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CELLULOSE CHEMISTRY AND TECHNOLOGY**CELLULOSE CHEMISTRY AND TECHNOLOGY**

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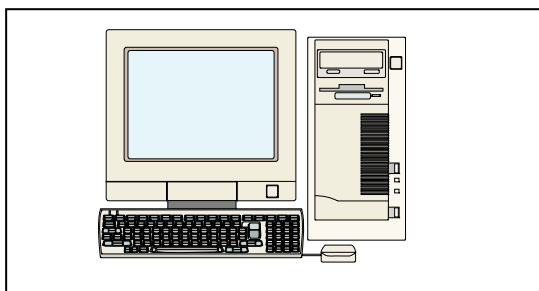
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CARACTERIZAREA TULPINILOR DE RAPIȚĂ (*Brassica napus*). 2. DATE BIOMETRICE ȘI COMPOZIȚIA CHIMICĂ

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Rezumat

Suprafețele cultivate cu plante anuale tehnice și mai ales, suprafețele semănate cu rapiță pentru ulei au însumat peste 537 000 ha în anul 2010, iar cantitatea de tulpini de rapiță a fost estimată la peste 1 200 000 t. Tulpinile de rapiță rămân pe câmp pentru rotația culturilor sau li se dă foc pentru a elibera terenul pentru culturile din anul următor. Se impune găsirea unor direcții de valorificare superioară a tulpinilor de rapiță, una dintre acestea fiind procesarea pe cale chimică pentru separarea materialului celulozic și obținerea materialelor fibroase, dar și pentru izolarea altor substanțe valoroase. Lucrarea de față prezintă date referitoare la natura fibrelor din tulpinile de rapiță și caracteristicile dimensionale ale acestor fibre. Se investighează și compoziția chimică a tulpinilor și se compară cu alte specii vegetale folosite la fabricarea celulozei. Se analizează și potențialul papetar al fibrelor din tulpini de rapiță.

Cuvinte cheie: *tulpini de rapiță; fibre; celuloză; lignină.*

Abstract

Areas cultivated with technical crops and especially areas with rapeseeds totaled more than 537000 Ha in 2010, and the amount of rapeseed stalks has been estimated at 1,2 million tonnes. Rapeseed stalks remain on the field for crop rotation or are set on fire to clear the land for the next crop. It is necessary to find ways of higher valorization of rapeseed stalks, one of which being their chemical processing to separate the cellulosic material and to obtaining fibrous materials, but also to isolate other valuable substances. The paper presents data regarding the type of fibers of rapeseed stalks and the dimensional characteristics of these fibers. The chemical composition of rapeseed stalks is investigated and it is compared with the chemical composition of other vegetal species used in pulp manufacture. The papermaking potential of rapeseed fibres is also analyzed.

Key words: *rapeseed stalks; fibers; cellulose; lignin*

1. INTRODUCERE

Factorul primordial care determină utilizarea plantelor anuale și a deșeurilor vegetale în industria celulozei este înlocuirea lemnului, o materie primă deficitară și scumpă.[1]. Celulozele cu fibră scurtă sunt din

ce în ce mai acceptate la fabricarea multor sortimente de hârtie, ceea ce face posibilă extinderea bazei de materie primă prin valorificarea plantelor anuale [2,3]. Creșterea suprafețelor cultivate cu plante anuale tehnice și mai ales cu cele din care se obțin biocombustibili (rapița, floarea soarelui,

porumbul, grâul) pune problema găsirii unor metode eficiente de valorificare a tulpinilor.

După recoltarea semințelor, tulpinile de rapiță rămân pe teren. Valorificarea lor se realizează fie prin încorporarea în sol, prin arderea miriștilor sau prin colectarea tulpinilor și eliberarea terenului [4]. Încorporarea în sol duce la creșterea conținutului de humus și încorporarea, imobilizarea și transformarea azotului și sulfului la forme organice stabile în solurile sărace în substanțe nutritive [5]. În multe țări cultivate, la combină sunt montate dispozitive speciale pentru tocarea tulpinilor și împrăștierea acestora pe teren, concomitent cu recoltatul. Ulterior, pentru o descompunere mai rapidă a reziduurilor și mineralizarea resturilor vegetale [6], se încorporează tulpinile bine mărunțite în sol, prin arătură, eventual împreună cu doze moderate de îngrășăminte cu azot pentru a facilita descompunerea carbonului organic în sol și fixarea azotului. Totuși, mai mult de 2/3 din carbonul organic nu se descompune nici după 270 de zile, iar fixarea azotului mineral se

2. PARTEA EXPERIMENTALĂ

Materii prime - tulpinile de rapiță

Materialul vegetal care a fost folosit pentru determinările în faza de laborator a fost reprezentat de tulpini de rapiță, rămase pe câmp după recoltarea semințelor în luna iunie, cu umiditatea relativă de 15%. Înălțimea tulpinilor analizate a fost cuprinsă între 1 și 1,5 m. Diametrele la bază au avut variații mici, majoritatea tulpinilor având 20-30 mm. Măsurând grosimea secțiunilor în lungul tulpinii s-au constatat valori ale diametrelor de 15-25 mm la 0,5 m înălțime, de 10-20 mm la 1 m înălțime și 5-10 mm la vârf.

Din analiza dimensională rezultă că din tulpini mature se obține 97% tocătură normală (fracție masică) cu dimensiuni de 5-10 cm lungime, restul fiind format din 3% pleavă, alcătuită din fragmente de tulpină și material mărunț. Conținutul de tulpină desmedulată reprezintă 84%, iar măduva reprezintă 13% din greutatea tulpinilor integrale.

Dintre proprietățile fizice ale materiilor prime celulozice, densitatea materialului vegetal influențează în mod direct comportarea la delignificare. Tocătura de rapiță are greutatea volumetrică mult mai mică decât a tocăturii din lemn și anume 42 kg/m³ pentru tulpini întregi și 75 kg/m³ pentru tocătura de 5-7 cm lungime. Se observă că tocătura are la aceeași umiditate greutatea volumetrică aproape dublă față de

face numai până la 10-12% din cantitatea disponibilă din sol [7]. Pierderile de azot sunt minore prin recoltarea tulpinilor și nu au impact negativ asupra balanței de nutrienți din sol, iar impactul asupra pierderilor globale este nesemnificativ [8]. Altă utilizare a tulpinilor de rapiță o reprezintă folosirea ca resurse lignocelulozice pentru obținerea de materiale fibroase, produse chimice, biocombustibili sau bioenergie [9].

Prima etapă a acestui studiu a avut în vedere caracterizarea structurii morfologice și anatomice a tulpinilor de rapiță și a cuprins studii detaliate prin intermediul microscopiei optice, digitale și electronice, analizându-se elementele de structură ale țesuturilor vegetale [10]. În partea a doua se determină valorile dimensiunilor fibrelor, indicii morfologici de calitate, precum și compoziția chimică, caracteristici importante pentru evaluarea potențialului papetar al fibrelor din rapiță.

tulpinile normale. Prin comparație, tocătura de rășinoase are densitatea de aproximativ 200 kg/m³.

Analiza microscopică a structurilor morfologice și anatomice

Pentru caracterizarea calității materiei prime pentru industria de celuloză și hârtie, principalele elemente anatomice ale materialului vegetal ce au rolul cel mai important sunt fibrele și de aceea s-au determinat caracteristicile dimensionale ale fibrelor tulpinilor de rapiță.

Metoda de lucru, conform standardului TAPPI T259 sp09 - *Species Identification of Nonwood Plant Fibers* [11], a presupus pregătirea probelor pentru observațiile la microscopul digital, achiziția de imagini și măsurări liniare ale dimensiunilor fibrelor.

Pentru analiza morfologică s-au folosit: microscopul electronic cu scanare (Scanning Electron Microscopy - SEM) JSM 5500 Jeol, microscopul optic digital AXIO Imager A1m Zeiss și STEMI 2000-C. Pentru analiza prin microscopie electronică cu scanare, probele au fost metalizate cu aur (gold-coated), iar pentru analiza prin microscopie optică, fibrele au fost dispersate în apă și depuse pe lamele pentru microscop. Imaginile au fost înregistrate cu o cameră video Leica DC300, cameră ce permite capturarea imaginilor folosind o vizualizare live și focalizarea precisă a imaginii pentru salvare lor în format BMP, JPG sau TIFF. Obținerea rezultatelor optime

privind datele biometrice ale fibrelor de rapiță s-a realizat prin interpretarea datelor cu programul software Optika Vision® Pro, special elaborat pentru achiziția, prelucrarea și analizarea imaginilor microscopic. Datele obținute au fost prelucrate statistic, calculându-se pentru fiecare parametru măsurat media, deviația standard și distribuția fibrelor pe grupe de mărimi [12].

Metode analitice folosite pentru studii chimic

Următoarele metode experimentale au fost utilizate pentru analiza compoziției chimice a tulpinilor de rapiță și a fibrelor celulozice obținute din acestea. Metodele de analiză sunt cele standardizate de Technical Association of the Pulp and Paper Industry (TAPPI) [11], sau sunt metode clasice utilizate pe scară largă în literatura de specialitate. Deoarece aceste metode sunt descrise în colecții de standarde sau în literatura citată, ele sunt prezentate doar în principal. Schematic, etapele procedurii experimentale pentru studiul chimic al tulpinilor de rapiță sunt prezentate în figura 1.

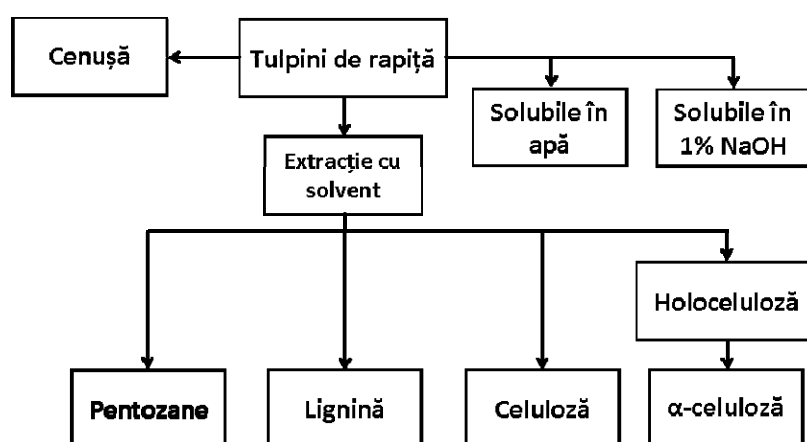


Fig. 1 Schematizarea etapelor procedurii experimentale folosită la determinările de compoziție chimică a tulpinilor de rapiței

Pregătirea probelor de tulpini pentru analiza chimică s-a făcut conform metodei TAPPI T257 cm-02 - *Sampling and preparing wood for analysis* [11], prin măcinare în stare uscată în dezintegrator. Materialul măcinat a fost sortat printr-o sită cu ochiurile de 0,4 mm, pentru analiză reținându-se fracțiunea rămasă pe sită.

Celuloza. Determinarea cantitativă a celulozei se bazează pe stabilitatea relativă a celulozei față de acțiunea unor reactivi chimici – acizi, alcooli, baze, etc. – care dizolvă sau descompun restul polizaharidelor și ligninei din materialul vegetal, transformându-le în substanțe solubile.

Celuloza (metoda Kürschner-Hoffer). Metoda nitrică de dozare a celulozei în mediul alcoolic se bazează pe acțiunea la temperatura de fierbere a unui amestec, format din 1 volum acid azotic concentrat și 4 volume alcool etilic absolut, asupra materialului vegetal, în prealabil extras cu solvenți organici. Celuloza obținută se

raportează procentual la materialul absolut uscat luat în lucru [13].

Celuloza (metoda Seifert). Metoda constă în acțiunea unui amestec compus din acetil-acetonă, dioxan și acid clorhidric asupra materialului vegetal extras în prealabil cu solvenți organici. Rezultatul se exprimă în procente raportat la materialul absolut uscat luat în analiză [14].

α-Celuloza. Principiul metodei constă în tratarea succesivă a holocelulozei materialului vegetal la temperatura de 25°C cu o soluție de hidroxid de sodiu 17,5% și apoi diluarea ei la 9,45%. Materialul dizolvat se filtrează și se va folosi ulterior pentru determinarea β- și γ-celulozei, iar reziduul de pe filtru se usucă în etuvă până la pond constant. Conținutul în α-celuloză se calculează procentual față de materialul vegetal absolut uscat (metoda TAPPI T203 cm-09 - *Alpha-, beta-, and gamma-cellulose in pulp* [11]).

Holoceluloza. Holoceluloza reprezintă complexul de polizaharide rămas după

îndepărtarea ligninei din materialul vegetal extras în prealabil cu solvenți organici, adică celuloza, pentozanele, hexozanele și acizii poliuronicici.

Dozarea holocelulozei prin metoda Jayme și Wise [15, 16] constă în tratarea materialului vegetal, în prealabil extras cu solvenți organici, cu clorit de sodiu în mediu acid la temperatura de 80-90°C. După cel puțin trei tratamente succesive și când materialul vegetal este de culoare albă, delignificarea se consideră terminată, iar amestecul se filtrează și se usucă în aer și apoi în etuvă la 105±3°C până la pond constant. Rezultatul se exprimă procentual față de materialul inițial absolut uscat luat în lucru.

