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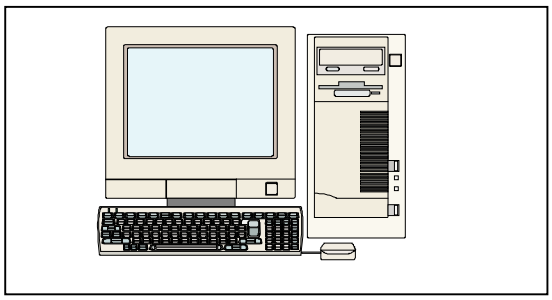

MANAGEMENTUL DEŞEURILOR. ANALIZA SITUAȚIEI DIN JUDEȚUL SUCEAVA

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Rezumat

Lucrarea prezintă date statistice actualizate privind gestionarea deşeurilor în județul Suceava, pe categorii de deşeuri, dintre care pentru noi prezintă interes tendințele privind colectarea şi valorificarea maculaturii. Sunt analizate evoluțiile colectării deşeurilor din diferite surse, îndeosebi a celor municipale, precum şi aspecte privind tratarea şi valorificarea deşeurilor.

Cuvinte cheie: *deşeuri, deşeuri municipale, colectarea maculaturii*

Abstract

The paper presents updated statistics on waste management in Suceava county, categories of waste, of which for us is interesting trends regarding the collection and use of waste paper. I analyzed the evolution of waste collection from various sources, especially those municipalities and waste treatment and recovery issues.

Key Words: *waste, waste paper collecting, domestic waste*

1. INTRODUCERE

Județul Suceava se confruntă cu mari probleme legate de sistarea depozitării pe depozitele de deşeuri neconforme în condițiile în care depozitele de deşeuri zonale aflate în lucru prin proiectul „Sistem integrat de gestionare a deşeurilor municipale în județul Suceava" nu sunt încă funcționale. În ultimul timp şi-a sistat activitatea depozitului de deşeuri Antileşti - Fălticeni, la data de 16 iulie 2010, iar dintre depozitele de deşeuri municipale vechi, neconforme, au mai rămas în funcțiune pe teritoriul județului Suceava doar depozitele Gura Humorului şi Câmpulung Moldovenesc, care mai pot funcționa până la data de 16 iulie 2011. În aceste condiții costurile de gestionare a deşeurilor menajere cresc prin eliminarea lor pe depozitele neconforme din afara județului din Botoşani, Săveni, Darabani, Târgu Neamț. Pentru îmbunătățirea situației s-a demarat construirea în avans a primei celule din depozitul de deşeuri Moara, din fonduri proprii ale Consiliului Județean Suceava şi ale primăriilor arondate.

2. Fluxuri de deşeuri reciclabile

În Judetul Suceava sunt implementate Sisteme de colectare selectivă a deşeurilor reciclabile în 31 de localități prin finalizarea de proiecte PHARE CES şi fonduri proprii ale autorităților administrației publice locale.

Este regretabil că în unele localități, deşi există facilități pentru colectarea selectivă, nu se colectează separat deşeuri reciclabile, din cauza lipsei de participare a populației şi autorităților locale (ex Frasin, Valea Molodovei, Mânăstirea Humorului, Ostra şi Stulpicani).

În total s-au colectat 4027 tone de deşeuri de hârtie/carton de către agenții economici autorizați în colectarea/valorificarea deşeurilor reciclabile şi s-au valorificat prin fabricile de hârtie /carton din țară, inclusiv la SC AMBRO SA Suceava, care prin instalația proprie de prelucrare maculatură cu o capacitate de 300 tone/zi, a colectat/valorificat în perioada iunie-noiembrie 2010 cantitatea de 32409 t de deşeuri de hârtie/carton din toată țara**,** incluzând 3297 tone din județul Suceava.

Prezentăm în tabelul 1 fluxul unor categorii de deşeuri monitorizate de APM Suceava, pentru perioada iunie-noiembrie 2010.

