 % (g/g) cellulose/[Bmim]Cl during 130°C for 2 h at 400 W of microwave. The cellulose could be transformed into a gel or be carbonized, when the cellulose ratio was above 5 % (g/g) or reaction temperature was over 150°C. After ionic liquid pretreatment, the (sugar cane bagasse) SCB cellulose was dissolved in [Bmim]Cl to form a homogeneous solution. Then the solution was passed through high pressure homogenizer to prepare the nanocellulose. After homogeneous refining by HPH, the nanocellulose was regenerated by water, and the final recovery of cellulose was more than 90 %. In addition, the ionic liquid could be recycled and reused for several times. Therefore, it was concluded that homogeneous HPH process was an efficient method to isolate nanocellulose from SCB cellulose.

Isolation of cellulose nanowiskers from bio-residue resulted in bioethanol production

Bioethanol residue was also of interest to obtain nanowiskers.. The total yield of nanowiskers was measured as a percentage of the residue used as a starting material. The yield of pure cellulose from residue was measured to approx. 50 %. The further processing with a high-

pressure homogenizer yielded 96 % nanowiskers, whereas hydrolysis yielded 93 % based on purified cellulose. The lowest yield, 68 %, was measured for sonicated nanowiskers. The yield was measured after 30 min of sonication and removal of the sediment fraction. It might be possible to improve the yield in the sonication process by increasing the processing time.

The purified cellulose was isolated from biotehanol residue to obtain cellulose nanowiskers using three methods: (1) ultrasonication, (2) high pressure homogenization and (3) acid hydrolysis, which was tested to see if a further hydrolysis of the cellulose would increase the crystallinity (Figure 5) [9].

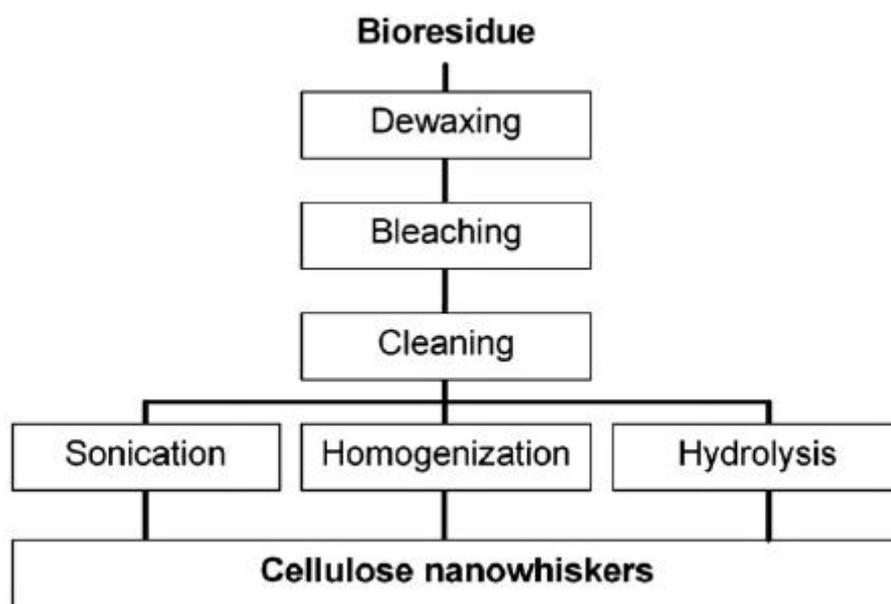


Fig. 5 Schematic diagram of the preparation process of cellulose nanowiskers from bio-residue

In the mechanical isolation process, a purified cellulose suspension of 1 wt % concentration was sonicated with a rod-type sonifier, with 24 kHz. The sonication time was set to 10 min and it was repeated 3 times. Homogenization was carried out using a high-pressure homogenizer with a pressure of 500 bar.

The acid hydrolysis was done following a method described by Bondeson et al.[10].

Cellulose nanowiskwers from coconut husk fibers

A large amount of cellulosic waste is generated yearly by the agro-industries.

There is a great demand to find other end uses for these “agricultural cellulosic wastes”. Unripe coconut husk is an example of such agro-industrial by-products for which end uses are needed [11].

Pretreatment of coconut fibers

Coconut fibers were subjected to a washing pre-treatment to remove impurities and waxy substances covering the external surface of fiber cell walls. First, fibers were chopped in a Wiley mill and sieved through a 40-mesh sieve. These fibers (100 g) were dispersed in distilled water (500 mL) for 10 min in a Waring

Laboratory Blender at full speed. This suspension was stirred for 2 h at 50 °C and filtered in order to remove soluble extractives in water. This procedure was repeated once more. The residue was dispersed in 500 mL of a 2 % NaOH solution and suspension was stirred for 2 h at 80 °C, filtered and washed with water. After washing, the alkaline treatment was repeated once more, and the fibers were dried at 50 °C for 24 h.

As lignin hinders fiber separation by acid hydrolysis, partial delignification (bleaching) was performed in order to facilitate further whisker extraction. Partial delignification was carried out so that the remaining lignin would help improve the thermal properties of the acid-extracted whiskers. Delignification was carried out in two levels: a less strong one-stage (1B) and an aggressive multi-stage (4B) bleaching. First, 5 g of dried pretreated fibers were heated between 60 and 70 °C in 150 mL water containing 1.5 g NaClO₂ and 8-10 drops of glacial acetic acid. The mixture was stirred at frequent intervals for 1 h, then cooled in ice bath, filtered quantitatively and washed with cold water. For stronger bleaching, this procedure was repeated three more times using the same conditions, i.e., treatment 1B was compromised of only one bleaching step while treatment 4 B had four steps. In the end, the bleached pulps were treated with 0.05 N nitric acid solution for 1 h at 70 °C, sieved in a 120 μm mesh size sieve and washed extensively with water.

Sulfuric acid hydrolysis

Cellulose whiskers were prepared by sulfuric acid hydrolysis. The bleached fibers were treated in a concentrated sulfuric acid (64 wt % sulfuric acid in water) at 45 °C. The ratio of fibers to acid solution was 1-10 g/mL. Since the higher the ratio of nanowhiskers-to- microfibrils the better their dispersion and stability in the aqueous medium, in order to compare both treatment hydrolysis was performed for 120, 150, and 180 min, under constant stirring. After treatment, the hydrolyzed cellulose samples were washed four times, separating the crystals from the solution

by centrifugation (10, 000 rpm, 10 min) after each washing step. The resultant precipitate was continuously dialyzed against water for 3 days until constant pH was reached. Subsequently, this precipitate was dispersed in water to obtain nanowhiskers suspensions which were used for further characterization.

Typically, coconut nanowhiskers had length ranging from 80 to 500 nm and widths of about 6 nm. A noteworthy observation is that the aspect ratio ranged from about 20 up to 60, with an average value of about 39 ± 16 , which lies in the range of long nanowhiskers which have great potential to be used as reinforcing agents in nanocomposites.

Nanocellulose structures from raw cotton linter

The amount of linter produced worldwide is around 2.5 million tons, considering the 42 million metric tons of cotton linter produced in 2010 [12]. Producing cellulose nanocrystals is an interesting use for linter. Nanocrystals of cellulose with diameters ranging from 2 nm to 20 nm and length ranging from 100 nm to 2.1 μm are called whiskers, nanowhiskers, or nanofiber, and they can be obtained from many natural fibers. The linter is an attractive source of nanowhiskers because it has more cellulose than other natural fibers commonly used such as: sisal (*Agave sisalana*) (67-78 %), banana (*Musa spp.*) (54-64.4 %), sugarcane (*Saccharum officinarum*) bagasse (44.9-45 %), bamboo (*Bambusa spp*) (41.8-54.0 %), and coconut (*Cocos nucifera*) husk (32.5-45.0 %).

Nanowhiskers preparation

The linter was ground in a Wiley mill and hydrolyzed without any chemical pretreatment. The method of acidic hydrolysis was applied with minor adaptation [13]. The linter was mechanically stirred at a ratio of 1:20 (w/v) of aqueous concentrated sulfuric acid (60 %,w/w) with a Teflon bar dispersing element, at 45 °C, for 60 min. The nanowhiskers suspension was centrifuged for 15 min at 13,000 rpm in a

High-speed Refrigerated Centrifuge and the precipitate was resuspended in distilled water and dialyzed with tap water until a pH (6-7) was reached. The process from centrifugation through dialysis was repeated three times.

The nanocrystal' dimensions are influenced by the hydrolysis conditions or pretreatment. However, it is widely accepted that the raw material is the most important factor. The aspect ratio (L/D) of the crystals extracted from linter is different from those extracted from coconut husks (35-44), sugarcane bagasse (32-64), sisal (43-60), regular cotton fiber (10-14), microcrystalline cellulose (11-13) and flax (*Linum usitatissimum*) (15). The aspect ratio of linter nanowhiskers does not overlap with any of those listed, and this raw material is an option if nanocrystals with specific dimensions are required by industry.