Pentozanele. Dozarea pentozanelor din materialul vegetal se realizează prin acțiunea acidului clorhidric asupra pentozanelor, rezultatul fiind hidroliza lor la pentoze și trecerea ulterioară a acestora în furfurool prin fierbere. Furfuroolul este distilat și în funcție de cantitatea acestuia se determină procentul pentozanelor din materialul vegetal absolut uscat (metoda TAPPI T 223 cm-01 - *Pentosans in wood and pulp* [11]).

Lignina. Izolarea și dozarea cantitativă a ligninei se realizează direct, prin hidroliza și trecerea în soluție a hidraților de carbon, obținând lignina sub forma unui precipitat insolubil. Metoda lui Klason, transpusă în standardul TAPPI T222 om-06 - *Acid-insoluble lignin in wood and pulp* [11], reprezintă prima variantă analitică de dozare a ligninei în două trepte:

- prima etapă la rece - reactivul (acid sulfuric 72%) hidrolizează polizaharidele greu hidrolizabile până la oligozaharide, care rămân adsorbite în materialul vegetal;

- a doua etapă la cald - la temperatura de fierbere cu reactivul diluat la concentrației de 3%, hidroliza zaharurilor se termină până la monozaharide care devin astfel separabile de proba de lucru și trec în soluție.

La terminarea fierberii, lignina se lasă să se depună și apoi se filtrează, se spală pe filtru și se usucă în etuvă la 105±3°C până ajunge la pond constant. Conținutul procentual de lignină se raportează la materialul vegetal absolut uscat luat în lucru.

Substanțele extractibile. Extracția constituie operația preliminară în analiza materialului vegetal pentru a preîntâmpina erorile în determinarea celorlalte componente ale sale. Cunoașterea conținutului de extractibile din materialul vegetal prezintă o importanță practică, îndeosebi la fabricarea celulozei

deoarece aceste substanțe măresc consumul de chimicale la fierberi, inhibă procesul de fierbere sau influențează negativ proprietățile celulozei obținute. S-a luat în considerare, pe de o parte substanțele însoțitoare hidrofile, solubile în apă sau în soluții slab alcaline, ca de exemplu polizaharide, zaharuri, amidon, hemiceluloze ușor hidrolizabile, gume vegetale, etc., iar pe de altă parte substanțe hidrofobe (ceruri, grăsimi, rășini etc.) solubile în solvenți organici.

Metodele folosite preconizează tratarea materialului vegetal cu solventul respectiv și stabilirea proporției de produse trecute în soluție prin diferența de masă înainte și după extracție.

Extracția cu amestec alcool-benzen.

Principiul metodei constă în extracția dintr-o probă de material cu aparatul Soxhlet a produselor solubile într-un amestec alcătuit din două volume de benzen și o parte alcool etilic. Metoda prevede ca durata de extracție să fie de 6-8 ore cu minim 6 sifonări pe oră (metodele TAPPI T204 cm-07 - *Solvent extractives of wood and pulp* și T264 cm-07 - *Preparation of wood for chemical analysis* [11]).

Extracția cu alcool. Metoda prevede extracția materialului vegetal cu alcool etilic într-un aparat Soxhlet pentru o perioadă de minim 4 ore (metoda TAPPI T264 cm-07 - *Preparation of wood for chemical analysis* [11]).

Extracția cu apă rece. Principiul metodei constă în stabilirea proporției de material dizolvat în apa distilată la temperatura de 23±2°C cu agitare continuă. După macerare timp de 48 de ore, materialul se filtrează. Cantitatea de substanță solubilă în apă rece se determină procentual prin diferența între masa absolut uscată a probei inițiale și a rezidului (metoda TAPPI T207 cm-08 - *Water solubility of wood and pulp* [11]).

Extracția cu apă caldă. Metoda constă în extracția materialului vegetal în apă distilată la temperatura de fierbere sub reflux timp de 3 ore, urmat de filtrarea rezidului rezultat. Cantitatea de substanță solubilă în apă caldă se determină procentual prin diferența între masa absolut uscată a probei inițiale și a rezidului obținut (metoda TAPPI T207 cm-08 - *Water solubility of wood and pulp* [11]).

Extracția cu soluția de 1% hidroxid de sodiu. Principiul metodei constă în stabilirea proporției de material din probă trecută într-o soluție de hidroxid de sodiu 1% la temperatura de fierbere timp de o oră. Materialul extras se aduce cantitativ pe un creuzet filtrant și se spală cu apă caldă până la neutralizare, se usucă apoi în etuvă la 105±3°C, urmărindu-se ajungerea la

greutate constantă (metoda TAPPI T212 om-07 - *One percent sodium hydroxide solubility of wood and pulp* [11]).

Cenușa. Conform prevederilor metodei TAPPI T211 om-07 - *Ash in wood, pulp, paper, and paperboard: Combustion at 525°C* [11], principiul metodei constă în separarea substanțelor minerale în urma arderii complete a elementelor combustibile dintr-o probă de material, înțelegându-se în mod convențional rezidul ajuns la masă constantă după combustia probei la $525\pm 25^\circ\text{C}$. Pentru analiză s-a folosit materialul la care s-a determinat în prealabil umiditatea.

Conținutul de dioxid de siliciu și silicați în cenușa s-a determinat conform metodei TAPPI T244 cm-99 - *Acid-insoluble ash in wood, pulp, paper, and paperboard* [11], prin tratarea repetată a cenușii cu acid clorhidric și evaporarea până la sec.

Umiditatea. Conform metodelor TAPPI T210 cm-03 - *Weighing, sampling and testing pulp for moisture* [11] și T258 om-06 - *Basic*

density and moisture content of pulpwood [11], umiditatea reprezintă pierderile de masă suferită de o probă de material prin uscare la etuvă la temperatura de $105\pm 3^\circ\text{C}$.

3. REZULTATE ȘI DISCUȚII

Datele biometrice ale fibrelor de rapiță

Pentru caracterizarea calității materiei prime pentru industria de celuloză și hârtie, principalele elemente anatomice ale plantelor anuale care au cel mai important rol sunt fibrele, alături de care coexistă traheide, vase și alte tipuri de celule. În majoritatea lucrărilor de specialitate atunci când se vorbește despre elemente fibroase și se indică valorile lor biometrice, se folosește numai termenul de fibre, indiferent dacă se face referire la traheide, fibre veritabile sau vase. În figura 2 se prezintă imagini SEM ale fibrelor de rapiță obținute la diferite magnitudini.

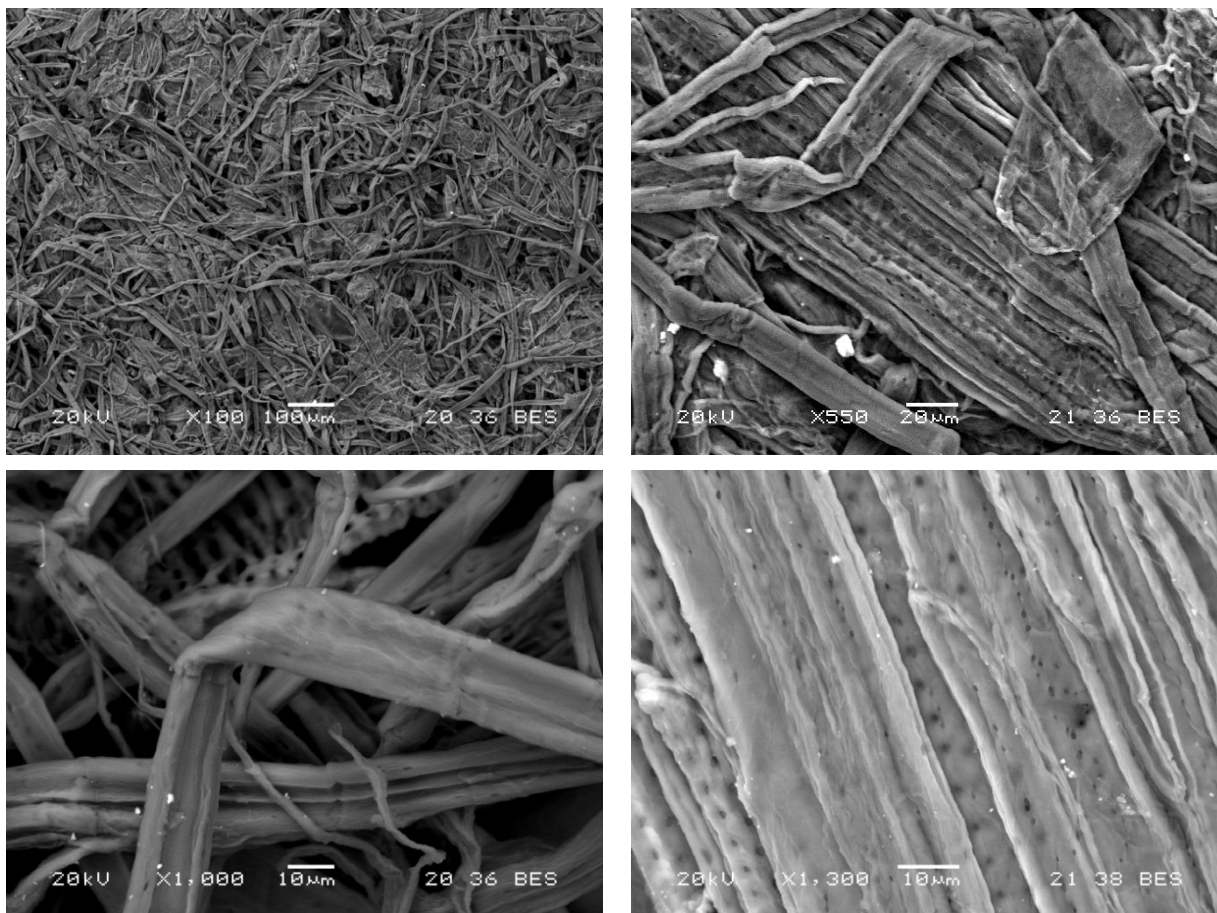


Fig. 2 Imagini SEM ale fibrelor de rapiță, obținute la diferite magnitudini

S-au determinat următoarele dimensiuni ale fibrelor: lungimea (L), grosimea peretelui celular (T), diametrul fibrei (D) și al lumenului

(d). Pe baza măsurătorilor efectuate asupra elementelor fibroase s-au calculat indicii morfologici de calitate, [17]:

- Indicele de flexibilitate, $E = d/D$;
- Indicele de împâslire, $S = L/D$;
- Criteriul Rünkel, $Ru = 2*T/d$;
- Criteriul Mühlsteph, $Mu = 100*(D^2-d^2)/D^2$;
- Coeficient de rigiditate, $R = 100*T/D$;
- Factorul F, $F = 100*L/T$.

Rapița se caracterizează prin eterogenitatea elementelor fibroase și prin conținutul ridicat de elemente nefibroase. Împreună cu fibrele celulozice, în materialul fibros obținut la delignificare se mai găsesc și

celule fine care pot fi elemente liberiene, traheide, celule parenchimatice, sclerenchimatice și epidermice datorită cărora celuloza obținută din plantele nelemnoase are un caracter mai eterogen decât cea obținută din lemn [18].

Fibrele de rapiță conțin mai multe tipuri de celule cu diferite dimensiuni și forme, care sunt marcate în figura 3.

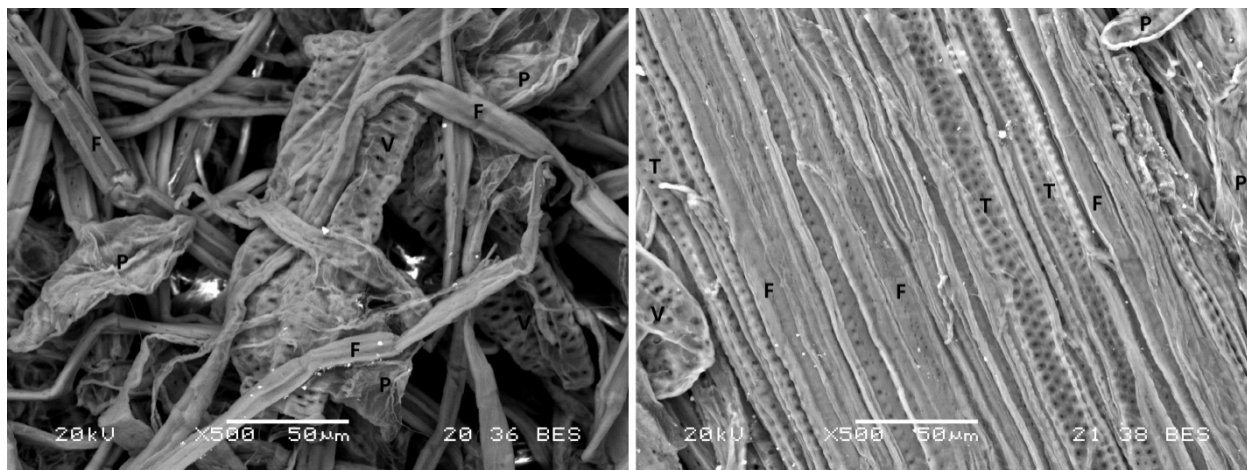


Fig. 3 Elemente anatomice în tulpina de rapiță:

F - fibre; V - vase; P – celule parenchimatice; T - traheide (mărire 500x)

Elementele anatomice prezente în tulpina de rapiță sunt:

- *Fibrele* propriu-zise sunt lungi, înguste, cu pereți groși, ascuțiți, fără perforații;
- *Vasele* sunt, de obicei, subțiri și marcate de numeroase perforații de diferite forme, capetele sunt retezate; perforațiile sunt simple sau scalariforme, iar vasele au un raport mic între lungime și diametru;
- *Traheidele* sunt lungi, înguste, cu pereți perforați;
- *Celulele parenchimatice* au dimensiuni variabile, cu pereți subțiri și formă de sac.