Tabel 1 Gestiunea fluxurilor principale de deşeuri din judeţul Suceava (iunie - noiembrie 2010

Denumire material	Cantitate (tone)			Stoc (tone)	
	Colectată	Valorificată	Eliminată		
1. Deşeuri municipale	57566	1123	56443	0	0
2. Sticlă	570.622	537.301	0	86.631	53.31
3. PET	476.271	463.099	0	40.5	27.328
4. PE	401.495	387.87	0	91.505	77.88
5. Hârtie / carton	4027,833	4027,833	0	0	0
6. Uleiuri uzate	70.225	64.623	0	87.998	82.396
7. PCB / PCT *(litri)*	-328*	0	0	21879	21879
8. Acumulatori auto	345.48	335.66	0	18.373	8.553
9. Anvelope uzate	771.467	158.255	0	3069.302	2456.09
10. Deşeuri lemnoase, din care:	171279.8	180221.3	0	19070.5	28012
11. Rumeguş	71704.3	59966.9	0	15729.4	3992
12. Deşeuri spitaliceşti	31.56	0	31.56		0

**cantitatea trecută cu minus reprezintă bucăţile eronat considerate câte două pe carcasă şi raportate anterior de către operatori economici*

3. Gestionarea substanţelor chimice şi deşeurilor periculoase

Prezentăm mai jos o serie de informaţii privind aspectele legale care privesc gestionarea substanţelor chimice şi deşeurilor periculoase şi modul în care au fost rezolvate în practică întrucât sunt situaţii cu care se confruntă majoritatea firmelor medii şi mari.

3.1. Importul şi exportul anumitor substanţe şi preparate periculoase - Procedura PIC

Legislaţia europeană în domeniul substanţelor şi preparatelor periculoase se referă la aspecte legate de clasificare, etichetare, cât şi la punerea pe piaţă (import/export), protecţia consumatorului, protecţia civilă.
Regulamentul nr. 689/2008/CE - PIC privind exportul şi importul de produse chimice periculoase (astfel cum a fost modificat prin Regulamentul nr. 15/2010/CE), pune în aplicare Convenţia de la Rotterdam şi este ultimul dintr-o serie de astfel de reglementări privind substanţele chimice pentru comerţul internaţional care datează din 1992.
Modalităţile de realizare a controlului exportului şi importului produşilor chimici periculoşi, precum şi modalităţile de colaborare dintre autorităţi sunt reglementate de HG 305/2007 si Ordinul nr. 1239/6.08.2007 iar produşii periculoşi sunt prevăzuţi în anexele I şi V ale Regulamentului.
Autoritatea Naţională a Vămilor a informat că în cursul sem II 2010 în judeţul Suceava nu s-au efectuat importuri/transporturi de substanţe chimice periculoase supuse procedurii PIC. De asemenea în judeţul Suceava nu există importatori/utilizatori de substanţe care să se regăsească in anexele acestui regulament.

3.2. Regimul substanţelor care diminuează stratul de ozon

În cursul sem. II 2010 au fost reinventariat agenţii economici - 37 de agenţi economici în jud. Suceava care se supun Regulamentului nr. 1005/2009 privind substanţele care diminuează stratul de ozon, intrat în vigoare la 1.01.2010. Prezentăm situaţia în tabelul 2.

Tabel 2 Agenți frigorifici - cantități utilizate în semestrul II 2010 în jud. Suceava

Județ	**Cantitate utilizată în sem II 2010 Agenți frigorifici (kg)**							
Suceava	CFC-12	CFC-13	HCFC-22	HCFC- 123	HCFC-141b	R 502	Alti HCFC	Clorura de metil
	3	-	156	-	-	2	-	-

3.3 Poluanți organici persistenți (POP)

Poluanții organici persistenți (POP) sunt substanțe chimice care persistă perioade lungi în mediul înconjurător, se bioacumulează în organismele vii şi prezintă riscuri pe termen lung lung pentru oameni, mediu şi animale.

Conform datelor transmise de către agenții economici din județ, în sem. II 2010 nu sau înregistrat operațiuni de import/export /utilizare de poluanți organici persistenți.

Referitor la regimul bifenililor policlorurati (PCB/PCT), s-a solicitat agenților economici deținători de echipamente cu conținut de PCB/PCT (condensatori electrici) actualizarea inventarului şi raportarea privind stadiul respectării planurilor de eliminare a echipamentelor şi materialelor cu conținut de PCB/PCT la nivelul sem II 2010.