Cellulose nanowiskers from cotton fibres

To produce cellulose nanowiskers by controlled hydrolysis of MCC, the fungus *T.reesei* was used under submerged fermentation process [14]. The MCC (microcrystalline cellulose) was prepared from cotton fibers (short staple cotton variety: *Bengal desi*) by conventional hydrochloric acid hydrolysis (4N HCl). This resulted in MCC with wide size distribution in the micrometer range. To have uniform size distribution, the MCC was sieved through various sieves and the size range of 45-53 μm was selected for further work.

Microbial hydrolysis of MCC

The 24 h inoculum of the fungus *T. reesei* (ATCC 13631) was prepared in potato dextrose broth by inoculation of spore suspension ($\sim 3 \times 10^6$ spores/mL). The optimized concentration (5 %) of inoculum was added in Mandel's medium having MCC as sole carbon source in 250 mL conical flask at 25°C/30°C under shaking conditions (150 rpm). After fermentation, the broth was subjected to differential relative centrifugal forces to optimize the sedimentation of all particles

size more than 1 μm . The resultant supernatant was filtered through 100 kDa ultrafiltration membrane by vacuum suction and the cellulose nanowiskers (CNW) trapped on the surface of membrane was removed with a jet of ultrapure water and freeze dried for further analysis. The cellulose content was determined and yield was calculated as percent of cellulose content to that of initial MCC concentration. For comparison, CNW was prepared by conventional process using 64 wt % of sulfuric acid hydrolysis of MCC at 35°C for 1 h. The acid hydrolyzed sample was neutralized with excess of water and washed with water by repeated centrifugation till pH was neutralized and freeze dried.

The penetration of fungus into ordered regions of MCC during incubation resulted in reduced crystallinity of CNW prepared by microbial hydrolysis compared to that of acid hydrolysis. The reinforcing effect of CNW in polymer composites is mainly due to very strong and rigid three-dimensional network of hydrogen-bonded whiskers. The traditional method of acid hydrolysis resulted in sulfation on the surface of CNW while the surface chemistry of CNW prepared by fungal hydrolysis remains unaltered; this in turn will improve its performance as nanofillers in composites. Also, this enhances the biocompatibility of CNW with its use in biomedical applications and pharmaceuticals.

Obtaining of cellulose nanocrystals from waste paper

The removal of the amorphous region by acid hydrolysis results in the formation of highly ordered (crystalline) structure, the cellulose nanocrystals (CNCs). Waste paper provides a potential source of raw material for the production of CNCs [15]. The extraction of cellulose particles from waste paper was carried out by its subjecting to alkali and bleaching treatments followed by controlled-condition of acid hydrolysis for the isolation of CNCs. The waste paper was cut in small pieces and boiled for more

than 12 h, during which distilled water was added periodically. It was then ground to form slurry, filtered and rinsed several times with 5 % (w/v) of reagent grade sodium hypochlorite. The slurry was then filtered and washed with distilled water until neutral pH was achieved. The CNCs were obtained by acid hydrolysis of the pretreated source material using 60 % (v/v) H₂SO₄ solution at 45°C with constant stirring. The optimum reaction time was fixed at 1 h with pretreated solution to acid ratio of 1:2 (v/v). The mixture was diluted with distilled water followed by centrifugation to remove spent acid. The suspension was then subjected to dialysis against distilled water until a constant pH was obtained. After this treatment more than 70 % of the CNCs have an aspect ratio in the range 20-50. The diameter of CNCs ranged from 3-10 nm while the length range from 100 to 300 nm with an average value of ~ 4nm and ~170 nm, respectively.

Isolation of cellulose nanocrystals and cellulose nanofibres from maize stalk residues

Cellulose nanocrystals (CNCs) and cellulose nanofibres (CNFs) (nanofibrillated cellulose) were successfully extracted from cellulose obtained from maize stalk residues [16]. The post-harvested maize stalks were grounded into a coarse powder by Hammermill. The maize stalk powder was then weighed and dried in an oven at 50°C overnight and treated with 1.5 % NaOH, 1.5 % NaClO₂, and 1.5 % KOH, respectively, for 1h. Each treatment was repeated four times with repeated washes using deionized water to remove excess chemicals and achieve a neutral pH. The schematic diagram of the extraction of cellulose from maize stalk residues and extraction of cellulose nanocrystals and nanofibers is shown in Figure 6.

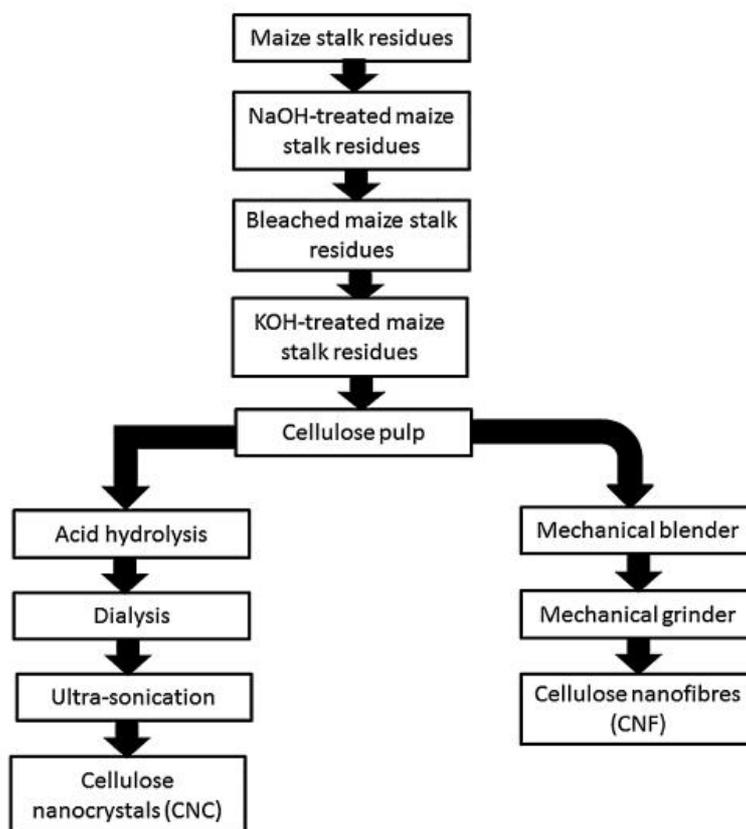


Fig. 6 Extraction of cellulose nanocrystals and nanofibres from cellulose obtained from maize stalk residues

Extraction of CNFs

Cellulose pulp (2 %) was agitated in a mechanical blender [Silverson L4RT-England] at 35000 rpm for 15 min. Then dispersed suspension was ground using a supermass colloidier [MKCA6-34-Masuko Sangyo Co, Ltd., Japan] at a speed of 1500 rpm for 20 min until a gel-like substance was achieved.

Extraction of CNCs

Cellulose obtained from maize stalk residues after KOH treatment was hydrolyzed using 50 % acid concentration under strong agitation of 1000 rpm, at 40°C for 30 min, keeping acid/pulp ratio at 20:1 (mL/g). The hydrolysis process was terminated by adding 10 folds (1000 mL) of deionized water. The suspension was then centrifuged at 8000 rpm for 10 min and dialyzed with deionized water for 3 days until the pH was neutral. Subsequently, the suspension was dispersed by ultrasonication for 1 min. Finally, the suspensions were stored in a refrigerator at 4°C with the addition of few drops of chloroform to avoid fungal growth and used to obtain micro- and nanopapers.

Nanocellulose from banana (pseudo stem), jute (stem) and pine apple leaf fibres

These raw materials were used to obtain nanocellulose. To study the feasibility of extracting cellulose from these wastes the steam explosion technique along with mild chemical treatment were adopted. These processes include usual chemical procedures such as alkaline extraction, bleaching and acid hydrolysis but with a very mild concentration of chemicals. Banana, pine apple leaf fibres (PALF) and jute were soaked with 2 % caustic soda and placed 6 h at a temperature of 30°C (step 1) [17].

Steam explosion technique was applied on the mercerized fibres at a pressure of 137 Pa, for 1h. Steam pre-treatment is performed by loading lignocellulosic material directly into steam gun and treating it with high pressure steam at temperatures within 200-250°C.

Substrates are then recovered by water washing (step 2).

Mercerized, stem exploded sample is then subjected to bleaching. After successive chemical treatments, the bleaching treatment with a chlorite (NaClO_2) solution (pH 2.3) for 1 h at 50°C was performed to remove the remained lignin (step 3).

The bleached sample is then subjected to mild acid treatment. 5 % oxalic acid was used for the acid hydrolysis and followed by second of steam explosion for 1h. 137 Pa pressure was used followed by sudden release of pressure. The fibres were then washed thoroughly and then subjected to mechanical stirring followed by sonication (step 4). The samples were further broken down into leaner fragments by the sonicator. The slurry obtained after sonication exhibited a remarkably high viscosity. It suggested that the synthesis of homogeneous dispersion of hydrophilic nanofibrils in water from natural fibres has been accomplished. The process provided high turbulence and shear that created the efficient mechanism of reduction in size nanocellulose level.