Analiza microscopică de ansamblu a elementelor fibroase arată că celulele de parenchim și vasele sunt în proporție neglijabilă, elementele principale fiind fibrele propriu-zise și traheidele.

Rezultatele prezentate în tabelul 1 arată că tulpinile de rapiță conțin fibre scurte cu proprietăți morfologice similare cu fibrele din

alte specii nelemnoase și lemnoase de foioase utilizate în mod uzual la fabricarea celulozelor.

Este cunoscut că rezistența hârtiei depinde de conținutul de celuloză cu fibră lungă. Rezistența în stare umedă a benzii de hârtie depinde de asemenea de conținutul de fibre lungi [19]. Totuși, celuloza cu fibră scurtă este de dorit în compoziția pastei de hârtie deoarece influențează favorabil caracteristicile de imprimare ale hârtiei, iar celuloza din rapiță poate fi o alternativă în acest sens [20].

Figura 4 prezintă distribuția lungimilor fibrelor de rapiță, determinată prin analiza de imagine cu microscopie optică. Lungimea medie a fibrelor este 1,2 mm, valoare similară cu alte fibre nelemnoase, cum sunt fibrele din paie de grâu, din stuf, precum și din speciile de foioase. Limitele valorilor dimensionale ale lungimii fibrelor de rapiță sunt cuprinse între 0,71 mm și 1,99 mm.

Tabelul 1 Dimensiuni ale fibrelor celulozice de rapiță și indicii morfologici corespunzători

	Valoarea minimă	Valoarea medie	Valoarea maximă	Deviația standard
Lungimea fibrelor (L), mm	0,71	1,198	1,99	0,26
Diametrul fibrelor (D), μm	9,10	13,10	19,60	3,34
Grosimea peretelui celular (T), μm	1,77	2,25	3,08	0,47
Diametrul lumenului (d), μm	4,34	8,60	13,44	2,82
Finetea fibrelor, mg/100m	6,75	8,84	10,52	1,54
Indicele de flexibilitate, E = d/D	0,48	0,64	0,72	0,09
Indicele de împâslire, S = L/D	61	91	132	23,28
Criteriul Runkel, Ru = 2*T/d	0,39	0,58	1,10	0,26
Criteriul Mühlsteph, Mu = 100*(D ² -d ²)/D ²	48,22	57,69	77,31	10,48
Coefficient de rigiditate, R = 100*T/D	14	18	26	4
Factorul F, F = 100*L/T	390	555	780	115

Lungimea fibrelor din tulpinile de rapiță, determinată prin analiză de imagine, poate fi împărțită în trei categorii (vezi tabelul 1 și figura 4):

- fibre lungi (peste 1,5 mm), grupul reprezentat de fibrele cu dimensiuni medii de 1,71 mm, care reprezintă 15% din totalul fibrelor de rapiță;
- fibre de lungimi medii (1 – 1,5 mm): fibrele cu dimensiuni medii de 1,19 mm, care reprezintă 56% din totalul fibrelor de rapiță;
- fibre scurte (sub 1 mm): fibrele cu dimensiuni medii de 0,94 mm reprezentând 29% din totalul fibrelor de rapiță.

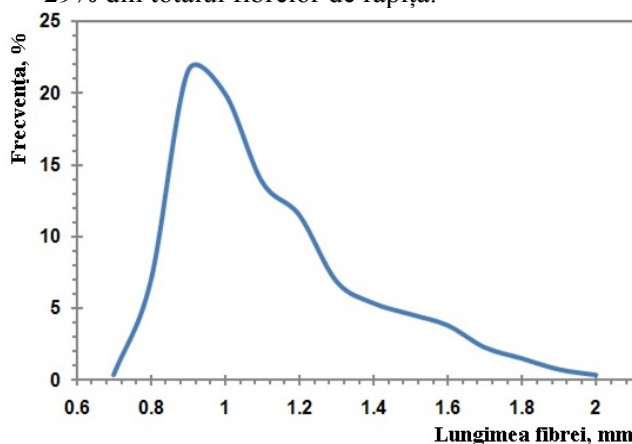


Fig. 4 Distribuția dimensională a lungimilor fibrelor de rapiță, determinată prin analiză de imagine

Datele privind clasarea fibrelor, indică asemănări între fibrele de rapiță cu fibrele de paie și stuf, îndeosebi în privința fibrelor scurte. În ordinea conținutului de fibre scurte, rapița se situează între stuf - 22% și paie - 25%. În cazul fibrelor de lungime medie, rapița conține un procent mai mare decât stuful - 35% și decât paiele - 44%. Valorile pentru fibrele lungi în cazul rapiței (16 %) se situează la mai puțin de jumătate atât față de stuf (43%) și paie (31%) [21].

Clasarea fibrelor pe grupe de lungimi, prin fracționarea pe site folosind clasorul Bauer-McNett este prezentată în figura 5. Lungimea medie gravimetrică a fibrelor calculată din greutatea uscată a fracțiunilor de fibre celulozice este de 16% fibre lungi, 57% fibre de lungime medie și 23% fibre scurte. Conținutul de material fin a fost de 4%. Se observă o bună concordanță între distribuția lungimii fibrelor determinată prin analiză de imagine și prin clasare.

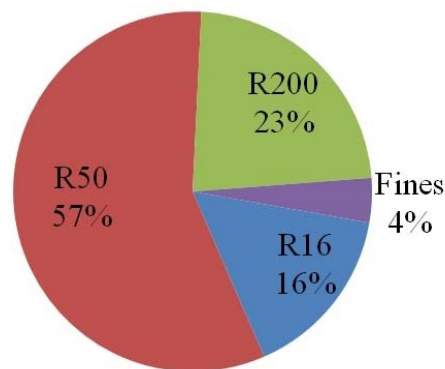


Fig. 5 Clasarea a fibrelor de rapiță (clasorul BauerMcNett)

Diametrul și grosimea peretelui celular dictează flexibilitatea fibrelor. Fibrele cu pereții groși influențează negativ numărul de duble îndoiri, plesnirea și lungimea de rupere a hârtiei. Pe de altă parte, hârtiile din fibre cu pereți subțiri vor fi mai bine formate și vor avea structura mai densă. Din acest punct de vedere, fibrele de rapiță se aseamănă cu fibrele din paie și din stuf. Diametrele fibrelor de rapiță, au fost cuprinse între 9,10 și 19,60 μm, cu o valoare medie de 13,1 μm. Din datele prezentate în

tabele 1 și 2 se constată că valorile medii ale diametrelor situează fibrele de rapiță deasupra celor de orez și de floarea soarelui, la același

nivel cu esparto și grâul, dar sunt inferioare stufului și fibrelor lemnoase.

Tabelul 2 Raporturi dimensionale comparative privind fibrele de rapiță, floarea-soarelui, paie și stuf [22-24]

	Rapiță	Floarea-soarelui	Paie de grâu	Stuf
Lungimea fibrei (L), mm	1,2	0,9	1,5	1,6
Diametrul fibrei (D), μm	13,1	11	13	19
Peretele celular (T), μm	2,25	4	2	5
Diametrul lumenului (d), μm	8,6	4	10	10
Indicele de flexibilitate, $E = d/D$	0,48-0,72	0,36-0,63	0,77-0,9	0,37-0,54
Indicele de împâslire, $S = L/D$	91	78	123	82
Criteriul Runkel, $Ru = 2 \cdot T/d$	0,39-1,10	0,5-1,7	0,2-0,57	1,3
Criteriul Mühlsteph, $Mu = 100 \cdot (D^2 - d^2)/D^2$	48-77	46-86	18-40	52
Referințe	Studiul actual		[24]	

La determinarea grosimii pereților celulari ai fibrelor de rapiță s-au obținut valori ce se situează între 3,08 și 1,77 μm, cu o medie de 2,25. Diametrul maxim al lumenului a fost de 13,44 μm, minimul de 4,34 μm, iar valoarea medie 8,6 μm.

În ansamblu, privind comparativ distribuția lungimii fibrelor, grosimea peretelui celular și diametrul lumenului la rapiță, stuf și paie, este de presupus creșterea vitezei de măcinare în cazul celulozei din rapiță, fapt dovedit și experimental. De asemenea, viteza mare de măcinare se explică și prin conținutul crescut de pentozane care favorizează atât umflarea fibrelor cât și prin fibrilarea intensă care determină creșterea suprafeței specifice a fibrelor [25].

Lungimea și diametrul fibrelor, grosimea peretelui celular și diametrul lumenului sunt caracteristici foarte importante pentru compararea diferitelor specii vegetale din punctul de vedere a potențialului papetar. Indicii specifici sunt indicele de flexibilitate, indicele de împâslire, criteriul Runkel și criteriul Mühlsteph. În plus, coeficientul de rigiditate și factorul F, deși mai puțin folosiți în literatura de specialitate, stabilesc corelația între însușirile fibrelor și caracteristicile hârtiei.

Indicele de flexibilitate, definit prin raportul dintre diametrul lumenului și diametrul fibrei, oferă indicații asupra numărului de legături ce se stabilesc între fibre [19]. Astfel, un număr mai mare de legături între fibre formează o structură mai densă și oferă posibilitatea hemicelulozelor să îndeplinească funcția de liant și să se dezvolte legături de hidrogen, în favoarea rezistenței hârtiei [26, 27].

Clasificarea speciilor fibroase după valoarea indicele de flexibilitate se face în 4 grupe:

- fibre foarte elastice - au indicele de flexibilitate mai mare de 0,75;
- fibre elastice - au indicele de flexibilitate cuprins între 0,50-0,75;
- fibre rigide - au indicele de flexibilitate cuprins între 0,30-0,50;
- fibre foarte rigide - au indicele de flexibilitate mai mic de 0,30.

Fibrele care au indicele de flexibilitate peste 0,5 pot da hârtii dense cu rezistențe mecanice superioare, pe când cele cu indicele de flexibilitate mai mic de 0,5 dau hârtii voluminoase, poroase și cu rezistențe reduse [19, 28, 29].

Procentual, 81% din fibrele de rapiță sunt din categoria fibrelor elastice, restul de 19% reprezentând fibre rigide. Valoarea medie a indicelui de flexibilitate pentru fibrele de rapiță este ridicată (64 %), fiind superioară fibrelor din fag, asemănătoare stufului și florii-soarelui, dar inferioară grâului și pinului [19, 24].

Indicele de împâslire reprezintă raportul dintre lungimea și diametrul fibrei, iar o valoare mare a acestui indice este de dorit pentru obținerea produselor papetare cu proprietăți de rezistență [30]. În cazul rapiței s-au obținut valori cuprinse între 61 și 132, cu 91 ca valoare medie.

Indicele de împâslire pentru fibrele din lemn de foioase este de 55-75, în timp ce pentru fibrele din conifere este de 95-120 [31]. Valoare medie de 91 situează fibrele de rapiță între fibrele de foioase și conifere. Comparativ cu alte plante anuale, indicele de împâslire este superior fibrelor de floarea-soarelui și stufului, respectiv inferior fibrelor de paie cerealiere.

Criteriul Runkel exprimă raportul dintre dublul grosimii peretelui celular și diametrul lumenului, valori obținut din măsurătorile realizate în secțiune transversală a fibrelor [32]. Criteriul Runkel clasifică fibrele în 5 grupe [19]:

- *grupa I* cu valori mai mici de 0,25 și *grupa a II-a* cu valori cuprinse între 0,25 și 0,5 reprezintă fibrele cu pereți subțiri și lumenul mare. Aceste fibre se aplatizează ușor, sunt foarte flexibile și de aceea formează legături interfibrilare dezvoltate. Hârtiile obținute au densitate ridicată și caracteristici de rezistență superioare;

- *grupa a III-a*, cu valori între 0,51 și 1,0 conține fibre la care lumenul are dimensiuni medii, iar pereții pot fi mai subțiri sau mai groși. Fibrele au flexibilitate, și e aplatizează ușor. Hârtiile vor avea caracteristici de rezistență ridicate;

- *grupa a IV-a* cu valoarea criteriului cuprinsă între 1,01-2 și *grupa a V-a* cu valoarea mai mare de 2,01 reprezintă fibre rigide cu lumenul îngust. Fibrele sunt rigide, iar hârtiile vor avea densitatea scăzută și caracteristici de rezistență inferioare.

În cazul fibrelor de rapiță, valoarea indicelui Runkel variază între 0,39 și 1,10. □inând seama de grupele de clasificare ale criteriului Runkel, 62% din numărul fibrele de rapiță se găsesc în *grupa a II-a*, 20% se găsesc în *grupa a III-a* și 18% se încadrează în *grupa a IV-a*. Valoarea medie a indicelui (0,58), clasifică fibrele de rapiță ca fiind favorabile privind potențialul papetar.

Fibrele de rapiță se aseamănă, din punct de vedere al criteriului Runkel cu paie cerealiere [24] și se plasează între fibrele de fag și cele de molid [33].

Criteriul Mühlsteph reprezintă valoarea raportului dintre suprafața pereților și suprafața fibrei în secțiune transversală și se referă la forma fibrelor din paste celulozice provenite din materiile prime vegetale [34, 35]. Criteriul Mühlsteph împarte fibrele vegetale în trei grupe [19]:

- *grupa I* cu valoarea raportului sub 30 sunt fibre în formă de panglică cu pereți subțiri și lumenul mare;

- *grupa a II-a* cu valoarea raportului cuprins între 31 și 80 sunt fibre cu forme intermediare între panglică și bastonaș;

- *grupa a III-a* conține fibre cilindrice, necolapsate, sub formă de bastonașe drepte cu valoarea raportului peste 81 datorită pereților celulari groși și lumenului mic.