Pe sem. II 2010, s-au eliminat un nr. de 1257 buc. condensatori electrici (conținând 21831 litri ulei cu conținut de PCB/PCT) de către agenții economici care aveau în planul de eliminare ca termene sem. II 2010 şi respectiv sfârşitul existenței lor utile.

3.4 Metale grele şi compuşi restrictionati: mercur, nichel, cadmiu, plumb, crom, staniu, arsen

Metalele în cantități foarte mici sunt necesare tuturor formelor de viață. Ele pătrund în celula vie sub formă de cationi, dar înglobarea lor este strict reglată, deoarece în cantități mari practic toate metalele sunt toxice.

Metalele restricționate se regăsesc în anexa XVII a Regulamentului nr. 1907/2006 privind înregistrarea, evaluarea, autorizarea şi restricționarea substanțelor chimice - REACH. Unele dintre substanțe şi preparate cu metale grele sunt interzise la comercializare şi utilizare.

La nivelul județului Suceava la nivelul sem. II 2010 exista următoarea situație privind metalele grele şi compuşii acestora prezentata in tabelele 3 si 4:

Tabel 3 Situația cantităților de mercur şi compuşi cu mercur existente la nivelul sem. II 2010 în jud. Suceava

Stocuri mercur (kg) la 1.11.2010				
Judet	Mercur total	Cantități de deşeuri de mercur	Compuşi cu mercur	Deşeuri compuşi cu mercur
Suceava	132,9	0	3,24	0

Tabel 4 Situația cantităților de metale şi compuşi ai metalelor restricționate la nivelul sem. II 2010 în jud. Suceava

Stocuri la 1.09.2010 (kg)							
Județ	Nichel metalic/ compuşi	Cadmiu metalic/ compuşi	Plumb metalic/ compuşi	Crom metalic/ compuşi	Staniu metalic/ compuşi	Arsen metalic/ compuşi	Deşeuri
Suceava	0/4	0/22	0/12	0/5,24	0,3/0	0/876,205	

3.5 Regulamentul nr. 1907/2006 privind înregistrarea, evaluarea, autorizarea şi restricţionarea substanţelor chimice - REACH

REACH stabileşte un sistem nou pentru înregistrare, evaluare, autorizare şi restricţionare a substanţelor chimice.

Preînregistrarea este prima etapă a unui proces de 11 ani de tranziţie a substanţelor actuale pe piaţa UE la acest nou sistem. Prezentam situatia in tabelul 5

Tabel 5 Situaţia privind substanţele ca atare, produse /importate în sem. II 2010 în jud. Suceava

Judeţ	Nr. operatorilor economici producători/importatori	Nr. operatorilor economici participanţi în SIEF '	Cantitatea de substanţe produse/ importate
Suceava	1/7	0	600/2000

De menţionat că o parte din producătorii/importatorii care s-au preînregistrat pe REACH nu au avut activitate în sem II 2010, iar o parte din cantităţile produse / importate raportate sunt de fapt doar cantităţi utilizate în sem. II 2010 (la utilizatori în aval).

3.6 Incinerarea deşeurilor

În cursul anului 2010 în judeţul Suceava au funcţionat instalaţiile de incinerare deşeuri aparţinând S.C. SUPER STAR S.A. Rădăuţi şi S.C. MONDECO S.A. Suceava.

Cantitatea totală de deşeuri medicale incinerate în cele 2 incineratoare, provenite de la unităţile sanitare din judeţul Suceava în sem. II 2010, este 72 tone.

3.7 Transportul deşeurilor periculoase

Conform HG 1106/2008, APM Suceava a eliberat în sem. II 2010 un nr. de 37 de autorizaţii pentru transportul intern al deşeurilor periculoase.