The steam exploded fibres from pine apple leaf were bleached using a mixture of NaOH and acetic acid (27 and 78.8 g respectively) and a mixture of 1:3 sodium hypochlorite solutions [18]. The bleaching was repeated six times. After the bleaching the fibres were thoroughly washed in distilled water and dried. The steam exploded bleached fibres were treated with oxalic acid of 11 % concentration in an autoclave until it attained a pressure of 20 lb. The pressure was released immediately. The autoclave was again set to reach 20 lb and the fibres were kept under that pressure for 15 min. The pressure was released and the process repeated eight times. The fibres were taken out washed until the washing no longer decolorized KMnO_4 solution to make sure that the washings are free from acid. The proceeded nanofibres were suspended in water and kept stirring with a mechanical stirrer of type RQ-1.27 A and 8000 rpm for about 4 h until the fibres are dispersed uniformly. The size distribution

of PALF nanofibres was established (Figure 7).

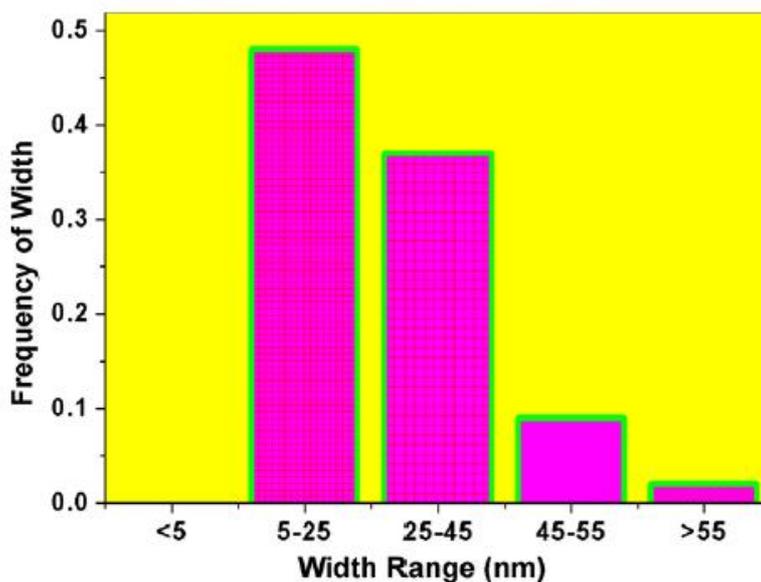


Fig. 7 Size distribution of PALF nanofibres

Isolation of cellulose nanocrystals from rice straw

Rice straw was thoroughly washed 3-4 times with warm tap water to remove dirt and aqueous soluble substances, followed by prolonged (about one week) air drying [19]. The dry clean rice straw was milled (Thomas –Wiley Laboratory Mill model 4, Thomas Scientific, USA) to pass through a 60-mesh screen. Rice straw powder (30 g) was first extracted with 2:1, v/v toluene/ethanol (450 mL) mixture for 20 h to remove wax, pigments and oils, followed by oven-drying at 55°C for 24 h. The dewaxed powder was then immersed in 1.4 % acidified NaClO₂ (1000 mL), with pH adjusted to 3.0-4.0 by CH₃COOH, at 70°C for 5 h to dissolve lignin. After quenching the reaction with ice and decanting the excess liquid, the light yellow solid was washed with copious amount of water until filtrate becoming neutral. Hemicelluloses and silica in the delignified powder were leached with 600 mL 5 % KOH at room temperature for 24 h and then at 90°C for 2 h. The white cellulose powder was centrifuged and washed with copious amount of water until filtrate reached neutral. The aqueous sample suspension (~300mL) was quickly

frozen by pouring liquid nitrogen (N₂) into the sample container and then freeze-dried (FreZone 1.0 L Benchtop Freeze DrySystem, Labconco, Kansas City, MO) to remove water.

Preparation of cellulose nanocrystal fibres

Cellulose isolated from rice straw was hydrolyzed using 64-65 wt% sulfuric acid at an 8.75 mL/g acid-to-cellulose ratio, and a temperature of 45 °C for 30 or 45 min.

Acid hydrolysis was stopped by diluting with 10-fold ice water. The resulting cellulose nanocrystal gel was washed once, centrifuged at 5000 rpm for 25 min at 10°C, and then dialyzed with regenerated dialysis membranes with 12-14 kDa molecular weight cut off (Fisherbrand, Pittsburgh, PA) against ultra-pure water (Millipore Milli-QUFPlus (until reaching neutral pH. The suspension was sonicated (Branson ultrasonic processor model 2510, Danbury CT) in an ice bath for 30 min and then filtered (Whatman 541, Maidstone, Kent, England) to remove large pieces of aggregates. The CNC suspension at about 0.06 wt % was quickly frozen by pouring liquid nitrogen into the sample container

and freeze-dried overnight to remove water the dried product was stored under vacuum for the following characterization.

Cellulose nanocrystals from chardonnay grape skins

This study is the first to isolate pure cellulose from grape skins generated from white winemaking process and to derive cellulose nanocrystals. Several chemical processes reported for biomass separation including solvent extraction, acid/base dissolution and oxidation/reduction over a wide range of reaction conditions were evaluated to design the most effective approach to isolate cellulose from grape skins collected from chardonnay winemaking process [20].

Isolation of cellulose from grape skins

The non-cellulosic components in grape skins were removed to isolate cellulose by incorporating and streamlining procedures applied for varied biomass sources. The as-received grape skin was milled (Thomas-Wiley Laboratory Mill) to pass through a 60-mesh screen, followed by oven-drying at 70°C for 2 days. The dry grape skin powders (30 g) were first extracted with 2:1 toluene/ethanol (450 mL) mixture for 20 h to remove wax, phenolics, pigments and oils, followed by oven-drying at 70°C for 24 h. The organic-extracted powders were then heated in 2 % H₂SO₄ (600 mL) aqueous solution under constant stirring at 90°C for 5 h to hydrolyze acid soluble polysaccharides and polyphenolics, filtered and washed with water to neutral pH. The acid treated powders were further leached with 5 % NaOH (600 mL) at ambient temperature for 24 h and continued at 90°C for 5 h to dissolve hemicelluloses and other base soluble polysaccharides, filtered and thoroughly washed to neutral pH.

The base treated sample was bleached by 5 % H₂O₂ (600 mL) with pH adjusted to 11.5 by NaOH at 45 °C for 8 h (more H₂O₂ as well as higher temperature, e.g., 70 °C, may be necessary according to the sample color change), then cooled to

ambient temperature for 24 h to oxidize and dissolve lignin and phenolics. The bleaching effect was enhanced by continuing the reaction in 1.4 % acidified NaClO₂ (1000 mL), with pH adjusted to 3.0-4.0 by CH₃COOH, at 70 °C for 5 h then at ambient temperature for 24 h to dissolve all residual lignin, phenolics and impurities. The final product was washed with water until neutral. The aqueous suspension (~ 300 mL) was quickly frozen by pouring liquid nitrogen (N₂) into sample container and freeze-dried to remove water.

Preparation of nanostructures from grape cellulose

Cellulose isolated from grape skins was hydrolyzed using 64-65 wt % sulfuric acid at an 8.75 mL/g acid-to-cellulose ratio as in the case for wood pulp and cotton, and at a temperature of 45 °C for 30 min. Acid hydrolysis was stopped by diluting with 10-fold ice water. The resulting cellulose gel was washed once, centrifuged at 5000 rpm for 15 min at 10° C, and then dialyzed using regenerated cellulose dialysis membranes with 12-14 kDa molecular weight cut off against ultra-pure water until reaching neutral pH. The suspension was sonicated in an ice bath for 30 min, and then filtered to remove larger pieces of aggregates. The suspension of cellulose nanocrystals (CNS) at about 0.01 wt % was quickly frozen by pouring liquid nitrogen into the sample container and freeze-dried overnight to remove water. The dried product was stored under vacuum for the following characterizations.

TEM observation of grape cellulose nanocrystals showed only nano-scale spheres or nanoparticles. The diameters of these spherical cellulose nanoparticles ranged from 10 to 100 nm, with majority between 30 and 65 nm. Based on 169 TEM images of CNCs these spherical cellulose nanoparticles have a calculated mean size of 48.1 (±14.6) nm. AFM further disclosed that most of spherical nanoparticles actually consisted of 50 nm long nano-rods as cores surrounded by abundant cellulose nano-fragments less than 5 nm in sizes as the

shells. It is highly possible that the core-shell cellulose nanostructure is created by self-assembly process of cellulose fragments and rods induced from their strong interfacial hydrogen bonds.