Conform acestui criteriu, prima grupă include fibrele cu flexibilitate mare și grad de împâslire ridicat, fiind cele mai potrivite pentru obținerea hârtiilor cu proprietăți mecanice superioare.

Criteriul Mühlsteph pentru fibrele din rapiță are valori cuprinse între 48 și 77, valori care includ aceste fibre în *grupa a II-a*, a

fibrelor cilindrice cu forme intermediare între panglică și bastonaș. Ele se aseamănă cu fibrele din paie și din stuf.

Coeficientul de rigiditate reprezintă raportul dintre grosimea peretelui și diametrul fibrei și se știe că pe măsură ce acest raport crește, proprietățile mecanice ale hârtiilor se înrăutățesc [35, 36]. Coeficientul de rigiditate al fibrelor de rapiță este cuprins între 14 și 26. Valoarea medie (18) este mai mică decât în cazul fibrelor de fag (26) și mai mare decât a fibrelor de pin (14) [81]. Rezultă că fibrele de rapiță se încadrează în privința rigidității între cele de fag și fibrele de pin.

Factorul F sau *coeficientul L/T* reprezintă raportul dintre lungime fibrei și grosimea peretelui celular. El se folosește pentru caracterizarea fibrelor din punctul de vedere al flexibilității [37-39]. Valoarea medie a factorului F pentru fibrele de rapiță este 555, cu variații de la 390 la 780. Fibrele de pin și cele de brad au valori medii 1170, respectiv 1030 [40], iar fibrele de fag și de mesteacăn au factorul F 207, respectiv 403 [41]. Ca și în cazul coeficientului de rigiditate, fibrele de rapiță se încadrează între fibrele de conifere și de foioase în privința rigidității.

Datele biometrice ale fibrelor de rapiță arată faptul că ele pot substitui fibrele de paie și de stuf în compoziția pastelor de hârtie, conferind hârtiei proprietăți asemănătoare.

Compoziția chimică a tulpinilor de rapiță

Din punctul de vedere al potențialului papetar, interesează nu numai datele biometrice tulpinilor și ale fibrelor ci și compoziția chimică. Determinarea compoziției chimice este utilă pentru compararea rapiței cu alte resurse vegetale ca materie primă pentru obținerea celulozei. Interesează mai ales componenții principali (celuloza, hemicelulozele și lignina), dar și unii componenți secundari cum sunt substanțele extractibile și cenușa. Este cunoscut faptul că cu cât conținutul de celuloză este mai ridicat, randamentul la dezincrustare va fi mai mare, iar cu cât procentul de lignină este mai mic, cu atât efortul necesar pentru delignificare va fi mai redus. [42, 43].

Tulpinile de rapiță s-au analizat privind compoziția chimică după metodologia obișnuită și folosind metodele uzuale, aplicabile atât la lemn cât și la plante anuale. Rapița conține o cantitate apreciabilă de măduvă și de aceea, caracterizarea chimică s-a efectuat pe tulpinile integrale, pe tulpinile libere de măduvă și la măduva separată din tulpini. În tabelul 3 se

prezintă rezultatele obținute la determinarea compoziției chimice a tulpinilor de rapiță.

Tabelul 3 Compoziția chimică a tulpinilor de rapiță

Component		Metoda de analizat	Tulpini integrale, %	Tulpini fără miez, %	Miez, %
Celuloză	α -celuloză	T203 cm-09	39,9	42,2	22,2
	Celuloză	Kürschner-Hoffer	41,0	44,5	25,0
	Celuloză	Seifert	34,5	36,4	18,4
Pentozane		T223 cm-01	23,4	21,8	33,7
Holoceluloză		Jayme și Wise	72,1	74,5	56,6
Lignina	Insolubilă în acid	T222 om-06	20,6	19,5	27,7
	Solubilă în acid	NREL laboratory	0,9	0,7	2,2
	Cenușă în lignină	T211 om-07	1,3	0,9	-
	Total		21,5	20,2	29,9
Extractibile	Etanol-benzen	T204 cm-07	2,8	1,4	1,9
	Etanol	T264 cm-07	1,6	1,0	5,5
	Apă	T264 cm-07	2,3	4,6	4,5
	Total		6,8	6,9	11,9
Solubile	Apă rece	T207 cm-08	7,5	6,4	14,6
	Apă caldă	T207 cm-08	8,6	8,0	12,5
	1% NaOH	T212 om-07	29,1	29,0	29,8
Cenușa		T211 om-07	5,8	2,5	7,1
Silicați		T244 cm-99	0,7	0,6	1,4

Din tabelul 3 se observă că procentul de holoceluloză este ridicat, 72,1 % la tulpinile cu tot cu măduvă și 74,5 % la tulpinile din care s-a eliminat măduva. Este interesant faptul că și măduva conține o cantitate ridicată de holoceluloză, 56,6 %. Celuloza Kürschner-Hoffer reprezintă 41,0 % la tulpinile integrale și 44,5 % la tulpinile fără măduvă. Măduva conține aproximativ 18 % celuloză. Tulpinile de rapiță conțin mai multă celuloză decât paiele de grâu (34-40 %), dar mai puțină decât stuful (44-46 %) [22, 23].

Conținutul de pentozane este 23,4 % la tulpinile integrale și 21,8 % la tulpinile din care s-a extras măduva. Din acest punct de vedere, rapița conține mai multe pentozane decât lemnul de rășinoase și chiar de foioase, dar mai puține decât paiele de grâu și aproximativ la fel cu stuful. Se remarcă conținutul ridicat de pentozane din măduvă (33,7 %). Pentru conținutul de lignină s-au găsit valorile medii de 20,6 % la tulpinile integrale și 19,5 % la tulpinile eliberate de măduvă. Măduva conține 27,7 % lignină. Din punctul de vedere al conținutului de lignină, rapița poate fi comparată cu stuful și cu unele specii de foioase (plopul, mesteacănul), dar conține mai multă lignină decât paiele de grâu.

Datele privind compoziția chimică arată faptul că din punct de vedere a componentelor principali, tulpinile de rapiță reprezintă o materie primă atractivă pentru fabricarea celulozei. Prezența măduvei, care conține multe pentozane și mai multă lignină decât tulpina, constituie un dezavantaj. Dintre

componentii secundari atrage atenția conținutul de cenușă. Acesta are valoarea de 5,8 % la tulpinile integrale, fiind sensibil mai mic decât cenușa din paiele de grâu (7-10 %), dar mai mare decât cenușa din stuf (3,5-5 %). Se remarcă faptul că cenușa conține o cantitate redusă de silicați (0,7 %), mult inferioară paielor de grâu (4,5-5,5 %).

4. CONCLUZII

- Rapița se caracterizează prin eterogenitatea elementelor fibroase (fibre veritabile, traheide, vase) și prin conținutul ridicat de elemente nefibroase. Împreună cu fibrele, se găsesc și celule fine care pot fi elemente liberiene, celule parenchimatice, sclerenchimatice și epidermice. Celuloza obținută din tulpinile de rapiță are caracter mai eterogen decât cea obținută din lemn;
- Celuloza de rapiță face parte din categoria celulozelor cu fibră scurtă, asemănându-se cu celulozele din paie și din stuf. În ordinea conținutului de fibre scurte, rapița se situează între stuf - 22% și paie - 25%. În cazul fibrelor de lungime medie, rapița conține un procent mai mare decât stuful - 35% și decât paiele - 44%. Proporția de fibre lungi în cazul rapiței (16 %) se situează la mai puțin de jumătate atât față de stuf (43%) și paie (31%);
- Compoziția chimică arată faptul că din punct de vedere a componentelor principali, tulpinile de rapiță reprezintă o materie primă atractivă pentru fabricarea celulozei. Prezența măduvei, care conține mai multe pentozane și mai multă

lignină decât tulpina, constituie un dezavantaj. Conținutul de cenușă are valoarea de 5,8 %, fiind sensibil mai mic decât cenușa din paie de grâu (7-10 %), dar mai mare decât la stuf (3,5-5 %). Cenușa tulpinilor de rapiță conține o cantitate de silicați mult inferioară cenușii din paie de grâu.

5. MULȚUMIRI

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CELLULOSE CHEMISTRY AND TECHNOLOGY

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MATHEMATICAL MODELING IN ELECTROSPINNING PROCESS OF NANOFIBERS: A DETAILED REVIEW

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Electrospinning represents an efficient and versatile technique for fabrication of very thin fibers from polymers or composites. Various polymers have been successfully electrospun into ultrafine fibers in recent years mostly in solvent solution and some in melt form. The efficiency of this process can be improved by adjusting the composition of the solution and the configuration of the electrospinning apparatus, such as voltage, flow rate etc., therefore optimizing the alignment and morphology of the fibers produced. In addition, several applications demand well-oriented and diameter and porosity controlled nanofibers. Thus, recently there has been great interest to optimize this method in order to solve the problems that make electrospinning uncontrollable. Mathematical and theoretical modeling and simulating procedure will permit to offer an in-depth insight into the physical understanding of complex phenomena during electrospinning and might be very useful for managing contributing factors toward increasing production rate. In this review article, we give a general outlook of the most common mathematical models for electrospinning, which have been introduced so far, and briefly point out their weak points.

Keywords: electrospinning, nanofibers, jet instability, modeling

RADIAL VARIATION IN WOOD STATIC BENDING OF NATURALLY AND PLANTATION GROWN ALDER STEMS

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This study was carried out to determine radial variation of wood density, modulus of elasticity (MOE), modulus of rupture (MOR) and stress at elastic limit in plantation and natural alder forests in the north of Iran. Testing samples were taken at breast height of the stem and in three radial positions (10, 50 and 90% of radius) from natural and plantation forests to determine wood mechanical strength properties, according to the ASTM standard. The analysis of variance indicated that planting conditions (natural and plantation forests), radial position and their interaction had no significant effects on the modulus of elasticity (MOE), modulus of rupture (MOR) and stress at elastic limit in alder wood, while only radial position had a significant effect on wood density. Wood density was increased along radial direction from the pith to the periphery for both planting conditions. Overall, the mechanical strength properties in the plantation forest were slightly higher compared to the natural forest. The relationship between wood density and mechanical properties were analyzed by linear regression. A positive relationship was found between wood density and mechanical properties for both planting conditions. This relationship was stronger in plantation grown, compared to naturally grown trees.

Keywords: *Alnus glutinosa*, static bending properties, natural forest, plantation forest

MECHANICAL CHARACTERIZATION OF MICROLAMINAR STRUCTURES EXTRACTED FROM CELLULOSIC MATERIALS USING NANOINDENTATION TECHNIQUE

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Nanohardness (H) and elastic modulus (E) properties of several biomass by-products (fruit shells) have been characterized by nanoindentation technique. Two procedures were followed: (i) 3D topographic images for the microstructure characterization and (ii) 2D mechanical mapping for density and mechanical distribution features analysis. Results revealed the typical cellulosic cell wall structures, indicating that the reduced modulus values (E_r) for the cellulosic cells and the amorphous matrix phases were of 6.2 GPa and 4 GPa, respectively, for the apricot shell. The single phases of the rest of structures were tested, showing differences in modulus due to the content of cellulose in the hierarchical structure, and various H and E_r features for each specimen and microstructure analyzed.

Keywords: nanoindentation, mechanical properties, cellulosic biomaterials

NON-LINEAR VISCOELASTIC BEHAVIOR OF NOVEL REGENERATED CELLULOSE FIBER IN DRY AND WET CONDITION

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Viscoelastic models were employed to analyze the mechanical properties of novel regenerated cellulose fiber from NaOH complex solution. The stress-strain curves of the dry and wet fiber were fitted. The models were composed of a Maxwell element, linear spring and non-linear spring. The tested results indicate that the regenerated cellulose fibers exhibit better tensile properties in dry and wet condition than those of viscose rayon. It can be explained by the high molecular weight of novel regenerated cellulose fiber ($\sim 1.1 \times 10^5$), compared to that of viscose rayon ($\sim 5 \times 10^4$), as well as high degree of crystallinity (60~65% to 30~40%).

Keywords: non-linear, viscoelastic, cellulose fiber, orientation, wet condition

RHEOLOGICAL RESEARCH OF SOME POLYSACCHARIDE GELS LOADED WITH NIGELLA SATIVA EXTRACTS

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Rheological properties of xanthan and carrageenan polysaccharides were investigated by means of dynamic shear oscillation measurements. These hydrogels were tested both with and without *Nigella sativa* extracts of different pH values. Although no major difference was noticed between the control samples and those loaded with the active ingredients, some of the new gels showed better rheological behavior.

Keywords: *Nigella sativa* extracts, xanthan and carrageenan, viscoelastic domain, cosmetic vehicles, polysaccharide gels

SOME ASPECTS OF THE CHARACTERIZATION OF VEGETABLE GUMS: *PRUNUS PERSICA* (PLUM) and *PRUNUS DOMESTICA* (CHERRY)

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The paper deals with the characterization of some vegetable gum exudates (plum tree, cherry tree) by FTIR spectroscopy, C^{13} NMR spectroscopy, thermo-gravimetric and rheological analyses of the dilute aqueous solutions. The functional groups and main components of the studied gums have been identified: galactan, xylan, arabinan. It is emphasized that there are differences in thermal stability between the two gums. For the dilute aqueous solutions of the analyzed gums, with a concentration ranging between 0.005-2.0 g/dL, Huggins constant values [K] and intrinsic viscosity $[\eta]$, which are dependent on the structure, molecular weight and interactions between existing functional groups, were established.