CONCLUZII

1. În judeţul Suceava se generează în continuare cantită□i mari de deşeuri municipale, care conţin hârtie şi carton. Cantitatea de maculatură asigură în jur de 10% din necesarul principalului reciclator zonal - AMBRO;
2. Dezvoltarea unui sistem integrat de gestionare a deşeurilor, eficient din punct de vedere economic şi care să asigure protecţia sănătăţii populaţiei şi a mediului este în curs de realizare prin proiecte gestionate de Consiliul Judeţean Suceava;
3. Gestionarea substanţelor chimice şi deşeurilor periculoase poate deveni o problemă dificilă pentru firmele mici şi medii întrucât legislaţia este complexă şi monitorizarea compuşilor chimici necesită specialişti locali dată fiind monitorizarea APM.

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BOOK REVIEW

BIONANOTECHNOLOGY

David S. Goodsell,

Lessons from Nature, Wiley-Liss, Inc., Hoboken, New Jersey, USA, 2004, 337 pages,

ISBN 0-471-41719-X

The subject of this book is another approach to nanotechnology, which is available today to anyone with a moderately equipped laboratory. This is bionanotechnology, nanotechnology that looks to Nature for its start.

In the chapter 1 bionanotechnology is defined as a subset of nanotechnology: atom-level engineering and manufacturing using biological precedents for guidance. It is also closely married to biotechnology but adds the ability to design and modify the atomic-level details of the objects created. Bionanomachines are designed to atomic specifications, they perform a well-defined three-dimensional molecular task, and, in the best applications, they contain mechanisms for individual control embedded in their structure.

The chapter 2 explores the bionanomachines made by living cells. Bionanomachines have been developed by the process of evolution and are selected to perform their tasks in a very specific environment and are subject to the unfamiliar forces imposed by this environment. At their small scale, bionanomachines are almost immune to the laws of gravity and inertia which are negligible at the nanoscale, and the world of bionanotechnology is unfamiliar, shifting world that plays by different rules. In general, biomolecules may be thought of as articulated chains of atoms that interact in a few well-defined ways. Bionanomachines operate in a chaotic environment being bombarded continually by water molecules. They will scatter randomly if not firmly held in place. Bionanomachines operate by forming interactions with other bionanomachines, fitting together and breaking apart in the course of action. If two molecules fit closely together and have the appropriate matching of chemical groups, they will interact over long periods of time. If the interactions are weaker, they will form only temporary interaction before moving on to the next. The form and function of biomolecules are dominated by two things; the chemistry of their component atoms and unusual properties of the water surrounding them. The energetics of this interaction are quite different from anything we experience in our macroscopic world. In this context the biological molecules (proteins, nucleic acids, lipids and polysaccharides) as structural ensemble are discussed. At the same time, some examples of natural bionanomachinery are evidenced.

The chapter 3 presents an overview of the many techniques that are available for the design, synthesis and analysis of biomolecules. The first example refers to the recombinant DNA technology which is the core capability of bionananotechnology. This technology allows us to construct any protein that we wish, simply by changing the genetic plans that are used to build it. Thus it is possible to modify and/or to create new proteins with specific functions (e.g. monoclonal antibodies). The understanding of the mechanics of biomolecular function and the ability to engineer them for new functions are possible by applications of techniques such as x-ray diffraction, NMR spectroscopy and electron microscopy. On the other hand, along with experiments, the molecular modeling can be used to study biomolecules and to predict biomolecular structure and functions.

The structural principles of bionanotechnology are presented in chapter 4.The first goal in nanotechnology is to build a stable nanostructure. To achieve this basic goal we need to understand the forces that link atoms together inside a nanostructure. The ways used by bionanomachines are based on their optimal function and stability when they are surrounded by water at temperatures of about 37^{o}C. Natural