Nanocellulose from citrus waste

Owing to the low energy consumption and the addition of significant value, nanocellulose extraction from agricultural waste is one of the best alternatives for waste treatment. Different techniques for the isolation and purification of nanocellulose have been reported and combining these techniques influences the morphology of the resultant fibres. Thus far, the motivation to explore more locally obtained residues has increased interest in nanocellulose production using cereal by-products such as wheat straw, soy hulls, soybean straw, sorghum fibres and rice straw, as well as other crop residues such as cassava bagasse, banana fibres, pineapple leaves, sugarcane bagasse and orange bagasse.

The most common hydrolyzing agent is sulfuric acid, which stabilizes the nanowhisker suspension by electrostatic repulsion avoiding fibril aggregation, but modifies the native cellulose surface. Moreover, acid hydrolysis under milder conditions using hydrochloric and oxalic acids has been successfully used for

pineapple, banana and jute lignocellulose materials.

The nanostructuration or dispersion of microcrystalline cellulose is typically the step that requires additional energy consumption, because it is generally achieved by various mechanical treatments, such as cryocrushing, high intensity waves (ultrasonication) and high-pressure homogenization. To reduce energy consumption an alternative has been proposed: an enzymatic hydrolysis step that provides a solid remnant with high content of microcrystalline cellulose with the resultant liquor content used for the production of second generation ethanol.

Pretreatment of citrus-waste biomass fibers

Bagasse from the *Citrus sinensis* (L) *osbeck* variety was ground, sieved to a particle size of 0.85-1.15 mm and oven-dried at 120° C. The resultant biomass was pretreated by delignification using NaOH (4 % w/v, 1:25 ratio) and subsequent bleaching with 1.7 % w/v sodium chlorite at pH 4.5. For each step, the samples were maintained at 120°C under a pressure of 1 atm for 30 min and the residual reagents were removed by vacuum filtration with hot water (Figure 8) [21].

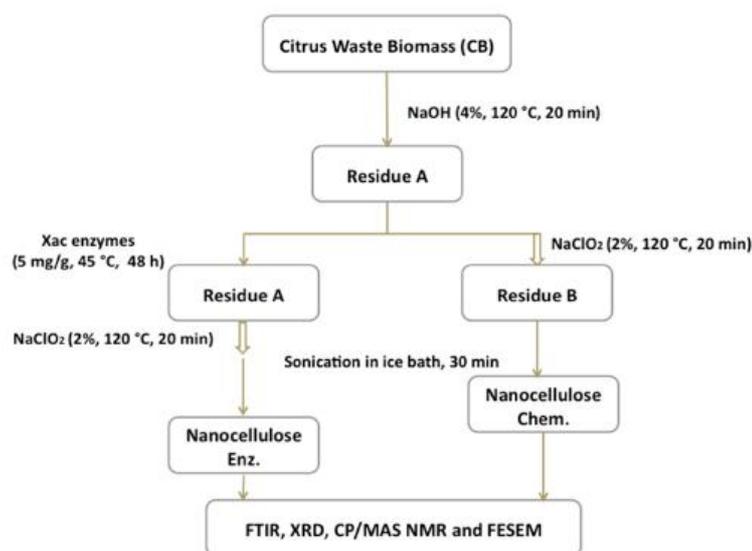


Fig. 8 Flowchart illustrating the key steps in the citrus-waste biomass processing used to produce nanocellulose fibers

Enzymatic hydrolysis and isolation of cellulose nanofibers

The fibers resulting from the pretreatment process were diluted in water until 17 % w/v was achieved, and this solution was adjusted to pH 5.0 for enzymatic hydrolysis. Then 5 mg of the *Xac* (*Xanthomonas axonopodis* pv.citri) protein solution were added per gram of CB. Enzymatic hydrolysis was performed at 45°C and 90 rpm for 48 h. The hydrolyzates were then filtered by vacuum filtration before dilution of the bioresidue to approximately 1 % w/v, and the dilute filtrate was subsequently dialyzed with water in a cellulose membrane (6-8 kDa cut off, Fischer *Sci.*). The sonication of the fibrous material was performed with a tip that delivered a power of 75 W (VCX-750, Vibra-Cell, Newtown, CT, USA) for 12 min. This sonication process was performed in triplicate.

III. CONCLUSIONS

The information presented in this review demonstrate that there is a lot of possibilities to obtain cellulose nanocrystals and microfibrillated cellulose using along with wood some residual lignocellulosics resulted in industry, agriculture and food processing. These examples could be associated with the biorefining which allow to recover the other compounds and opens new perspectives both for nanocelluloses obtaining and for their use in different fields.

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**CELLULOSE CHEMISTRY AND
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MODIFICATION OF β -CYCLODEXTRIN THROUGH SOLUTION RINGOPENING OLIGOMERIZATION OF β -BUTYROLACTONE

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β -cyclodextrin (CD) derivatives were prepared through ring-opening of β -butyrolactone (BL) in DMSO solution initiated by CD at relatively low temperature in the presence of (-)-sparteine (SP) as nucleophilic activator. The reaction was proved to yield a mixture of polyhydroxybutyrate (PHB) and 3-OH butyrate cyclodextrin derivatives (CD-HB). Following separation, the resulted products were thoroughly characterized through NMR spectroscopy and electrospray ionization mass spectrometry (ESI MS) coupled with liquid chromatography (LC). The CD-HB products are described in view of their substitution degree, substitution pattern at glycoside ring level and length of the oligomer chains attached to the CD, taking into account both NMR and ESI MS characterization methods. The kinetics of β -butyrolactone ring-opening in the presence of CD and SP is evaluated through ^1H NMR spectroscopy showing that secondary processes are contributing to the monomer conversion.

Keywords: β -cyclodextrin, β -butyrolactone, electrospray mass spectrometry, sparteine, polyester, liquid Chromatography

BINDING OF BILE ACIDS BY CELLULOSE-BASED CATIONIC ADSORBENTS

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One of the ways to regulate the cholesterol level in the blood is by adsorption of overproduced bile acids from the gastrointestinal tract. For this purpose, synthetic anion exchangers have been in clinical use for many years. The efficiency of these sorbents is rather low, because of their low binding capacity. In this work, cationic cellulose derivatives of different structure were evaluated as sorbents for binding of bile acids. It was found out that adsorption of bile acids is highly affected by pH. This was explained taking into account dissociation constants of the bile acids, as well as of the functional groups of the adsorbents. It has been showed that the cellulose-based adsorbents are more effective bile acid binders than the commercial ones, due to their more accessible structure. Comparing cellulosic adsorbents, the macroporous adsorbent DEAE-Granocel in all cases showed the best sorption capabilities.

Keywords: cellulose derivatives, cationic adsorbents, sorption of bile acids, cholesterol

IMPROVING THE YIELD OF TRIMETHYLSILYL CELLULOSE BY ACTIVATION OF CELLULOSE WITH ETHYLENEDIAMINE

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Trimethylsilyl cellulose (TMSC), an important precursor of regenerated cellulose, is difficult to obtain since cellulose is difficult to react with hexamethyldisilazane (HMDS) due to its low solubility in common solvents. Therefore it is necessary to activate cellulose prior to the reaction. In this investigation, alkali and ethylenediamine (EDA) were used for cellulose activation prior to TMSC production and their effects were evaluated by TMSC yields. Initially, cellulose was pretreated by either alkali or EDA, and then activated cellulose was dissolved in LiCl/DMAc solution. At last, HMDS reacted with the prepared homogenous cellulose to produce TMSC. The results showed that the yield of TMSC obtained from cellulose activated by alkali and EDA was 50.1% and 86.7%, respectively. It means cellulose pretreated by EDA improves the yield of TMSC by up to 36.6%, comparing with that treated by NaOH under the same reaction conditions. XRD results unveiled that the allomorph transformation and the associated crystallinity reduction of cellulose when treated by EDA may contribute to the easy dissolution of cellulose and improved yield of TMSC.

Keywords: cellulose, trimethylsilyl cellulose, ethylenediamine

CATIONIZATION OF PERIODATE-OXIDIZED COTTON CELLULOSE WITH CHOLINE CHLORIDE

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To find a more efficient and practically feasible cationization process for cellulose, periodate oxidation followed by a reaction with choline chloride was carried out in cotton. FTIR spectra revealed the presence of aldehyde carbonyl groups in periodate-oxidized cotton. The cationized cotton fabrics were dyed by acid dye to confirm the presence of cationic groups. Elemental analyses also indicated the presence of cationic groups. In general, oxidation temperature is an important factor in determining the oxidation effectiveness and, consequently, cationization. This oxidation/cationization process proved to be practically feasible and environmentally desirable as an alternative cationization of cotton.