Keywords: vegetable gums, termogravimetric analysis, intrinsic viscosity, C^{13} NMR, FTIR

MORPHOLOGICAL AND SURFACE ASPECTS OF CELLULOSE-LIGNIN HYDROGELS

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Cellulose-lignin hydrogels (CL), prepared by a two-step procedure consisting in dissolving the cellulose in an alkaline solution at low temperature, followed by the crosslinking reaction with lignin in the presence of epichlorohydrin, were subjected to experimental approaches, additional to those reported before, for their in-depth characterization. Thus, the morphology was examined by optical and scanning electron microscopy (SEM), while some surface properties (surface area, average pore size, and sorption capacity) were estimated by dynamic water vapor sorption (DVS) analysis. The changes in crystalline structure of the samples were confirmed by X-ray diffractometry (XRD). It has been found that these characteristics are influenced by the lignin whose presence leads to increased porosity of the material.

Keywords: cellulose-lignin hydrogel, dynamic water vapor sorption, X-ray diffraction, optical microscopy, scanning electron microscopy, structural characterization

ANTIOXIDANT AND ANTIBACTERIAL ACTIVITIES OF SOME NATURAL POLYPHENOLS

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The present study provides information on separation and identification of natural bioactive compounds from different vegetal materials with potential applications as antibacterials and plant growth modulators. Natural extracts were obtained by alcoholic and water extraction from spruce bark, grape seeds, *Crataegus monogyna* (hawthorn) and *Asclepias syriaca* (milkweed). HPLC-DAD analysis revealed that gallic acid (12.54 mg/100 g) and catechin (85.52 mg/100 g) were the most abundant compounds in hawthorn and grape seed extracts, vanillic acid (71.9 mg/100 g) was found in high concentrations in spruce bark wood, while milkweed extracts were characterized by the presence of hydroxycinnamic acids and flavonoids. The DPPH assay indicated that the highest radical scavenging activity was registered by grape seeds ($EC_{50} = 45.75 \mu\text{g}$) and hawthorn ($EC_{50} = 17.8 \mu\text{g}$) alcoholic extracts.

The same extracts exhibited antibacterial properties on *Staphylococcus aureus*, while the samples obtained from spruce bark and milkweed extracts inhibited the development of *Escherichia coli* and *Pseudomonas aeruginosa* species. Furthermore, the toxicity of the natural extracts was evaluated by their application in germination tests of *Phaseolus vulgaris*. The obtained results demonstrated that a high concentration of polyphenols has an inhibitory effect on plant development, while lower concentrations determine a considerable stimulation of plantlet elongation.

Keywords: polyphenols, extraction, characterization, HPLC, radical scavenging, antibacterial activity, seed germination

SYNTHESIS AND CHARACTERIZATION OF PECTIN-DEHYDROGENATION POLYMER COMPLEX BY ISOTOPIC LABELING METHOD

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Coniferin is closer to natural lignin precursors than coniferyl alcohol. Both conventional and α - ^{13}C labeled coniferin were polymerized in the presence of pectin to obtain a pectin-dehydrogenation polymer (pectin-DHP) complex under a closer approximation condition of the natural process for the formation of macromolecular lignin in the cell wall. A pectin-DHP complex was isolated and purified by extraction, hydrolysis, centrifugation and gel-adsorption method. The structure of the complex was analyzed by ^{13}C carbon nuclear magnetic resonance (^{13}C -NMR) spectroscopy. The results of ^{13}C -NMR spectroscopy indicate that DHP was covalently linked to the pectin by benzyl ether bonds, ester bonds and acetal bonds. It was also found that the structure of the pectin-DHP complex approximated that of native lignin more closely than did the structure of the DHPs prepared from coniferyl alcohol. By these results, it was demonstrated that the lignin-pectin complex occurs in plant cell during lignin formation.

Keywords: pectin, coniferin, isotopic labeling method, ^{13}C -NMR

SPECTROSCOPIC COMPARISON OF ORGANOSOLV LIGNINS ISOLATED FROM WHEAT STRAW

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Glycerol lignin (LIG-Gly), dimethylformamide lignin (LIG-DMF) and mixed solvents (glycerol and dimethylformamide) lignin (LIG-Gly, DMF) were isolated from wheat straw by organosolv pulping. The physical characterization of three different lignins isolated under laboratory conditions from wheat straw was performed. The structures of lignins were studied by three non-destructive (FT-IR, ¹H and ¹³C NMR spectroscopy) methods. The examination of FT-IR and ¹H NMR spectra did not show changes in the main structure of lignins, but based on ¹³C NMR spectra of lignin obtained from glycerol (LIG-Gly), C- α , C- β and C- γ in β -O-4 and carbon-carbon bonds, such as β - β , β -5, were observed. In the case of lignin that was obtained from mixed solvents (LIG-Gly, DMF), the signals for C- β and C- γ in β -O-4 and β -1, β -5 and 5-5 type structures were detected. In the ¹³C NMR spectra, signals relating to the ester groups obtained from the linkage of *p*-coumaric acids, ferulic acids and an ether linkage from ferulic acid and lignin were observed. In the lignin obtained from DMF (LIG-D), no fractures occurred.

Keywords: organosolv, wheat straw, lignin, FT-IR, NMR

STUDY ON THE MODIFICATIONS IN THE COMPOSITION OF SUGARS FROM LIGNOCELLULOSIC SUBSTRATES EXPOSED TO THE ACTION OF FUNGI

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The paper presents the results concerning the modifications in the sugar composition resulted from lignocellulosic substrates subjected to the action of lignolytic fungi: *Pleurotus ostreatus* and *Phanerochaete chrysosporium*. The substrates used were formed by various mixtures of corn cobs and oak tree leaves, oak tree sawdust and oak tree leaves, and oak tree bark – oak tree

leaves, all in ratios of 2:1 (marked as mixtures I, II and III). The evaluation of the sugar composition of the substrates biodegraded by the above-mentioned fungi, for 30 days, was performed after hydrolysis, using 1N sulfuric acid at 120 °C, for one hour, followed by sodium carbonate treatment until a pH of 5.8 was reached. The quantitative determinations were performed through gas chromatography. The gathered data showed that the highest degree of the heteropolysaccharide degradation corresponded to *Pleurotus ostreatus*, while the fungus *Phanerochaete chrysosporium* cultivated under the same conditions degraded carbohydrates at a lower level. Also, a large consumption of pentoses was recorded, evaluated through the variation of the xylose amounts, which rapidly decreased in case of the *Pleurotus ostreatus* microorganism, in comparison with the substrate inoculated by *Phanerochaete chrysosporium*.

Similarly, the hexoses consumption levels (mainly of glucose) were quite modest in the case of *Pleurotus ostreatus* and quite significant for *Phanerochaete chrysosporium*.

Keywords: lignocellulosic substrates, lignolytic fungi, carbohydrate degradation

IMPACT OF HEMICELLOSES PRE-EXTRACTION ON PULP PROPERTIES OF SUGARCANE BAGASSE

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The extraction of hemicelluloses, which otherwise would be wasted in the black liquor, can be integrated with chemical pulping processes in a biorefinery approach that will generate a sugar-rich feedstock for production of fuels and chemicals. Extractions of hemicelluloses from sugarcane bagasse under dilute sulphuric acid or mild alkaline conditions were performed, using a central composite experimental design. Selected solid residues obtained after dilute acid, hot water (zero acid) or mild alkaline pre-extractions were subjected to soda or soda-AQ pulping, and kraft pulping of the dilute acid pre-extracted solid residue was also performed. The integration of hemicelluloses pre-extraction by alkaline methods into a soda-AQ-based pulping process was preferred for sugarcane bagasse as feedstock, since it enabled xylan recovery of 69.1%, while providing pulps with superior tear strength and brightness.

Keywords: biorefinery, xylan extraction, sugarcane bagasse, chemical pulping, pulp quality, handsheet strengths

WHEAT STRAW PULP FRACTIONATION PART 1. THE EFFECT OF CELLS, VESSELS AND FINES ON PAPER PROPERTIES

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A study on the effect of fractionation of wheat straw pulp shows the effects of various wheat straw pulp components on paper strength. An industrial type pressure screen and hydrocyclones of two different sizes were used to produce fines and coarse fractions containing different amounts of parenchyma, vessel and epidermal cells. The vessels were found to behave more like fibers in the fractionation process, and this made it possible to create parenchyma and epidermal cell-rich fractions. By gradually replacing the original pulp with the different fractions, it was seen that certain paper physical properties do not necessarily follow the expected trends. For instance, the fines fractions behaved very differently and, by fractionating the suspension, better bulk-strength ratios were obtained. The coarsest fiber fraction had the highest tensile and tear strengths, but the finest fines fraction gave the highest Scott bond values. By utilizing this information, the fractionation process and dosing ratios can be used to obtain high-strength papers without any negative effects on dewatering or densification.

Keywords: non-wood, straw pulp, parenchyma cell, epidermal cell, vessel, paper property

EFFECT OF ADDING SECONDARY FIBERS TO KRAFT PULP ON STRENGTH PROPERTIES AND AIR RESISTANCE

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This paper deals with the utilization of secondary fibers as one of possible furnishes for the production of sack paper. The effect of the addition of waste papers to the virgin kraft pulp upon the tensile properties, paper porosity, and bonding ability was investigated. Waste papers, namely postconsumer corrugated board (quality grade A5), and cut-offs obtained from never-used

corrugated board (quality grade A6), were chosen as secondary fibers. The results obtained were evaluated using statistical methods and compared with those reported for sack papers. The addition of waste papers to virgin kraft pulp increased air resistance, but lowered tensile strength from 7.99 km for virgin kraft pulp to 3.83 and 4.13 km for waste paper of quality grades A5 and A6, respectively.

Keywords: waste paper, kraft pulp, tensile energy absorption, air resistance

RECENT DEVELOPMENT IN COMBINING FLAME-RETARDANT AND EASY-CARE FINISHING FOR COTTON

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Flame retardancy and easy-care properties are desired in several articles produced from cotton fiber. Therefore, chemical finishing of cotton fiber, using reduced consumption of water and energy, is obviously important. Apparently, developments in combining the flame-retardant finishing and easy-care finishing would be useful for the textile finishing sector. Any similarity in the type of reagents used in the finish bath and processing conditions, including padding, drying and curing, presents interest as to combining the two separate finishing processes. Flame-retardant and easy-care finishing of cotton fibers requires an appropriate cross-linking agent and catalyst. The finish composition may be applied through the pad-dry-cure processing sequence. Studies have shown the possibility of achieving flame retardancy and crease recovery properties in cotton fiber through combined flame-retardant, and easy-care finishing. Low-formaldehyde based cross-linking agent, or formaldehyde-free cross-linking agent including dimethyloldihydroxyethyleneurea and selected polycarboxylic acids are used. This paper describes some of the important recent development achieved in producing the flame-retardant and crease recovery properties in cotton fabric using combined finish liquor application.

Keywords: easy-care finishing, flame-retardant finishing, cellulose, phosphorous, cross-linking agents, catalysts, polycarboxylic acids

SOLID-PHASE EXTRACTION OF Pb FROM COMMON SALT AND WATER SAMPLES BY CELLULOSE MODIFIED WITH ANHYDROUS EDTA

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A regenerated cellulose fiber functionalized by anhydrous EDTA has been synthesized, then it was employed as a solid-phase extraction material for preconcentration and determination of trace Pb in common salt and water samples. The chelating cellulose (Cell-EDTA) was characterized by infrared spectrometry and elemental analyses. In order to obtain quantitative recoveries of Pb, various analytical parameters, such as pH, amounts of solid-phase, equilibration rate, sample volume, eluent volume, flow rate etc. were investigated. The effects of some metal ions on the sorption of Pb were also examined. The maximum sorption capacity of 0.68 mmol/g was obtained. A preconcentration factor 200 (using 2000 mL of sample and 10 mL of eluent) was achieved. The proposed method was applied to determine the trace amount of Pb in common salt and water samples. The detection limit of Pb was $1.5 \mu\text{g L}^{-1}$ as the concentration in 500 mL solution (20-fold preconcentration).

Keywords: EDTA-type chelating cellulose, Pb, solid-phase extraction, preconcentration, common salt

EFFECT OF DIFFERENT CONDITIONS ON THE AVERAGE DEGREE OF POLYMERIZATION OF BACTERIAL CELLULOSE PRODUCED BY *GLUCONACETOBACTER INTERMEDIUS* BC-41

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The average degree of polymerization (DP) of bacterial cellulose (BC), which was secreted by selected *Gluconacetobacter intermedius* BC-41, was studied using the viscosity measurement method under five different sets of conditions, with varying media, cultivation modes, fermentation time, carbon sources and surfactants. The DP of BC produced in A9 medium was 22.9% higher than that produced in Schenk and Hildebrandt (SH) medium. Meanwhile, there was not a significantly different DP under static and shaking culture conditions. However, the DP was remarkably influenced by fermentation time. The BC produced with glycerin or xylose as carbon source exhibited lower DP than that produced with glucose. Adding Tween 20 or Tween 80 in A9 medium had little effect on the DP, while adding Triton X-100 decreased it. The results presented

here would provide some experimental data for BC production with different DP in practical applications.