bionanomachines are also constructed to be stable over a typical biological time scale. There are four strategies for the construction of nanostructure: sequential covalent synthesis, covalent polymerization, self-organizing synthesis and self-assembly. These aspects are discussed in the case of proteins. Self-assembly is used throughout biology. It is made necessary by the bottom-up assembly technique used in living cells. They specify the building of three-dimensional bionanomachines with only the one-dimensional information held in DNA. Self-assembly requires specific geometry of interaction and unique interaction between subunits and it is spontaneous. On the other hand natural bionanomachines are designed for optimal function under crowded conditions. In some cases a less concrete building material is needed. Self-organization is a perfect method for creating structures that are flexible, resilient and self-repairing. In natural systems, self-organization is used primarily to create lipid membranes and in current bionanotechnology, a number of self-organized forms of lipids and lipid like molecules are being explored to create novel infrastructure and to create delivery vehicles for nanomedicine. Natural bionanomachines combine a stable, global structure of arbitrary precision and a few local regions specified to high precision. At the same time flexibility at all levels is used to enhance the function of bionanomachines. This include harnessing of thermal motion for chemical catalysis, use of induced fit for recognition, design of different conformational states for use in regulation, and incorporation of selective flexibility to link several separate functionalities. Biomolecular flexibility will provide one of the greatest challenges and potential benefits of bionanotechnology.

Functional principles of bionanotechnology are developed in chapter 5. The natural tools available in living cells – ribosomes, enzymes, DNA – are involved to build nanomachines. Looking in cells there are working assemblers, sensors, motors, factories, rigid and elastic materials, adhesives and the list goes on. All biological processes are based on information stored in DNA. The information stored in DNA is not used directly by ribosomes to build proteins. Instead, an intermediary molecule is used. For use, the information is copied, or transcripted, into a strand of RNA. This RNA strand is then used directly by the ribosome to direct the construction of proteins. The flow of information from DNA to RNA to protein demonstrates that information may be densely stored at the nanoscale. But, many desirably nanoscale processes do not occur spontaneously. In these cases energy is added to force the process to occur in the wanted way. There are involved three sources of energy-chemical, light and electrical energies to drive difficult chemical reactions and to power directed motion. ATP (adenosine triphosphate) is the most common biological fuel molecule. Several methods are used to construct ATP with energy from the breakdown of food or capture of light. Cleavage of ATP is then used to power most unfavorable biomolecular processes. The light capturing event is performed by a class of proteins termed photosynthetic reaction centers. These proteins capture a photon of light and use it to create a high energy electron, which is then used for power. Biological systems move electrons one at time from one carrier to the next in well-defined bionanocircuits. The process is termed charge transfer. The transfer of single electrons along complex paths is widespread in biological systems. Thus, the cells create specific molecules by an ordered set of small chemical transformation using bionanomachines –enzymes- that perform each step efficiently and accurately. Enzymes are a priceless gift from nature, providing the starting point for all of bionanotechnology. Based on the activity of enzymes all components of the cell are synthesized. Further the cells are assembled by filaments, fibrils, biominerals and bioadhesives to create strong, resilient composite materials. In the biological systems the power strokes are correlated with the binding of ATP and/or the release of ADP and phosphate. At the same time, cells have developed machines that capture thermal energy and use it to do work. Thus different kinds of motions at cell level are explained. Another aspect refers to the containment in natural biological systems assured by lipid membranes which are flexible, self-healing and impermeable to the molecules that must be contained. This creates the problems of transport objects across the barrier. The cells build a wide variety of active and passive transport systems to traffic molecules across membranes. These are based on channels, selective channels, specific transporters, proton pumps and in some cases pumps powered by electron flow or light are included. In biological systems the sensing is very important which is performed by receptor protein. Depending on the nature of the compounds and receptor there are different ways to transmit the stimuli (chemicals or physical-light, mechanical).

All cells on Earth are built according to a similar molecular plan, using a similar mechanism to self-replicate. Self-replicating cells contain five basic functionalities: an information driven

assembler, an information storage medium, an information duplicator, a set of synthetic machinery for creating construction materials, and a general infrastructure. Thus bionanomachines are created at the nanoscale and then combined through random diffusion inside cells to perform the more orchestrated tasks of life.