Keywords: periodate oxidation, cationization, choline chloride, FTIR analysis

EFFECT OF COMBINED TREATMENT METHODS ON THE CRYSTALLINITY AND SURFACE MORPHOLOGY OF KENAF BAST FIBERS

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Kenaf bast fibers were treated by combined methods with steam (steam-chemical-ultrasonic treatment) and without it (chemical-ultrasonic treatment). The crystallinity and morphological properties of these treated fibers were compared with the untreated ones. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were employed to appraise crystallinity. Morphological features were examined by scanning (SEM) and transmission (TEM) electron microscopies. The fibers treated with steam had a higher degree of crystallinity than those without steam treatments and the untreated fibers. However, steam pre-treatment tended to reduce the fiber surface roughness. The fibers treated without steam showed surprising morphology, which is characterized by the formation of nanofibers on the surface of microfibers. Such morphology should enhance surface roughness and improve the performance of the corresponding composite.

Keywords: kenaf bast, steam pre-treatment, crystallinity, morphology

PRESWELLING OF CELLULOSE PULP FOR DISSOLUTION IN IONIC LIQUID

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The effect of cellulose preswelling with dimethyl sulfoxide (DMSO), dimethylformamide (DMF), formamide (FA), diethyl ether (DEE) and ethyl acetate (EAc) on cellulose dissolution in the ionic liquid (IL) 1-butyl-3-methylimidazolium acetate (BMIMAc) was studied. The solutions were analyzed by ¹H and ¹³C NMR spectroscopy and rheological methods. The preswelling of cellulose accelerated its dissolution in the IL without significant changes of the degree of polymerization. Volatile, aprotic and organic liquids appeared to be the most effective at cellulose activation.

Keywords: cellulose, activation, swelling, ionic liquids, dissolution

A THREE-STAGE KLASON METHOD FOR MORE ACCURATE DETERMINATIONS OF HARDWOOD LIGNIN CONTENT

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A three-stage Klason, or 72 wt% sulfuric acid, method is described for hardwoods. As compared to the traditional twostage method, the primary hydrolysis (PH) stage was modified to improve mixing of the wood meal into the 72% H₂SO₄. The PH stage was followed by two 1 h secondary hydrolysis (SH) stages. The 72% H₂SO₄ slurry was first diluted to 40 wt% H₂SO₄ and heated at 80 °C then diluted to 3 wt% H₂SO₄ and refluxed. When equivalent PH stages were used, convincing evidence was obtained showing that the hydrolytic intensity in the cleavage of lignincarbohydrate complexes (LCC) was much higher for the modified SH stages, as compared to the traditional refluxing of a 3% H₂SO₄ slurry for 4 h. The accuracy in lignin content determination should be equal or superior for the threestage method, which takes approximately 2 h less time. Results are presented for 4 hardwoods from 3 different genera.

Keywords: hardwoods, lignin content, sulfuric acid hydrolysis, acid insoluble lignin, acid soluble lignin

HPLC METHOD FOR THE EVALUATION OF CHROMATOGRAPHIC CONDITIONS FOR SEPARATION OF NEW XANTHINE DERIVATIVES

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The aim of this study is to develop a suitable HPLC method to determine with efficiency and selectivity the individual components of a series of 8 xanthine derivative compounds. HPLC analysis was performed using a high performance liquid chromatography system and a Phenomenex C18 column (octadecylsilyl) with 250 mm length, 4.6 mm internal diameter, 5 μm particle size and high pH stability. The UV spectra for the eight new xanthine derivatives were drawn. The retention times, number of theoretical plates and purity factor in different solvents were also established by using the HPLC method. The method is suitable for determining the xanthine derivatives from different pharmaceutical coated matrices, based on their physicochemical properties, such as the affinity to polar compounds or vegetable proteins.

Keywords: HPLC, methylxanthines

CO-PYROLYSIS OF VARIOUS LIGNINS WITH POLYCARBONATE

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The co-pyrolysis of bisphenol A polycarbonate with lignins of various origin and obtaining procedures (Klason annual plants, Organosolv hardwood and Lignoboost softwood lignin) were comparatively studied with a focus on product yield and oil composition. Similarities and differences among studied lignins were observed and discussed. Lignoboost lignin gave the highest oil yield and the lowest amount of residue. Organosolv hardwood yielded significant amounts of syringol, methylsyringol and isovanillic acid, while Lignoboost lignin yielded more guaiacol and its methyl- and ethyl derivatives. Residual acetic acid and sulphur compounds from the obtaining procedures were found for Organosolv hardwood and Lignoboost lignin.

Keywords: co-pyrolysis, Klason, Organosolv, Lignoboost, polycarbonate

HYDROLYTIC HYDROGENATION OF CELLULOSE TO SUGAR ALCOHOLS BY NICKEL SALTS

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Direct and selective hydrolytic hydrogenation of cellulose was carried out over catalytic amounts of nickel salt. C4-C6 polyols were obtained with an 87.9% yield in a neutral aqueous solution without an aid of liquid phase acid at the temperature of 150°C in the presence of NiSO₄.

Keywords: cellulose, hydrolytic, hydrogenation, polyols

CHEMICAL CHANGES IN FIR WOOD FROM OLD BUILDINGS DUE TO AGEING

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Wood is a biological material and changes in its molecular structure during exposures usually have a negative influence on its strength and other mechanical and physical properties. In this work, wet chemical and physico-chemical methods have been used to determine the changes in the cellulose, hemicelluloses, lignin and

extractives of the 108 to 390-yearold visually undamaged fir wood taken from beams situated in the Rychvald castle in Czech Republic. Natural ageing of the fir wood without activity of biological agents caused a significant increase of the extractives content (twofold, or for the oldest beam, even fourfold) and a decrease of the hemicelluloses (by maximum 24%), while the amounts of lignin and holocellulose were quite stable (decreased only by 4%). The molecular weights, respectively, degrees of polymerization, were stable in cellulose, decreased in hemicelluloses, while in lignin increased due to condensation reactions.

Keywords: historic wood, fir, ageing, lignin, cellulose, hemicelluloses, size exclusion chromatography

INVESTIGATION OF THE EFFECT OF SUPERCRITICAL CARBON DIOXIDE RETREATMENT ON REDUCING SUGAR YIELD OF LIGNOCELLULOSE HYDROLYSIS

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Supercritical carbon dioxide (scCO₂) was used to pretreat corncob, cornstalk and rice straw at the temperature of 80-160°C and pressure of 5-20 MPa, with the raw materials moisture content of 0-75% for the durations of 15-60 min. It was found that the reducing sugar yield of all the three materials showed a maximum with the increase of the moisture content and pretreatment temperature. The optimum experiment result was obtained at 100°C, 15 MPa with the duration of 30 min and moisture contents of 50%. The reducing sugar yield was 39.6%, 27.4% and 36.6% for corncob, cornstalk and rice straw, respectively, while for untreated materials it was 26.2%, 22.5% and 30.9%. High Performance Liquid Chromatography (HPLC) analysis for hydrolysates of corncob and rice straw indicated that scCO₂ pretreatment had a positive effect on the hydrolysis of both cellulose and hemicelluloses. Among the three materials, the reducing sugar yield of corncob was improved the most after scCO₂ pretreatment, which could be demonstrated by the X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) analyses.

Keywords: lignocellulose, supercritical carbon dioxide, pretreatment, reducing sugars

INFLUENCE OF FUNGAL DECAY ON CHEMI-MECHANICAL PROPERTIES OF BEECH WOOD (*FAGUS ORIENTALIS*)

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The mechanical and chemical properties of beech (*Fagus orientalis*) heartwood and sapwood after incubation with rainbow white-rot fungus (*Coriolus versicolor*) (for 14 weeks by the Kolle flask method) were determined. Also, the weight loss of the samples was measured after exposure to the white-rot fungus. The results indicated

that the highest weight loss (36.08%) was observed for sapwood samples and the lowest (32.98%) occurred in heartwood samples. The highest and the lowest compression strength parallel to the grain were noted in heartwood and sapwood decayed samples, respectively. The highest and the lowest Brinell hardness perpendicular to tangential and radial surfaces were observed in heartwood and sapwood decayed samples, respectively. The chemical analysis showed that the major changes occurred in lignin content, i. e. 54.4% and 47.10% lignin reduction for sapwood and heartwood, respectively. Also, alcohol-benzene solubility decreased, while 1% sodium hydroxide solubility and hot water solubility increased in the decayed wood samples.

Keywords: beech, rainbow white-rot fungus, heartwood, sapwood, lignin

CHEMICAL COMPOSITION AND MORPHOLOGICAL PROPERTIES OF CANOLA PLANT AND ITS POTENTIAL APPLICATION IN PULP AND PAPER INDUSTRY

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In this research, the chemical composition and morphological properties of canola plant cultivated in Iran were investigated. Canola straw was collected from a cultivation farm near Babul, Mazandaran, Iran. Average width, fiber length, lumen diameter and cell wall thickness were measured as 27.95, 860, 18.86, and 4.42 μm , respectively. The typical chemical composition, involving the amounts of cellulose, lignin, ash and ethanol/acetone extractives, was determined as 44, 19.21, 6, and 13 wt%, respectively. Optimum pulping conditions were selected applying a cooking temperature of 170°C, and cooking time of 30 min, in addition to the introduction of a 20% sodium sulfite (based on Na_2O). The pulps were refined by a PFI mill. The obtained results showed that the mechanical properties of the handsheets made from canola NSSC pulp exhibited better properties, in comparison with mixed hardwood NSSC pulp in production of corrugating paper.