Keywords: *Gluconacetobacter intermedius* BC-41, average degree of polymerization, bacterial cellulose, viscosity method, different conditions

QUANTIFICATION OF CELLULOSE CONTENTS BY TRANSMISSION SPECTRA OF PLANT TISSUES

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Determination of cellulose is a part of numerous scientific studies and provides an interlinked base for many developmental and physiological variations among living entities. So, quick and accurate quantification of cellulose can never be over-emphasized. The present study leads towards the development of a method for quantification of cellulose contents under microscope. It is basically dependent upon transmitted color spectrum of plant tissues and assesses accurate cellulose quantity with an error of $\pm 0.46\%$. By adopting this method, inter- and intracellular variations in cellulose concentrations can efficiently be determined by measuring variations in color intensity. Moreover, it introduces a technique of physiological studies and also provides a base for development of similar formulas for other biochemicals of living tissues.

Keywords: transmission spectrum, cellulose staining, colorimetric analysis, equation of line, area under line, percentage error

FUNCTIONALIZATION OF CELLULOSE: SYNTHESIS OF WATER-SOLUBLE CATIONIC CELLULOSE DERIVATIVES

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One of the trends of modern cellulose chemistry is the functionalization of known cellulose derivatives in order to expand their application area. In this work, water-soluble cationic cellulose derivatives containing up to 4% coupled nitrogen were obtained by the amination of hydroxyethylcellulose (HEC) with two different etherification agents, diethylepoxypropylamine (DEEPA) and (2-chlorethyl) diethylamine hydrochloride (DEAE). The influence of the composition of the reaction mixture on the degree of substitution was investigated by using mathematical planning of the experiments and was

described by regression equations. The effect of the etherification agent on the composition of cationic groups of the obtained derivatives was examined. It was found that the HEC reaction with DEEPA resulted in a monofunctional cationic polyelectrolyte containing tertiary amino groups, which could be assigned to cationic groups of intermediate basicity (pK_a approx. 8.2). On the contrary, the amination of HEC with DEAE gave polyfunctional derivatives containing a mixture of weakly and intermediately basic amino groups with pK_a 6.0-6.2 and 8.2-8.6, respectively. The synthesized derivatives are soluble in polar aprotic solvents, as well as in water, and the solutions possess high stability at elevated temperature and a high concentration of salts.

Keywords: cellulose derivatives, aminocellulose, cationic polyelectrolytes, water-soluble polymers, cationic cellulose derivatives

ULTRASOUND-ASSISTED MODIFICATION OF BEET PULP CELLULOSE WITH PHTHALIC ANHYDRIDE IN IONIC LIQUID

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Cellulose phthalates were synthesized from beet pulp cellulose and phthalic anhydride in ionic liquid (IL) 1-butyl-3-methylimidazolium chloride assisted by ultrasound. The parameters investigated included ultrasound time (from 15 to 60 min), temperature (between 95 and 120 °C), the molar ratio of phthalic anhydride/anhydroglucose units in cellulose (from 2:1 to 6:1), and reaction time (from 30 to 70 min). The results showed that the synergy of the combined use of ultrasound and IL successfully enhanced the degree of substitution of cellulose phthalates under the experimental conditions of the present study. After the chemical modification, the results of FT-IR and solid-state CP/MAS ^{13}C NMR showed the appearance of hydroxyl groups and reduction of OH bonds on the cellulose. The TGA data indicated that the cellulose phthalate showed lower thermal stability than native cellulose.

Keywords: ultrasound-assisted, cellulose, beet pulp, phthalation, ionic liquid (IL)

DOUBLE-DIFFUSION BEHAVIOR BETWEEN PHOSPHORIC ACID COMPLEX SOLVENT AND ORGANIC COAGULANT AND THEIR INCORPORATION INTO CELLULOSE FILM

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The double-diffusion behavior between phosphoric acid complex solvent (PACS) and organic coagulant was evaluated. In addition, the properties and micro-structure of cellulose films regenerated in PACS and organic coagulants were investigated by scanning electron microscope (SEM), water contact angle (WCA), tensile test, X-ray diffraction (XRD), and fourier transform infrared spectroscopy (FTIR). SEM images demonstrated that the film prepared in ethanol/methanol exhibited a mostly non-uniform morphology mainly resulting from the highest double-diffusion rate during coagulation. The best hydrophobicity of the film prepared in ethanol/glycol, as determined by WCA measurements, was also better explained by the corresponding lowest double-diffusion rate. The cellulose solution seemed favored by ethanol/acetone to be processed into film with satisfactory mechanical properties and crystallinity, which was probably attributed to the neither too fast nor too slow double-diffusion rate. FTIR analysis confirmed that no drastic change occurred in the micro-structure of cellulose films irrespective of the coagulation bath.

Keywords: double-diffusion behavior, phosphoric acid complex solvent (PACS), cellulose film, coagulation, morphology, wettability, tensile strength

IMPACT OF CELLULASE ENZYME TREATMENT ON STRENGTH, MORPHOLOGY AND CRYSTALLINITY OF DEINKED PULP

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In recent years, enzyme applications in the pulp and paper industry have become remarkable. In this research, *Trichoderma* cellulase was used on deinked pulp and its effects on fiber morphology, crystallinity and strength of pulp were studied. Three parameters were considered: dosage of enzyme, time and temperature of enzymatic treatment. The results showed that the enzymatic treatment enhanced the mechanical properties of the treated pulps. Also, water retention value and drainage were improved by the cellulase treatment. The effect of the enzymatic treatment on the drainage of pulp

showed that pulp drainability was improved. The results of handsheet and pulp evaluation indicated that 0.3% cellulase treatment for 60 minutes at 30 °C were the optimum treating conditions. In treated pulps, structural changes, such as fibrillation, were observed by SEM. The measurement of X-ray diffraction indicated that the crystallinity index of treated pulp was lower than that of the control pulp.

Keywords: enzyme, cellulose, deinked pulp, drainage degree, WRV, strength, morphology, crystallinity

POTENTIAL APPLICATIONS OF WASTES FROM ENERGY AND FORESTRY INDUSTRY IN PLANT TISSUE CULTURE

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Two industrial by-products, deuterium depleted water (DDW) and polyphenolic extract from spruce wood bark (SB) were tested as bioregulators for maize callus cultures. The effects of deuterium depleted water alone or in combination with spruce bark extract on *in vitro* growth and development of callus maize plant were studied. Specific parameters, including biomass accumulation, adventitious roots and aerial adventitious roots organogenesis, formation of new callus, as well as activity of enzymes, such as peroxidase, superoxide dismutase, catalase, and total content of polyphenolic compounds accumulated in callus have been closely monitored. The results have shown that the tested solutions stimulated the fresh biomass accumulation, adventitious roots organogenesis and formation of new callus by comparison with the control sample. The most significant stimulatory effect on callus biomass accumulation and total content of polyphenolic compounds was observed when the deuterium depleted water, combined with spruce bark polyphenolic extract, was used for the performed treatments.

Keywords: deuterium depleted water (DDW), spruce bark polyphenols (SB), callus maize, physiological parameters, enzyme activities, polyphenol biosynthesis

LOW TEMPERATURE ACID HYDROLYSIS OF GRASS-DERIVED LIGNOCELLULOSE FOR FERMENTABLE SUGARS PRODUCTION

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Fermentable sugars from food crops have been used for ethanol biofuel production. However, a major food security concern has led to an increase in the research of non-food crops as biomass for biofuels. Lignocellulosic materials (biopolymers) have been considered as biomass, but their use involves challenging production processes to release fermentable sugars. Several approaches using high temperatures and pressures have been used to facilitate the breakdown of lignocellulose. In this study, Kikuyu grass was investigated as a low-cost source of fermentable sugars. The lignocellulosic material from grass was subjected to pretreatment and then hydrolysed by sulphuric acid at comparatively low temperatures of below 100 °C at atmospheric pressures to produce fermentable sugars. A simple and low-cost method for the removal of some inhibitors (by-products produced during hydrolysis) using wood shavings packed in a chromatographic column was developed. The yield of fermentable sugars obtained after hydrolysis was 22.26 g/L (38.4% w/w).

Keywords: lignocellulose, biomass, acid hydrolysis, bioethanol, hydrolysate, fermentable sugars

IDENTIFICATION OF FACTORS INFLUENCING THE MAXIMUM FLEXURE OF BEECH WOOD PLASTICIZED BY MICROWAVE HEATING

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This paper reports on the influence of selected factors and their interactions on maximum flexure after plasticizing beech wood by microwave heating. To our knowledge, the use of microwave heating has not been reported for plasticizing wood yet. Therefore, a proper procedure was developed to verify the use of microwave heating for the purpose of plasticizing. The determination of maximum flexure was based on the principle of static bending with three-point loading. Maximum flexure was monitored in beech test samples with dimensions of 25 x 25 x 400 mm (cross-sectional dimensions were selected according to standard testing samples). Samples were divided into three groups of initial moisture contents of 65%, 30% and 20%. Our research confirmed only the influence of plasticizing time and moisture content on the maximum flexure of

wood plasticized by microwave heating, exactly as we expected. The other two factors, orientation (radial and tangential) and placement (in the center or on the side), had small or no effect on the value of maximum flexure. Microwave heating is quite intense, therefore for this kind of heating, it is better to have higher moisture content in an appropriate power device and minimal plasticizing time. The biggest advantage of microwave heating is the short plasticizing time, a few minutes, while steaming requires tens of minutes or even hours.

Keywords: microwave heating, plasticizing, maximum flexure, moisture content, plasticizing time, orientation, placement

KRAFT PULPING COMBINED WITH GREEN LIQUOR PRE-EXTRACTION OF BEECH WOOD

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Beech wood chips were extracted with green kraft liquor at different alkali charges of 1, 2, 3 and 4% on dry wood mass and with hot water. The extractions were performed at 160 °C and different time to achieve 10% wood mass loss. The total content of monosugars in hydrolysed extracts decreased with increasing green liquor charge, but lignin and insoluble solids content increased. The kraft pulp yields from pre-extracted chips with 2, 3 and 4% green liquor charge were similar with those from original wood chips. Effective alkali charges in the pulping process were about 1% to 3.5% lower than in control kraft pulping and reduced with increasing green liquor charge in the extraction process. The addition of AQ in the extraction or pulping process increased pulp yield, especially in extraction. Limiting viscosity numbers of the pulps from chips pre-extracted with green liquor were slightly higher than those of control kraft pulps. Tensile, burst and tear strength of the pulp handsheets from chips pre-extracted with 2, 3 and 4% green liquor charge were the same as or slightly higher than those for original wood chips. The optimal green liquor charge in the extraction process was 2% or 3%, in terms of extraction and pulping process effectiveness.

Keywords: beech wood, pre-extraction, hemicelluloses, kraft pulping, viscosity, strength properties

KRAFT PULPING AND BLEACHING OF PAULOWNIA SUN TZU 104® WOOD

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A trihybrid clone of Paulownia from the varieties *fortunei x tormentosa x elongate* was used for obtaining cellulosic pulp and paper by a kraft process and bleaching. Both bleached and unbleached pulps were subjected to a refining study between 0 and 3000 revolutions in a PFI mill. A fiber length (0.97 mm) similar to that of Eucalyptus, a high holocellulose content (71.4%), a low ash content (0.9%), a lignin content comparable to that of other varieties of Paulownia and an α -cellulose content slightly lower than that of Eucalyptus, but greater than that of other varieties of Paulownia were observed. Also, paper sheets showed good strength properties, comparable to or even greater than those obtained with Eucalyptus or other varieties of Paulownia at comparable refining degrees, between 30 and 40 °SR. The pulp was successfully bleached in all cases with a value of brightness >90%.

Keywords: Kraft pulp, Paulownia, paper, pulp, bleaching

ORANGE TREE PRUNINGS AS RAW MATERIAL FOR CELLULOSE PRODUCTION BY THE KRAFT PROCESS

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The aim of this work was to study the influence of operational variables in the orange tree pruning kraft pulping, such as temperature (155-185 °C), processing time (40-90 min) and active alkali concentration (10-16%) at constant values of liquid solid ratio, anthraquinone and sulfidity concentration of 8:1, 1% and 20%, respectively, on the pulp yield, lignin content, Kappa number and viscosity of the pulps and the tensile index, burst index, tear index and brightness of the paper sheets. The experimental data obtained were used to estimate the parameters or constants in the equation for the neural fuzzy model. The predictions for the yield, Kappa number, lignin content, viscosity, tensile index, burst index, tear index and brightness differ by less than 9, 8, 21, 14, 17, 21, 9, and 6% from their respective experimental values.

Keywords: orange tree prunings, kraft pulp, neural fuzzy model

ALKYL-CHITOSAN AS PAPER COATING MATERIAL TO IMPROVE WATER BARRIER PROPERTIES

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The aim of this study was to obtain and evaluate alkyl-chitosan derivatives as paper coating materials in developing water barrier properties. Three alkyl-chitosans, differing by alkyl chain length and at two substitution degrees each, were tested in two coating formulas – polymer and polymer/CaCO₃. Water barrier properties of paper were evaluated by contact angle (CA), water absorption capacity (Cobb₆₀ index) and water vapour transmission rate (WVTR). The polymer formula based on alkyl-chitosans improved consistently water barrier properties, which were positively influenced by substitution degree and negatively by alkyl chain length: the alkyl-derivative with the shortest alkyl chain and the highest substitution degree led to the highest increase of CA (82.1%) and the highest decrease of Cobb₆₀ index (82.6%). The WVTR, which depended less on surface hydrophobicity, showed only a slight reduction (only 20.3%) when using the polymer formula. Coating formulas based on alkyl-chitosan/CaCO₃ were more effective than the polymer formula in reducing Cobb₆₀ index and WVTR, suggesting a more uniform film formation, with lower porosity.