Bionanotechnology is a reality today (chapter 6). The first glimmerings of nanomedicine are allowing researchers to make tailored changes to the mechanisms of human body, correcting defects and curing disease. Familiar biomaterials, such as wood, bone and shells are providing the principles needed to create materials tailored at the nanoscale to fit our needs. Biological methods of nanoscale information storage and retrieval are being harnessed to solve computational problems and convict criminals. In this chapter different examples are presented: synthesis of proteins, computer-aided drug design, immunotoxins, delivery of drugs with liposomes, artificial blood, gene therapy and transformation of general medicine into personalized medicine. There are also discussed the following practical aspects: self-assembly at many scales, harnessing molecular motors, DNA computers, molecular design using biological selection, artificial life, hybrid materials and biosensors. The future of bionanotechnology is analyzed in chapter 7.Three case studies are presented. They refer to the nanotube synthase, nanoscale assembler and nanosurveillance. The author underline that the potential of bionanotechnology for feeding the world, for improving our health, for providing rapid and cheap manufacturing with environmental mindfulness, is immense. But we have to take into account two topics: the respect for life and possible dangers. Therefore, **Bionanotechnology: Lessons from Nature** shows both students and practitioners how the lessons that may be learned from biology can be applied to nanotechnology today.

Valentin I. Popa "Gheorghe Asachi" Technical University Iasi

CELLULOSE ALLOMORPHS: STRUCTURE, ACCESSIBILITY AND REACTIVITY

Diana Ciolacu, Valentin I. Popa,

Polymer Science and Technology Serie, Nova Science Publisher, Inc., New York, 2010, 70 pages, ISBN 978-1-61668-323-8

The trend towards cellulose and the tailoring of innovative products for science, medicine, and technology has led to a global renaissance of interdisciplinary cellulose research and the use of this abundant organic polymer over the last decade.

The progress in understanding of cellulose structure has continued during recent decades and will be ongoing in the future. A significant importance is the capacity of cellulose to aggregate in a wide variety of secondary and tertiary structures.

The polymorphism of cellulose always intrigued us through the non-elucidated aspects regarding both the obtaining and the structural organization of allomorphic forms. Although until today, the polymorphism of cellulose was proved through a series of techniques of investigation, an approach through a systematic study of the influence of crystalline forms of organization over the structural accessibility and the reactivity of cellulosic substrata has never been put into practice.

That is why this book analyzes the current knowledge in research and application in the field of allomorphs of cellulose. It performs both a systematization of the no elucidated elements in classical representations and the current hypotheses of the supramolecular organization of cellulose allomorphs. Particular attention has been paid to the understanding of the hydrogen bonding system of various structural organizations of cellulose allomorphs. Although, information about this subject has been published, the book is focused on what the authors considered to be the most important and representative knowledge. The advantages and limitation of the structural architectures of the cellulose allomorphs which are reflected on the accessibility of these are discussed. The accumulation of knowledge on the versatile transformation of crystalline forms of cellulose leads to the understanding of the region-chemical difference in reactivity.

This book has been structured into seven main chapters, as follow:

Chapter 1 - Molecular structure of cellulose – which describes the structure of cellulose at the molecular level, from the point of view of chain polarity, the equatorial positions of the hydroxyls groups on cellulose macromolecules, and also of the chain length expressed in the number of constituent AGUs.

Chapter 2 – Cellulose allomorphs – reviews four major types of cellulose allomorphs focused on the crystal structure of these, especially on the formation of intra- and inter-molecular hydrogen-bonding, the packing of the chains (parallel or antiparallel) and the unit-cell dimensions:

- cellulose I - represents the largest biomass on the earth and is the major structural component of all plant cell walls. Further, was found that cellulose I is a composite of cellulose Iα and Iβ crystalline forms, discovery which led to a revival of interest in the study of cellulose chemistry. The cellulose Iβ is close to the model proposed in literature for cellulose I, while the crystalline structure for cellulose Iα it is still in discussion because the difficulties in obtaining of pure cellulose Iα;
- cellulose II - the second crystalline form of cellulose, obtained by regeneration or mercerization processes;
- cellulose III - prepared with anhydrous liquid ammonia, at -80ºC or organic amine;
- cellulose IV - is known to be prepared by thermal treatments (in glycerol, at about 260ºC).

Chapter 3 - Alkali cellulose - tries to elucidate the mechanism and the intermediate structures which appear during the mercerization process.

Chapter 4 - Amorphous cellulose – focuses on amorphous cellulose which has often been used for model experiments to understand the behavior of the noncrystalline domains in cellulose under various conditions. Thus, this

chapter discus the preparation methods and the conformational and/or hydrogen bonding structure of this cellulose.