Keywords: canola, chemical composition, morphological properties, pulp and paper

FORMIC ACID/ACETIC ACID/WATER PULPING OF AGRICULTURAL WASTES

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In this paper, mustard branches, mustard stems and lentil stalks were characterized in order to evaluate them as pulping raw materials. These agricultural wastes are characterized by relatively moderate amounts of lignin (20-23%), reasonably low amounts of α -cellulose (35-37%) and relatively high amounts of ash content (4-7%). In this study, pulping of lentil stalks, mustard stems and mustard branches was carried out at atmospheric pressure using a mixture of formic acid, acetic acid, and water (FA/AA/H₂O). Increasing formic acid concentration in the acid mixture improved the delignification rate. A higher pulp yield was obtained from lentil stalks with higher residual lignin than those of mustard stems and branches after FA/AA/H₂O treatment. It was found that the delignification of FA/AA/H₂O treated pulp was improved in an efficient and selective manner by using peroxyacid, which facilitated chlorine free bleaching. After prebleaching with peroxyacid, pulp from mustard branches showed the lowest kappa number among the three raw materials. Prebleached pulps were bleached by alkaline peroxide bleaching and final pulp yields reached 47.2%, 45.3% and 41.3% for lentil stalks, mustard stems and mustard branches, respectively. The bleached pulp from mustard stems and branches showed ISO brightness above 80% after alkaline peroxide bleaching, while lentil stalks bleached pulp showed 76% ISO brightness. Acceptable papermaking properties were obtained from these agricultural wastes by organic acid pulping at atmospheric pressure, followed by chlorine free bleaching.

Keywords: formic acid/acetic acid pulping, agricultural wastes, delignification, peroxide bleaching, paper strength

ELEMENTAL CHLORINE FREE BLEACHING OF WHEAT STRAW CHEMIMECHANICAL PULP

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Production of bleachable CMP pulp from wheat straw using different dosages of NaOH and chemical treatment time was investigated. The yield after chemical treatment varied between 64.6 and 72.7% and the total yield after defiberizing was measured between 53.4% and 62%. The pulp produced applying 10% NaOH, 40 minutes pulping time and 95 °C pulping temperature was selected for bleaching trials. Elemental Chlorine Free (ECF) bleaching sequence was used for bleaching the selected pulp. Applying 3% (based on oven dry weight of the unbleached pulp) chlorine dioxide in D0EPD1 bleaching sequence (2% in D0 stage and 1% in D1 stage) improved the brightness to 62.2% ISO. The kappa number of the ECF bleached pulp was reduced from the value of 40.1 to the final value of 13.4 for bleached pulp.

Keywords: wheat straw, CMP, yield, strength, totally chlorine free, elemental chlorine free

MITIGATION OF ADSORBABLE ORGANIC HALIDES IN COMBINED EFFLUENTS OF WHEAT STRAW SODA-AQ PULP BLEACHED WITH CELLULASE-POOR CRUDE XYLANASES OF *COPRINELLUS DISSEMINATUS* IN ELEMENTAL CHLORINE FREE BLEACHING

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Novel cellulase-poor crude xylanases from strains SH-1 NTCC-1163 (enzyme-A), and SH-2 NTCC-1164 (enzyme-B) of *Coprinellus disseminatus*, mitigated kappa number (56.27 and 58.41%) of wheat straw soda-AQ pulp after OXAE and OXBE bleaching stages, respectively. Significant reductions in AOX (25.00 and 22.05%), with a slight decrease in some strength properties, owing to removal of hemicelluloses, was observed. The removal of hemicelluloses was further validated by an increase in pulp viscosity (6.82 and 4.93%), COD (43.15 and 43.15%) and colour (51.99 and 62.99%) for OXAE1D1E2D2 and OXBE1D1E2D2 sequences, respectively, compared to their respective controls. Compared to controls, AOX reduction was higher in OXAE1DE2P (38.75%) and OXBE1DE2P (36.25%) than OXAE1D1E2D2 (25.00%) and OXBE1D1E2D2 (22.05%) bleached pulps, but at the cost of brightness. AOX, COD and colour were significantly reduced on the 6th day of incubation of combined bleaching effluents.

Keywords: *Coprinellus disseminates*, biobleaching, wheat straw pulp, AOX

SYNTHESIS OF 2-HYDROXY ETHYL METHACRYLATE GRAFTED COTTON FIBERS AND THEIR FASTNESS PROPERTIES

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In this study, 2-hydroxy ethyl methacrylate (HEMA) monomer was grafted onto cotton fibers, using a benzoyl peroxide (BPO) initiator. The effects of grafting temperature, grafting time, monomer and initiator concentrations on grafting yield (GY) and grafting efficiency (GE) percentages were investigated and the optimum grafting conditions were determined. Maximum GY value was obtained as 47.6%. From swelling tests, it was observed that GY positively affected the swelling percentages of grafted fibers. SEM analyses of grafted and ungrafted fibers were performed in order to characterize fiber morphology. The dyed fibers were subjected to fastness tests and higher fastness ratings were observed for grafted fibers, compared to ungrafted samples.

Keywords: cotton fibers, 2-hydroxy ethyl methacrylate (HEMA), grafting, swelling test, fastness

SONICATION AND CONVENTIONAL DYEING PROCEDURES OF FLAX FIBRES WITH *ALLIUM CEPA* ANTHOCYANIN EXTRACT

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The aim of this paper was to improve the dyeability of flax fibre substrates by a previous modification *via* their grafting and explore the mechanism of such an improvement. The comparative results of the dyeing efficiency of grafted flax fabrics, using both ultrasound and conventional dyeing methods, are presented. The dyeing process involved the use of a natural red dye extracted from red onion (*Allium cepa*). Morphological, structural and chemical properties of the obtained samples were examined, in terms of a coassisted investigation system: scanning electron microscopy (SEM) images for the morphology and energy-dispersive X-ray spectroscopy (EDX) analysis for surface composition. The obtained results showed the superiority of sonication dyeing over the conventional dyeing procedure. Moreover, the research emphasizes the idea of the mesoporosity of the inclusion complex formed by encapsulating dye molecules inside the cavity of monochlorotriazinyl- β -cyclodextrin (MCT- β -CD).

Keywords: flax textile support, anthocyanin extract, morphology, natural dye, ultrasonication, colour fastness

NON-DESTRUCTIVE ANALYSIS OF KRAFT PULP BY NIR SPECTROSCOPY

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A fast and convenient analytical technique is needed for quality assessment and precision management in pulp production. The main objective of this study was to evaluate the ability of NIR spectroscopy to predict diverse pulp properties. Near-infrared reflectance spectra of handsheets, prepared from unbleached beech kraft pulps obtained under different pre-extraction and pulping conditions were evaluated. The pulp characteristics were modelled using the first derivatives of optical density [$\log(1/R)$] and the application of the partial least squares (PLS) method. The models were verified by using cross-validation and validation methodology. Kappa number, tensile index, burst index, tear index and brightness were successfully predicted by NIR spectroscopy ($R > 0.90$). The results indicate that NIR spectroscopy can be used as a rapid analytical technique to simultaneously estimate several characteristics with acceptable accuracy and can reduce time in conventional methods, so it could be suitable for direct applications, where “real time” data are needed.

Keywords: NIR spectroscopy, multivariate calibration, validation, unbleached beech kraft pulp, kappa number, tensile index, burst index, tear index, brightness

INFLUENCE OF STRUCTURAL CHANGES INDUCED BY OXIDATION AND ADDITION OF SILVER IONS ON ELECTRICAL PROPERTIES OF COTTON YARN

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This paper is focused on investigating the electrical behavior of cotton yarn oxidized with nonselective oxidation agent, hydrogen peroxide, through measurement of structural changes in cotton, and elucidating the influence of these changes on electrical resistance. Significant connection between the nature of the introduced polar groups, crystallinity index, water retention ability, silver sorption and electrical resistance was found. The measurement and possible control of electrical resistance could help anticipate and control the textile materials' tendency to generate static electricity, since these two parameters are closely connected and mutually dependent.

Keywords: cotton, oxidation, silver, electrical resistance, structure–property relations

ACETYLATION MODIFICATION OF RICE STRAW FIBER AND ITS THERMAL PROPERTIES

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The esterification of rice straw fiber with acetic anhydride, using sulphuric acid as catalyst, under mild conditions in glacial acetic acid, has been investigated. Acetylation conditions, such as dosage of chemicals and catalyst, and time and temperature of acetylation, were optimized. The preferred reaction parameters of acetylation reaction are described as follows: weight ratio of rice straw and acetic anhydride was 1:3, using sulphuric acid as catalyst in glacial acetic acid at 50 °C for 2 h, the dosage of catalyst and solvent was, respectively, 9.0% and 9 times to rice straw powder, in which the acetylation weight percent gain of 40.1% was obtained. The characterization of acetylated rice straw was performed by Fourier transform infrared (FTIR), Nuclear Magnetic Resonance (¹H NMR), X-ray diffractometer (XRD), Scanning electron microscope (SEM). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed a slow decomposition rate, compared to raw rice straw, and an endothermic peak at 188°C. These results demonstrated that the thermal properties of rice straw can be improved by acetylation.