Keywords: chitosan, alkyl-chitosan, functional coating, barrier properties

DUAL-ADSORPTION OF POLY(ALLYLAMINE HYDROCHLORIDE) AND LIGNOSULFONATE ONTO RECYCLED CELLULOSIC FIBERS

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The effects of the dual-polyelectrolyte adsorption of poly(allylamine hydrochloride) (PAH) and lignosulfonate (LS) on a recycled unbleached softwood kraft pulp were studied and the method used for the determination of LS concentration was discussed. Adsorption isotherms of LS on untreated and on previously PAH-treated pulps at neutral pH, and different ionic strengths were built, and the effects of the amount of PAH on LS adsorption were considered. It was found that even at low dosages of PAH, for which fibers remain anionic, high levels of LS adsorption at room temperature and short adsorption time can be achieved. Besides, it was found that the increase in ionic strength also increased the amount of LS adsorbed. The highest values on papermaking properties were obtained using only PAH. Nevertheless, when compared to the reference pulp, the PAH/LS system clearly improved the wet tensile strength and the compressive strength, avoiding paper non-uniformity or

charge-reversal problems.

Keywords: recycled unbleached softwood kraft pulp, dual-polymer treatment, poly(allylamine hydrochloride), lignosulfonate, adsorption isotherms, papermaking properties, paper uniformity

NONLINEAR BEHAVIOUR OF ONE-SIDE COATED PAPER: STATIC AND DYNAMIC VISCOELASTIC PROPERTIES

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The research presented in this paper is the result of a study on the dynamic and static viscoelastic properties of one-side coated papers for the purpose of offset printing. During their formation and the technological processes of coating and printing, paper substrates are exposed to various traction forces, which cause not only nonlinear time dependence, but also a permanent irreversible deformation. Paper, which is basically a composite material, also demonstrates viscoelastic properties. Viscoelastic materials characteristically adjust and respond to external forces, i.e. stresses and strains, in the form of a continuous rearrangement of molecular, supramolecular and other hierarchical morphological structures.

Keywords: static, dynamic viscoelasticity, strain relaxation, creep, DMS, coated paper

BIOSORPTION OF METHYLENE BLUE ONTO FOUANAT TEA WASTE: EQUILIBRIUM AND THERMODYNAMIC STUDIES

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The sorption of methylene blue (MB) from an aqueous solution by Foumanat tea waste was studied in a batch system. Three widely used isotherms (Langmuir, Freundlich and Temkin) were examined for MB sorption at different temperatures. The four Langmuir linear equations were discussed, and the Langmuir parameters were obtained from them. Langmuir-1 is the most popular linear form and it has the highest coefficient of determination, compared with the other Langmuir linear equation. The maximum saturated monolayer sorption capacity of tea waste for MB was 244 mg/g at 303 K. Various thermodynamic parameters, such as ΔG° , ΔH° , ΔS° and E_a , were calculated. The findings of this investigation suggested that physical sorption plays a role in controlling sorption. We investigated the adsorption mechanism by FTIR and SEM techniques. FTIR data indicated that MB binding occurred mostly at –OH and C=O groups of tea waste.

Keywords: biosorption, methylene blue, tea waste, isotherm, thermodynamic, adsorption mechanism

SWELLING AND DISSOLUTION OF CELLULOSE IN NaOH AQUEOUS SOLVENT SYSTEMS

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As a fundamental step towards creating a new class of cellulose engineering materials, the proposed research investigated swelling and dissolution of cellulose in NaOH aqueous solvent systems (NaOH/H₂O, NaOH/thiourea/H₂O and NaOH/thiourea/urea/H₂O). The dependence of swelling and dissolution behavior of cellulose fibers on the quality of the solvent was investigated in detail. For the two cellulose samples – cotton linter and spruce wood fibers – the swelling and dissolution mechanisms in NaOH-water and NaOH-water-additives stayed the same. Adding thiourea to NaOH-water produced the same ballooning mechanism, but with a larger expansion of the balloons, indicating a better solvent. The cotton fiber could not completely dissolve in NaOH/H₂O and NaOH/thiourea/H₂O. However, the cotton fiber swelled evidently showing no balloon formation and then disintegrated into rod-like fragments in NaOH/thiourea/urea/H₂O, which was an indication of the best solvent of all the NaOH aqueous solutions used.

Keywords: cellulose, swelling, dissolution, NaOH, urea, thiourea

PYROLYSIS OF PINE AND BEECH WOOD SAMPLES UNDER ISOTHERMAL EXPERIMENTAL CONDITIONS. THE DETERMINATION OF KINETIC TRIPLETS

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The pyrolysis process of pine and beech wood samples was investigated by the isothermal thermogravimetric technique, at five different operating temperatures, in nitrogen flowing stream. It was found that the isothermal pyrolysis process of wood samples can be described by the three-dimensional diffusion mechanisms, with different reaction geometry (Jander's type for pine, and Ginstling-Brounstein's type for beech). The evaluated models for both processes represent the global one-step reaction mechanisms. Some differences in the values of the kinetic parameters and diffusion geometry of the volatile products were established, probably resulting from sensitive alterations of the structure and the chemical composition of the investigated wood samples, occurring during the pyrolysis process.

Keywords: wood, pyrolysis, kinetics, diffusion mechanism, apparent activation energy

BENZYLATED HEMICELLULOSIC POLYMERS FROM *TRIPLOID POPULOUS*: CHARACTERIZATION OF PHYSICOCHEMICAL, STRUCTURAL FEATURES AND THERMAL STABILITY

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Chemical modification is one of the most important strategies to obtain novel biomaterials from the abundant biomacromolecules and to tailor the properties of biopolymers as desired macromolecules for specific application. In this study, a novel functional biopolymer was synthesized from *Triploid populus* hemicelluloses with benzyl chloride in dimethyl sulfoxide (DMSO) using NaOH as catalyst. Biopolymers with degrees of substitution (DS) between 0.08 and 0.34 were obtained by varying reaction temperature, reaction time, and the molar ratio of benzyl chloride to anhydroxylose unit in hemicelluloses. The chemical structure of benzylated hemicelluloses (BH) was characterized by FT-IR and ¹³C NMR spectroscopies. The results showed that the M_w and M_n of BH were lower than those of the native hemicelluloses. The BH with a low DS had less thermal stability than the native hemicelluloses, whereas the BH with a high DS had higher thermal stability than the native hemicelluloses. Moreover, BH showed porous surface with small irregular slices, as evidenced by scanning electron microscope (SEM), which was ascribed to the disruption of intermolecular and intramolecular hydrogen bonds. These findings indicated that BH with hydrophobic groups could open up new opportunities for potential application in thermoplastic industries.

Keywords: *Triploid populus*, hemicelluloses, benzylation, thermal properties, FTIR spectroscopy, NMR

IMPROVING THE DISPERSIBILITY OF CELLULOSE MICROFIBRILLATED STRUCTURES IN POLYMER MATRIX BY CONTROLLING DRYING CONDITIONS AND CHEMICAL SURFACE MODIFICATIONS

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The aim of this paper was to investigate some possibilities to improve the compatibility of cellulose microfibrillated structures at the fibre-polymer matrix interface level, when they are used as reinforcement in polymer composite materials. The cellulose microfibrillated structures isolated from bleached softwood pulp by chemical-mechanical methods were subjected to surface modification by acetylation, aiming to reduce their hydrophilic character. Fourier transform infrared spectroscopy (FTIR) analyses indicated the acetylation of the hydroxyl groups of cellulose; the increase of the elastic modulus of the polymer composite materials was due to the good dispersion of the surface modified cellulose microfibrillar elements in the polymer matrix. Another method that was tested to reduce the hydrophilic character of cellulose microfibrillated structures in contact with a polymer matrix was the spray drying, using the atomization of cellulose microfibrils. This method produces particulate materials with unchanged size and very good potential as reinforcement in composite manufacturing, utilizing conventional thermoplastic compounding techniques. The improvement in the mechanical properties of the composites reinforced with spray dried cellulose microfibrillar elements shows that this drying method is the most suitable for cellulose fibres that are used as reinforcement in hydrophobic polymer matrix, because this procedure reduces the advanced irreversible hornification phenomenon, which occurs during the oven drying process.

Keywords: cellulose microfibrillar structures, surface modification, drying, acetylation, polymer matrix, composites

A STUDY OF THE INFLUENCE OF CROSSLINKING DEGREE ON THE PHYSICOCHEMICAL PROPERTIES OF GELATIN MICROPARTICLES

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The application of the microencapsulation technique in medicine and pharmacy has been extensively studied in recent years. The microencapsulation of small particles in polymeric, waxy or other kind of protective shells has become a well-established technology for coating and isolating various substances. The present paper presents the results obtained in a study concerning the influence of crosslinking degree on the physicochemical properties of gelatin microparticles containing xantinol nicotinate. The microparticles have been prepared by emulsifying a gelatin solution in an oily phase (sun flower oil). So far, gelatin microparticles have been widely evaluated as an excellent drug carrier. Nevertheless, gelatin dissolves rather rapidly in aqueous environments, making the usage of the polymer quite difficult for producing extended release delivery systems. Therefore, in obtaining extended release gelatin microparticle formulations, the usage of a crosslinking agent generating non-soluble networks is necessary. Glutaraldehyde was selected as crosslinking agent. The crosslinking process was completed either by maintaining the test microparticles in glutaraldehyde vapors for various periods of time, or by using a 35% glutaraldehyde solution in acetone. The test gelatin microparticles were characterized *in vitro* in terms of both physical and chemical properties (such as particle size, density, drug content, swelling dynamics and drug release). The experimental data confirmed that the crosslinking degree significantly influenced drug loading, swelling kinetics, as well as the mechanism of drug release kinetics.

Keywords: microparticles, gelatin, crosslinking, glutaraldehyde, xantinol nicotinate

LIGNIN REMOVAL FROM AQUEOUS SOLUTIONS USING Fe₃O₄ MAGNETIC NANOPARTICLES AS RECOVERABLE ADSORBENT

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In the present study, the use of Fe₃O₄ magnetic nanoparticles as recoverable adsorbent for lignin removal from aqueous solutions has been investigated. Fe₃O₄ magnetic nanoparticles (MNPs) were chemically synthesized. The size and cross-section shapes of the synthesized particles were determined by scanning electron microscope (SEM) and X-ray diffraction analysis (XRD). The effects of some different parameters, including the amount of adsorbent, pH of solution, salt effect and adsorption time, on the removal efficiency of lignin were investigated and optimized. The kinetic studies on lignin showed rapid sorption dynamics by a pseudo-second order kinetic model. According to the isotherm studies, lignin adsorption equilibrium data were fitted well to the Langmuir isotherm. The maximum monolayer capacity (q_{max}) and the Langmuir constant (K_L) were obtained from the Langmuir model as 2554.42 mg g⁻¹ and 0.812 L mg⁻¹, respectively. The simple synthesis method and the recoverability of Fe₃O₄MNPs recommend it as a good adsorbent for lignin removal from aqueous solutions.

Keywords: lignin, Fe₃O₄ magnetic nanoparticles, adsorption, Langmuir isotherm

TECHNOLOGICAL PROPERTIES OF IRANIAN CULTIVATED PAULOWNIA WOOD (*PAULOWNIA FORTUNEI*)

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P. fortunei was imported into Iran from China and was planted at different spacings in the forest of the north of Iran, for wood production. In this research, physical, chemical, mechanical properties and morphological characteristics of Iranian cultivated paulownia (*Paulownia fortunei* L.) wood were investigated. Paulownia has acceptable Runkel, flexibility and slenderness coefficients, which are in the same range as those of hardwood and softwood. In general, the results of the chemical and morphological analyses indicate that Iranian cultivated paulownia fibers are a promising fibrous raw material for paper production. The species is not suitable for uses requiring mechanical strength. The values obtained for physical properties were as follows: oven-dry density – 0.261 g cm⁻³, basic density – 0.242 g cm⁻³, air-dry density – 0.291 g cm⁻³, volumetric shrinkage – 7.54%,

percentage of cell wall – 17.41%, porosity – 82.59%, fiber saturation point – 31.15%, and maximum moisture content – 349.72%. The means of holocellulose, cellulose, lignin and extractives were of 80.1, 51, 23.5, and 11.8%, respectively. The average values of mechanical properties were the following: modulus of rupture – 41.07 MPa, modulus of elasticity – 3.74 GPa, and compression strength parallel to the grain – 14.61 MPa. The mean value of fiber length was 996 μm , fiber width – 30.55 μm , width of lumen – 25.30 μm , and cell wall thickness – 5.25 μm .

Keywords: *Paulownia fortunei* L., physical properties, chemical properties, mechanical properties, morphology properties

ROLE OF PRETREATMENT WITH A COMPOSITE MICROEMULSION IN SACCHARIFICATION OF BAMBOO

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The highly dense biostructure and complex coating of biomass, which can decrease saccharifying efficiency and increase production cost, has been the bottleneck of biomass utilization. In this study, a self-designed composite microemulsion was used for lignocellulose (bamboo) pretreatment. The improvement of physicochemical properties and saccharifying efficiency after pretreatment was studied. The results showed that a stable composite microemulsion was obtained with an optimal mass ratio of 1:2:1:3:3, corresponding to cetyltrimethyl ammonium bromide/n-butyl alcohol/BminCl/ammonia. Lignocelluloses yielded a reducing sugar content of 57.8% via pretreatment with the composite microemulsion under the following material conditions: particle size between 0.25 mm to 0.38 mm, temperature of 70 °C, and reacting time of 16 h. The relative crystallinity of lignocellulose increased marginally and thermal stability improved obviously, while cellulose was protected well after pretreatment.