Chapter 5 - Accessibility of cellulose – discusses briefly the known methods used to evaluate the accessibility of cellulosic substrata. Also, are presented different possibilities to increase the accessibility of cellulose, classified as, mechanical, chemical and enzymatic treatments, persisting on the enzymatic hydrolysis, as a topic of great interest, with a major influence on solving the problems connected with protecting natural environment. Moreover, it was shown that the experiments involving the enzymatic hydrolysis of the main allomorphic forms of cellulose proved that both the morphological structure and the crystalline one are crucial aspects to the process and the rate of the reaction and implicitly regarding the accessibility.

Chapter 6 - Reactivity of cellulose - presents the factors which have an important role on the reactivity of cellulose and the broad industrial applications for each crystalline form of cellulose.

Chapter 7 - Concluding remarks – discuss briefly the important findings of each chapters and concluded that knowledge gained about the structure, accessibility and reactivity of crystalline forms of cellulose are important to understand the behavior of this natural polymer keeping in mind the large area of application in industrial, medical and pharmaceutical fields.

The book is a valuable source of information which contribute to the understanding of the complexity and uncertainties that still exist about polymorphism of cellulose and to synthesize the old knowledge and the developments of different studies which contribute to elucidate the structure of cellulose allomorphs.

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"Petru Poni" Iasi

CURRENT TRENDS OF SUPERCRITICAL FLUID TECHNOLOGY IN PHARMACEUTICAL, NUTRACEUTICAL AND FOOD PROCESSING INDUSTRIES

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The book "Current Trends of Supercritical Fluid Technology in Pharmaceutical, Nutraceutical and Food Processing Industries" provides an overview of basic principles of SFE and potential application in pharmaceutical and food industries.

Because of their unique properties and relatively low environmental impact, supercritical fluids have proven highly useful in the extraction and separation of organic compounds, in particle production, as reaction media, and for the destruction of toxic waste. During the last decades, more attention was focused on the extraction of organic compounds using supercritical fluids. In "Current Trends of Supercritical Fluid Technology in Pharmaceutical, Nutraceutical and Food Processing Industries", experienced practitioners present detailed accounts of a wide variety of techniques using supercritical fluids.

The book is divided in 4 parts and it comprises 10 chapters. Compiling contributions from international experts in the field, the book presents the state-of-the-science in the application of innovative technologies using supercritical fluids.

In the first chapter *Introduction to Supercritical Fluids: Basic Principles and Applications (by*

M. Nunes da Ponte) a concise and understandable scientific presentation of the basic principles, proprieties and potential application of supercritical fluids is related.

In the second chapter *Applications of Supercritical Expansion Processes for Particle Formation*

(by Ana Rita and C. Duarte) an overview of the supercritical expansion processes applied to pharmaceutical purposes is presented. The principles of these technologies and the advantages and disadvantages of the methods are clearly discussed.

Because supercritical processes are often referred and classified as "green" and "environmental friendly" processes, a number of applications and some examples of the use of supercritical fluid technology for the preparation of controlled release systems are reported.

In chapter 3 *Supercritical Anti-Solvent Micronization: Control of Morphology and Particle Size* (by Ernesto Reverchon and Iolanda De Marco), SAS precipitation used to micronize different kinds of materials is approached considering that AntiSolvent (SAS) precipitation has been largely used in many distinct research areas such as: pharmaceuticals, superconductors, coloring matters, explosives, polymers, biopolymers, etc. Furthermore, SAS experimental apparatus, several procedures and the optimal operating parameters are described along with details of the morphologies of the expanded microparticles.

Chapter 4 *Particles from Gas-Saturated Solutions and Related Methods for Particle Engineering* (by A.R. Sampaio de Sousa and Catarina M. M. Duarte) provides information on one of the most promising methods for particle engineering using supercritical fluids– Particles from gas saturated solutions (PGSS) and derived methods. The authors clearly described the basic principles, the modeling process, related methods and their application in pharmaceutical, cosmetic and nutraceutical field.

This chapter presents an overview of the basic principles of the method, several developments that were further undertaken, and a compilation of different examples and systems.