Keywords: acetylation, modification, rice straw, thermal properties

MONOMER REACTIVITY RATIOS OF CELLULOSE GRAFTED WITH NCYCLOHEXYLACRYLAMIDE AND METHYL METHACRYLATE BY ATOM TRANSFER RADICAL POLYMERIZATION

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The atom transfer radical polymerization (ATRP) of N-cyclohexylacrylamide (NCA) with methyl methacrylate (MMA) was performed in dimethylformamide (DMF) at 130°C, in the presence of cellulose chloroacetate (Cell.ClAc) macro initiator, Cu(I)Cl/2,2'-bipyridine catalytic system. The graft copolymers were characterized by elemental analysis, FTIR spectra and thermal analysis. Thermal stabilities of the graft copolymers were determined by the TGA method and it was found that the thermal stability of the copolymers increased with the increase of MMA units, while it decreased with the increase of NCA units. In order to investigate the effect of NCA interactions with MMA monomers on grafting, graft copolymerization was also studied using different feed compositions, ranging from 0.15 to 0.85. The reactivity ratios of NCA and MMA by ATRP on cellulose were determined using the Finemann-Ross (F-R), inverted Finemann-Ross (inverted F-R), Yezrielev-Brokhina-Roskin (Y-B-R), Kelen-Tüdös (K-T) and extended Kelen-Tüdös (extended K-T) linearization methods. The reactive ratios of r_1 and r_2 were obtained to be 0.004-0.128 and 0.657-0.907, respectively; $r_1 \cdot r_2$ of the graft copolymers on cellulose is close to zero.

Keywords: cellulose, monomer reactivity ratios, ATRP, graft copolymer

HOMOGENEOUS GRAFTING COPOLYMERIZATION OF METHYLMETHACRYLATE ONTO CELLULOSE USING AMMONIUM PERSULFATE

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The homogeneous grafting of methylmethacrylate (MMA) onto cellulose was carried out by using ammonium persulfate as initiator. DMAc/LiCl was used as solvent for the dissolution of cellulose and medium for the homogeneous graft copolymerization. The efficient reaction conditions of the grafting reaction were confirmed by weighing methods. The results showed that the efficient reaction conditions were as follows: reaction time, 2 h, mass ratio of MMA/cellulose, 1/1 (g/g), mass ratio of initiator/cellulose, 6/50 (g/g), and reaction temperature, 80°C. Under these conditions, the GP of cellulose under homogeneous conditions reached 76%, higher than that obtained under heterogeneous conditions. The grafted polymer was characterized by FTIR, SEM, TG-DTA and XRD. The results showed that the original crystalline structure was destroyed during the dissolution process of cellulose, which helped to improve the effectiveness of the grafting copolymerization reaction.

Keywords: homogeneous grafting, cellulose, methylmethacrylate, grafting percentage, N,N-dimethylacetamide/ lithium Chloride

THERMO-RESPONSIVE BEHAVIOUR OF CELLULOSIC MATERIALS

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Thermo-responsive hydrated macro-, micro- and submicro-reticular systems, particularly polymers forming hydrogels or similar networks, have attracted extensive interest as they comprise biomaterials, smart or intelligent materials. Phase transition temperature (low or upper critical solution temperature) of the thermo-responsive hydrated reticular systems, which exhibit a unique hydration-dehydration change, is a typical characteristic. The macro-reticular systems with weak bonding are represented by papermaking pulp slurries composed of cellulosic or ligno-cellulosic fibres. During wet pulp beating, it was found that the characteristic decrease of the pulp drainability with increasing the input of beating energy abruptly enhanced if the temperature of the beating pulp slurry was higher than 40 °C. Similar observations have been made during pulp slurry drainage at higher temperatures. The drainability of pulp slurries not only improves at temperatures higher than 40 °C, but also it tends to be higher than that obtained when decreasing water viscosity only.

Keywords: thermo-responsive hydrated system, hydrogel, phase transition temperature, beating, drainability

CELLULOSE-GRAFT-POLY(L-LACTIDE) AS A DEGRADABLE DRUGDELIVERY SYSTEM: SYNTHESIS, DEGRADATION AND DRUG RELEASE

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A cellulose-based degradable material, cellulose-graft-poly(L-lactide), was successfully attained via ring-opening polymerization (ROP) in an ionic liquid. The microsphere was prepared by the phase separation method, and the optimum reaction conditions were established as follows: dispersant dosage, 15% (g/g cellulose/AmimCl solution); oil/water volume ratio, 4:1; stirring speed, 350 r/min. Using wide-angle X-ray powder diffraction (WAXD), swelling and degradation tests, the changes resulting from degradation in the crystalline structure were also investigated. The hydration and degradation of cellulose-g-PLLA demonstrate significantly different characteristics, which dominated the drug-release mechanism of the cellulose-g-PLLA microspheres. It showed that the drug-release rate increased with the decrease in the grafting degree of the cellulose-g-PLLA, which may be due to the increased hydration ability of the cellulose-g-PLLA microspheres. Consequently, the cellulose-g-PLLA microspheres might be used as a potential polymer for the controlled release of drugs.

Keywords: cellulose, poly(L-lactide), microsphere, degradable, drug delivery

LOADING AND RELEASE OF A MODEL CATIONIC DYE ONTO/FROM CHITOSAN/POLY(ACRYLIC ACID) OLYELECTROLYTE MULTILAYERS

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Polyelectrolyte multilayers of chitosan (CS) and poly(acrylic acid) (PAA) were constructed onto glass slides by the deposition from aqueous solution containing NaCl as support electrolyte. After construction, the CS/PAA multilayers were post-treated, changing the water pH and the ionic strength in order to generate pores inside the polymer matrix. A thermal treatment was further used to stabilize the film morphology. The morphological modifications of the multilayers surface, before and after the post-treatments, were monitored by atomic force microscopy as a function of the number of double layers deposited. The capacity of the CS/PAA multilayer thin films to sorb/release cationic species was evaluated using Toluidine Blue O as a model dye. The stability of the post-treated multilayer thin films in successive sorption/desorption cycles was explained by the formation of amide bonds between ionic groups of CS and PAA.

Keywords: polyelectrolyte multilayer, chitosan, poly(acrylic acid), Toluidine Blue O, loading/release

ISOLATION AND CHARACTERIZATION OF LIGNIN FROM *STIPA TENACISSIMA L.* AND *PHOENIX DACTYLIFERA*

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This paper is devoted to the isolation of lignin from *Stipa tenacissima L.* and *Phoenix dactylifera* by three different processes, namely, CIMV, MILOX and Acetosolv, and its characterization. The Acetosolv process was found to be the most efficient cooking process, as deduced from the combined severity values and the pulp yield. The UV spectroscopy revealed that the lignin obtained from *Phoenix dactylifera* is more pure than that arising from *Stipa tenacissima L.* In fact, the latter presents higher amounts of carbohydrate impurities. Also, several techniques were used in order to characterize the obtained lignin from the two raw materials, namely: ¹³C-NMR and FTIR spectroscopy. Moreover, the chemical study of the structure of lignin isolated from *Stipa tenacissima L.* demonstrated that it is composed of HGS type and characterized by a high content of syringyl units. Instead, the lignin isolated from *Phoenix dactylifera* presents a higher content of the guaiacyl units.

Keywords: *Stipa tenacissima L.*, *Phoenix dactylifera*, lignin, NMR, UV spectroscopy

FLAXSEED CAKE – A SUSTAINABLE SOURCE OF ANTIOXIDANT AND ANTIBACTERIAL EXTRACTS

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Flaxseed cake, a by-product of the oil cold pressing technology, was subjected to extraction and acidic hydrolysis to obtain extracts rich in polyphenols and especially in lignans. The second step was to assess the extracts in order to evaluate their potential to be used as additives in the food and cosmetics industries. The identification and quantification of secoisolariciresinol (SECO), matairesinol (MATA) and lariciresinol (LARI) in the said extracts was accomplished using the HPLC method. The total polyphenol content, radical scavenging activity and antimicrobial activity were determined. The total polyphenol content for the samples extracted with 60% ethanol, hydrolyzed at 80 °C, was comparable to that of the extracts obtained from spices or medicinal plants. The radical scavenging ability of the extract correlates well with the total polyphenol content and is comparable to that of common synthetic phenolic antioxidants used in foods and cosmetics. Flaxseed cake extracts also contain up to 7.08 mg SECO/L, 0.06 mg MATA/L and 0.03 mg LARI/L. Both crude and hydrolysed extracts exhibited antibacterial activity against *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Escherichia coli*. The ability to extract agro fine chemicals from flaxseed cake provides the flaxseed industry with value-added co-products.