Keywords: composite microemulsion, ionic liquids, pretreatment, enzymatic hydrolysis

FUNGAL PRETREATMENT OF OIL PALM EMPTY FRUIT BUNCH: EFFECT OF MANGANESE AND NITROGEN

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Oil palm empty fruit bunch (OPEFB) was biologically pretreated using *Pleurotus floridanus* LIPIMC996 supplemented with various concentrations of manganese and nitrogen and incubated for 35 days at 30°C, and enzyme activities of manganese peroxidase (MnP) and laccase were examined. When OPEFB was supplemented with manganese, the highest lignin reduction was achieved up to 25.0±5.6% at the addition of 200 µg Mn²⁺/g OPEFB. In addition, *Pleurotus floridanus* LIPIMC996 grew best on OPEFB supplemented with 800 µg Mn²⁺/g OPEFB. When OPEFB was supplemented with nitrogen, the highest lignin reduction was achieved up to 27.2± 3.5% at the addition of 20 mM nitrogen. The best growth of *Pleurotus floridanus* was also achieved with the addition of 20 mM nitrogen. The addition of nitrogen and manganese on OPEFB did not significantly affect the activity of MnP and laccase.

Keywords: oil palm empty fruit bunch, pretreatment, ligninolytic enzymes, glucosamine, fungal growth, *Pleurotus floridanus*

INFLUENCE OF MECHANICAL OPERATION ON THE BIODELIGNIFICATION OF *EUCALYPTUS TERETICORNIS* BY *TRAMETES VERSICOLOR*

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In the biological pulping process, the removal of lignin can be achieved through treatment of lignocellulosic materials with white rot fungi. The main biological challenge in biopulping is that fungal hyphae are not able to penetrate in the core of the chips and only a surface phenomenon occurs. Therefore, the surface area of eucalyptus wood chips was increased by passing through an impressafiner. An impressafiner compresses the chips and converts them into spongy material. In the present study, biological pretreatment of eucalyptus non-structured (chips) and structured samples (spongy) was carried out with *Trametes versicolor*. During the

study, it was found that the lignin loss was approximately 8.90% higher in the destructured samples, compared to the non-destructured samples, within 21 days under optimum conditions. The fungal pretreatment decreased the kappa number of the treated destructured samples by as much as 10.29 points, compared to the untreated non-destructured samples. Thus, the study has provided an insight into economically feasible conditions to reduce pollution load.

Keywords: biopulping, delignification, white rot fungi, lignin, cellulose

INFLUENCE OF OPERATING CONDITIONS IN SODIUM HYDROXIDE AND ANTHRAQUINONE PULPING ON THE MORPHOLOGY OF CELLULOSE FIBERS OF TAGASASTE

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This paper discusses the potential for improving paper characteristics by controlling fiber properties. To this end, we examined the most salient changes in tagasastefibers as a function of the operating conditions during their soda– anthraquinone cooking. Using high anthraquinone concentrations and medium cooking times provided paper with good strength-related properties. These operating conditions were compatible with those required to obtain the best values of the properties dependent on fiber morphology. Thus, obtaining the optimum fiber length would require to use short cooking times or medium times if a medium alkali concentration is used. A high anthraquinone concentration in combination with a high soda concentration and temperature would provide the best conditions for maximizing the number of fibers obtained. A high soda concentration additionally reduces coarseness and increases the number of fibers; also, medium and high temperatures avoid excessive curling and kinking, increase the number of fibers and decrease coarseness.

Keyword: tagasaste, soda anthraquinone pulping, fiber morphology

DISPLACEMENT WASHING OF KRAFT PULP WITH AQUEOUS SOLUTIONS OF SURFACTANTS

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The aim of this work was to investigate the effect of the addition of surfactants to the wash liquid on the washing efficiency during displacement of black liquor from the fibre bed of unbleached kraft pulp. Aqueous solutions of two non-ionic surfactants and an anionic one were used. For comparison, distilled water was also used as wash liquid. Laboratory displacement washing experiments were performed in a cylindrical glass cell. A step change response method was chosen to describe the displacement of black liquor. The breakthrough curves were measured for alkali lignin using ultraviolet spectrophotometry. The flow of the wash liquid through a pulp bed was described by the dispersion model involving one dimensionless parameter known as the Péclet number. In order to characterize the displacement washing efficiency with aqueous solutions of surfactants, not only was the wash yield correlated with the Péclet number, but also a new dimensionless criterion involving intrinsic properties of aqueous solutions was derived.

Keywords: kraft pulp, displacement washing, surfactants

ENVIRONMENTALLY FRIENDLY AND COST-EFFECTIVE METHOD FOR MANUFACTURING ABSORBENT GRADE PAPER

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Absorbent paper is characterized by some of its important specific properties like water klemn, castor oil penetration and wet strength. An absorbent grade pulp was manufactured from a mixture of *Eucalyptus tereticornis* and veneer waste of poplar (15:85) by three distinct processes: (a) delignification at high alkali dose and longer cooking time (at 170 °C), followed by enzyme treatment (method-I), (b) delignification under normal pulping conditions, followed by semi-bleaching (CE_{OP}) (method-II), and (c) delignification under normal pulping conditions, followed by oxygen treatment (method-III). Method-I required 7.15 h for pulp processing and the cost of pulp was US\$ 2481.72/digester. The cost of pulp produced by method-II was comparatively lower (US\$ 2272.69/digester). However, it required a longer time (9.45 h) and was not environmentally benign because of generation of chloro-organic compounds. The pulp produced by method-III was environmentally friendly, required a cooking time of 12.45 h, and was also economical (US\$1936.32/digester), compared to the other methods.

Keywords: *Eucalyptus tereticornis*, veneer waste of poplar, pulping, semi-bleaching, oxygen delignification, cost effectiveness, absorbent grade paper

STUDY OF NON-IONIC SURFACTANT AND FOAMING AGENT CHARGE IMPACT ON FLOTATION DEINKING OF LASER-PRINTED WASTE PAPER

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The present contribution deals with the impact of a charge of a non-ionic surfactant and soft soap on the efficiency of printing ink removal from a suspension of recycled fibres at various flotation times. To determine the optimum conditions, a 3-factor experimental design using a Statgraphics software was used. The efficiency was evaluated by the image analysis using a Motic Images 2.0 software. An equation relating the flotation efficiency and variables (such as surfactant, soap, time), influencing significantly the flotation efficiency, was derived. A flotation efficiency of up to 96% can be attained via 5% surfactant addition, and 2% soap addition to oven-dry pulp for a flotation time of 25 minutes.

Keywords: recycling, flotation, surfactant, statistical modelling

EQUILIBRIUM STUDIES ON THE REMOVAL OF ACID GREEN 9 DYE FROM AQUEOUS SOLUTIONS BY CHITOSAN ADSORBENT: BATCH STUDIES

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Chitosan is a natural, renewable, nontoxic and biodegradable polymer. This unique natural cationic polymer has been evaluated as adsorbent for removing Acid Green 9 (AG9) dye from aqueous solutions. The experiments were performed in a batch system, at room temperature (20 ± 0.5 °C) and the effects of various experimental parameters (pH, contact time, initial dye concentration, adsorbent dosage, temperature, ionic strength) on adsorption capacity were investigated. The results have shown the effectiveness of dye removal is mainly dependent on the ratio between initial concentration of AG9 and chitosan dosage. At a given ratio of AG9: chitosan, an acid pH range of 4-6 was identified as optimal for dye removal. The temperature raising and presence of sodium sulphate (Na_2SO_4) resulted in a decrease of adsorption yield. The experimental data were analyzed for possible agreement with the Langmuir, Freundlich and Temkin isotherm equations. The Langmuir model was demonstrated to provide the best correlation with the experimental data.

Keywords: Acid Green 9, chitosan, adsorbent, isotherms, cationic polymer

HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF BOEHMITE/TITANIA HYBRID MATERIALS ON COTTON FABRICS

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A series of novel boehmite/titania hybrid materials was synthesized from aluminum isopropoxide and titanium-n-butoxide using a hydrothermal synthesis process. Grey cotton fabrics were dyed, and the hybrid materials were combined with the pre-treated cotton fabrics through a padding-drying-curing process. The structures of the hybrid materials were analyzed using FTIR and ²⁷Al-NMR. Moreover, the morphological structures of the processed cotton fabrics were evaluated using scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) analyses. Our data show that the electric conductivity of the processed cotton fabrics was improved in the fabrics processed with a higher amount of aluminum isopropoxide and all the processed fabrics had a good water repellent performance.

Keywords: boehmite, titania, hydrothermal, cotton fabrics, conductivity, water repellent

BOOK REVIEW

WOOD FIBERS FOR PAPERMAKING, Maria Cristina Area and Valentin I. Popa, Smithers Rapra Technology Ltd, Shawbury, Shropshire, SY4 4NR, UK, 2014, 106 pp., ISBN 978-1-90903-086-2

Paper is one of the oldest known and probably the most used bio-based material. By having multiple uses, from information support to high-tech material, it has become an important part of our every day life. The book *Wood Fibers for Papermaking* authored by Maria Cristina Area and Valentin I. Popa is dedicated to the most intensive raw material source of the papermaking industry and is aiming at reviewing the most important characteristics of these fiber sources.

Chapter 1, *Natural Forests and Forest Plantations* outlines the most important points in the timeline of wood use as fiber source for the papermaking industry. Natural coniferous forests have historically been an important log source and have been preferred due to the purity of the forests and also due to good characteristics of the fibers. The increase of raw material demand at the beginning of the 1950's has turned the interest of the paper industry towards usage of hardwoods. Overcoming of some technological problems related to the diversity of species in natural forests and to the differences in fiber dimensions has led to an increase in hardwoods usage for pulp production to over two thirds of the total wood quantity used for pulping.

The concern on overexploitation of the natural forests and the increase of wood consumption in the papermaking sector has determined the implementation of forest plantations as a method of ensuring the raw material supply. The most important criteria in selection of the tree species are chemical composition, quality of fibers, the age of maturity and the adaptability to the environmental conditions. As an example, in case of hardwoods the *Eucalyptus sp.* are preferred in warm humid areas, while the *Salicaceae* hybrids are preferred in the temperate regions. Achievements in forestry practices, genetic engineering and improvement of forest management systems have led to a

share of about 38% of forest plantations wood in the total raw wood used by the pulping industry in 2004.

Nonwood fibers may complete the need of virgin fiber for the production of paper, especially in parts of the globe where wood is a scarce resource. Several alternative types of fiber sources are also discussed: natural growing plants, agricultural wastes (mainly straws and stalks) and industrial crops (bast fibers, cotton and sisal). Several potential problems in using nonwoods as fiber sources are also pointed out together with the most used pulping processes.

The second book chapter, *Anatomy, Structure and Chemistry of Fibrous Materials* provides the most important information on the role of tree stem as the most used part as pulping feedstock. The main anatomical features of the tree trunk and their role in the living tree are described in a comprehensive and handy manner. Chemical composition, cell structure are also outlined together with the most important differences between softwood and hardwood species.

In chapter three, the most important categories of *Abnormal Wood* are depicted. Reaction wood is the result of the interactions of the tree to extreme or abnormal stress existing in the growth environment. While compression wood is mostly considered undesired due to lower quality fibers, tension wood fibers are generally considered acceptable. Reaction wood differs from normal wood in fiber distribution, mechanical properties and also in chemical composition. Compression wood has a higher lignin content than normal wood and has higher compressive strength. Tension wood is characterized by a higher alpha cellulose and extractives content than normal wood.

Although the content of juvenile wood was not considered an important feature during the period in which the pulping feedstock was

ensured by naturally grown trees, its importance became obvious when the plantation forests started to become a source of raw material. The most important differences between the juvenile wood and the mature wood are cell dimensions, specific gravity and strength. These are usually lower in juvenile wood when compared to mature wood. Both juvenile and compression wood tend to generate higher consumption of pulping chemicals, lower yield and poorer quality fiber than normal or mature wood.

Paper mechanical properties may vary significantly as a result of the fibers used in the papermaking process. The fourth chapter focuses on the relationship between *Characteristics of Cells and Properties of Pulps*. The dimensions of fibers vary significantly between tree species and also in the same tree. Softwoods have been preferred in the first half of the 20th due to the higher length of the fibers and narrower distribution in terms of fiber dimensions.

The correspondences between the fibers' dimensions and some mechanical properties is briefly emphasized. It is also

pointed out that the studies on the effect of fiber dimensions on paper properties have evidenced similar relationships for both wood and nonwood species. Among other factors that influence paper properties there are pulping process and yield and also the intensity of refining. Intrinsic fiber strength measured by the zero span tensile test and related to basis weight provides a measure of the fiber strength. The factors influencing paper strength are also mentioned.

In the end of the authors' work, the provided final remarks reinstate the most important ideas discussed in the previous chapters. By providing key information on wood as raw material for papermaking, the correlations between this renewable resource characteristics, the obtained paper properties and its behavior in different applications, the book constitutes as fundamental work of great use for all people working in the field of bio-resources.

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