Keywords: flaxseed cake, lignans, polyphenols, HPLC, antimicrobial activity

FAST PYROLYSIS OF POPLAR WOOD SAWDUST WITH LA-CONTAINING SBA-15 CATALYST BY PY-GC/MS ANALYSIS

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The catalyst was prepared by immobilizing lanthanum rare element on the periodic mesoporous channels of siliceous SBA-15. Powder X-ray diffraction data and ICP-AES revealed that the host retains its hexagonal mesoporous structure after immobilization and most of the lanthanum species are better dispersed in the calcinated materials. The surface area and pore size of La/SBA-15 were considerably decreased, indicating the intrapore confinement of the lanthanum species. La-containing SBA-15 catalyst was employed for catalytic cracking of Poplar Wood Sawdust (PWS) fast pyrolysis vapors, using analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The La/SBA-15 catalyst displayed prominent capabilities to crack the lignin-derived oligomers to phenol or monomeric phenolic compounds without the carbonyl group and unsaturated C-C bond on the side chain. Moreover, the catalyst also significantly decreased the linear aldehydes and decarbonylated furan compounds. In addition, the catalyst slightly decreased the acids, while benzene or aromatic derivative hydrocarbons were increased. The above catalytic capability of La/SBA-15 catalyst was enhanced with the introduction of La into SBA-15 catalyst.

Keywords: lanthanum containing SBA-15, poplar wood sawdust, Py-GC/MS

OPTIMIZATION OF CELLULASE PRODUCTION UNDER SOLID-STATE FERMENTATION BY *ASPERGILLUS FLAVUS* (AT-2) AND *ASPERGILLUS NIGER* (AT-3) AND ITS IMPACT ON STICKIES AND INK PARTICLE SIZE OF SORTED OFFICE PAPER

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Out of 12 fungal strains, two fungal strains, namely *Aspergillus flavus* AT-2 and *Aspergillus niger* AT-3, were found to produce maximum cellulase production. The CMCase activities of *A. flavus* AT-2 and *A. niger* AT-3 under state solid fermentation (SSF) conditions were of 42.69 and 40.08%, respectively, which was higher than those obtained under submerged fermentation (SmF) conditions. A fungal inoculum dose of 5%, incubation period of 5 days, temperature and pH of 30 °C and 4.8 for *A. flavus* AT-2 and 35 °C and 5.3 for *A. niger* AT-3, respectively, solid substrate:moisture content 1:3, rice straw (treated) as carbon source, (NH₄)₂SO₄ + yeast extract as nitrogen source, KH₂PO₄ as phosphorus source, succinic acid as source of organic acid, Tween-80 as surfactant and cellobiose as source of soluble sugar might be taken as optimal for cellulase production for both fungal strains. The optimum CMCase (17.24 IU/mL), FPase (1.92 IU/mL), α -glucosidase (0.69 IU/mL) and xylanase activities (5.73 IU/mL) and fungal protein concentration (2.90 mg/L) for *A. flavus* AT-2 and CMCase (24.32 IU/mL), FPase (2.47 IU/mL), α -glucosidase (0.82 IU/mL) and xylanase activities (4.80 IU/mL) and protein concentration (3.07 mg/L) for *A. niger* AT-3 were taken as optimal under SSF conditions. *A. flavus* AT-2 and *A. niger* AT-3 were found active in the pH range of 4.0 to 7.5 and maximum cellulase activity was obtained at pH 5.0 for *A. flavus* AT-2 (17.31 IU/mL) and at pH 5.5 for *A. niger* AT-3 (24.50 IU/mL). The optimum temperature for the crude cellulase activities of both fungal strains (*A. flavus* AT-2, IU/mL and *A. niger* AT-3, IU/mL) was of 50 °C, and beyond it cellulase activities were found to decrease. Deinking of sorted office paper with cellulase reduced stickies level by 4%, compared to control and concoctions of different enzymes, i.e. cellulose, xylanase, amylase and lipase in different combinations, were capable of removing ink particles of all sizes from the pulp.

Keywords: *Aspergillus flavus* AT-2, *Aspergillus niger* AT-3, solid-state fermentation, cellulase activity, stickies, ink particle size

ENZYMATICALLY HYDROLYZED AND AGITATED BIOMASS SUSPENSIONS: EXPERIMENTAL DETERMINATION OF FIBER SIZE DISTRIBUTIONS AND FILTRATION CHARACTERISTICS

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Separation processes in general present a significant challenge in the production of bioethanol from lignocellulosic materials. Solid-liquid separation, prior to the concentration of ethanol (for instance, by distillation), is often essential and upstream process conditions may determine how effectively this separation can be performed. In this experimental study, the properties of a lignocellulosic solid residue, generated through the enzymatic hydrolysis of biomass, and solid-liquid separations after the hydrolysis stage were studied, focusing on the fiber and particle

size distribution (FSD and PSD) of the solids. During the course of enzymatic hydrolysis, fiber and particle size distributions of the biomass during and after enzymatic hydrolysis were measured using a fiber tester and a laser diffraction analyzer, respectively, in order to quantify the effect of enzymatic saccharification on the size distribution of the suspended solids. The main target, however, was to investigate the filtration properties of hydrolyzed and agitated suspensions using a pressure filter. The particle size distributions of the filtered samples were measured with the laser diffraction analyzer. Even though the filtration properties were strongly influenced by agitation, the effect on particle size distributions was found to be much smaller. During enzymatic hydrolysis, the most significant reduction in the size of the solid took place rapidly after the cellulase addition. The width of the fibers was not observed to decrease during the hydrolysis stage.

Keywords: enzymatic hydrolysis, fiber size, particle size, mixing, agitation, filtration

EFFECT OF DIFFERENT PRETREATMENT METHODS OF CORNCOB ON BIOETHANOL PRODUCTION AND ENZYME RECOVERY

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Efficient pretreatment and reuse of cellulase are effective methods to promote the cellulosic bioethanol commercialization. Corn cob was used as substrate in this study, and the effects of pretreatment methods, including dilute acid, sodium hydroxide, aqueous ammonia soaking and acid-base coupling (dilute sulfuric acid-aqueous ammonia) on glucose and ethanol concentration were analyzed during pre-hydrolysis and the simultaneous saccharification and fermentation (SSF) process. The influence of each pretreatment on the adsorption and desorption of cellulase and on the recycling effect of cellulase after re-adsorption by the fresh substrate were also discussed. The results showed that acid-base coupling pretreatment was much better than a single acid or alkali pretreatment, i.e. the cellulose content of the corn cob substrate reached 73.84% after pretreatment; the desorption percent and recycling percent of cellulase after 96 h of SSF and re-adsorption in the first round was 57.7% and 62.4% respectively; ethanol concentration amounted to 62.0% of the first time in the second round of SSF after the enzyme re-adsorption.

Keywords: corncob, pretreatment, cellulase, enzyme recycling, adsorption, simultaneous saccharification and fermentation

PROPERTIES OF CELLULOSE/TURMERIC POWDER GREEN COMPOSITE FILMS

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Cellulose was dissolved in an environment friendly aq.(7%NaOH/12% urea) solvent that was precooled to -12°C. Turmeric powder was added in different proportions and the composite films were cast on glass plates and regenerated in dilute sulfuric acid bath. The films were uniform and transparent of yellow color. The effect of turmeric powder loading on the tensile, optical, thermal degradation and cell viability was studied. The tensile properties, optical transparency and cell viability were found to be higher for the composite films. The films were thermally stable up to 350 °C.

Keywords: Green composites, tensile properties, cell viability, turmeric powder

EFFECTIVENESS OF CHITOSAN AS ANTIMICROBIAL AGENT IN LDPE/CS COMPOSITE FILMS AS MINCED POULTRY MEAT PACKAGING MATERIALS

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Low density polyethylene (LDPE)/chitosan (CS) composites and stratified composites have been tested for minced poultry meat packaging according to well-known standard methods used in food industry. It has been established that the composites containing 3-6 wt% CS or nanocomposites containing chitosan/nanoclay and 0.5 wt% vitamin E show superior properties (with respect to appearance, smell, bouillon after boiling and sedimentation, pH, reaction with H₂S and total number of germs), compared with commercially available foils, when applied to meat products. It was found that the number of germs decreased for meat packed in the obtained compositions by 104-105 times. The best values have been obtained with stratified composites obtained by covalent bonding and covered with chitosan by electrospraying. The major characteristics of the LDPE foils, such as rheological behaviour, variation in crystallinity and permeability by treatment with chitosan and vitamin E, were studied, as they are important for packaging applications. The sensory methods, XRD, rheological and oxygen transmission rate analyses proved that the films accomplished all the requirements for minced poultry meat packaging.