Chapter 5 *Fundamentals and Modeling of Supercritical Precipitation Processes* (by Ángel Martín and María José Cocero) deals with important informations on the fundamental

investigation and modeling of supercritical fluid precipitation processes. These aspects are extremely important in the development of a systematic procedure for the design and scale-up of these processes. Different approaches for the modeling of SCF precipitation processes have been also presented along with solubility and other phase equilibrium calculations.

Chapter 6 -*Supercritical Fluid Impregnation for the Preparation of Controlled Delivery Systems*

(by Ana Rita C. Duarte and Catarina M. M. Duarte) is focused on the impregnation using supercritical fluid technology, in the preparation of controlled release systems. The development of different successful controlled release systems is presented with the aim to obtain high purity products, free of residual solvents, since no organic solvents are involved in the impregnation process.

Chapter 7 *Ionic Liquids and Carbon Dioxide as Combined Solvents for Reactions and Separations: The Miscibility Switch* (by E. Kühne, G.J. Witkamp and C.J. Peters) refers to the use of Ionic liquids (ILs) and carbon dioxide (CO2) to replace volatile organic solvents in synthesis and extraction processes. When ILs are used simultaneously with carbon dioxide for reactions and extractions, the process will be based on non-toxic, non-flammable solvents and will be applicable for a wide variety of compounds.

Chapter 8 *Supercritical Antisolvent Fractionation of Plant Extracts* (by O. J. Catchpole, N. E. Durling, J. B. Grey, W. Eltringham and S. J. Tallon) contains valuable information regarding the fractionation of plant extract solutions using near-critical fluids to give two or more fractions containing bioactives with widely differing polarities.

In particular the authors describe the use of the SAFT process in detail for the solvent extraction and subsequent supercritical antisolvent fractionation of sage and onion.

In chapter 9 *Mathematical Modelling of Supercritical Fluid Extraction* (by H. Sovová) are discussed two of the most frequent types of models for supercritical extraction from plants and the factors influencing scale-up of the process. Considering that different mathematical models for supercritical fluid extraction have been developed in the last decades and it is difficult to choose the most suitable model for particular extraction this study presents concisely, a simple criteria based on time constants of mass transfer and characteristic time of equilibrium extraction.

In chapter 10 *Supercritical Fluid Processing in Food and Pharmaceutical Industries: Scale- Up Issues* (by Fabrice Leboeuf and Frantz Deschamps) the keys for the scale-up of extraction and fractionation processes, together with examples of applications are discussed briefly. Also, the scale-up issues of the particle engineering processes for industrial applications, the design of SFF Full Scale Plants and the cost estimations, are given. The accurate knowledge of mass transfer and nucleation processes will form the basis for efficient scale-up.

Versatile and comprehensive, the book "Current Trends of Supercritical Fluid Technology in Pharmaceutical, Nutraceutical and Food Processing Industries" combines basic fundamentals with industrial applications.

Enhanced concern for the quality and safety of food products, increased preference for natural products, and stricter regulations on the residual level of solvents, all contribute to the growing use of supercritical fluid technology as a primary alternative for the extraction, fractionation, impregnation and particle expansion, and this technology is the key in pharmaceutical, cosmetic, food and nutraceutical field.

Considering the scientific advancements, the improved technology and increased utilization of supercritical fluids it was required a comprehensive, single-source review of current and future trends in supercritical fluid technology.

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EVALUATION OF FORESTRY BIOMASS QUALITY FOR THE PRODUCTION OF SECOND-GENERATION BIOFUELS

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Different classes of wooden material were analysed as to their chemical composition, especially as to the content of fermentable sugars: softwood and hardwood unbarked wood, SRC, VSRC and different grades of forest chips. High hexose contents were preferably found in unbarked softwoods, which presented up to 4% more C6 sugars than unbarked hardwoods. However, some hardwood species, such as eucalyptus and poplar clones, presented very high hexose content values. Short rotation coppices present just slightly lower average hexose content compared to mature wood, but very short rotation coppices are poorer in hexoses, by 3% on the average. The hexose content of forest chips is significantly affected by the non-wood fractions. On the average, the gap between mature unbarked wood and forest chips is of 5% for hardwoods and of 8% for softwoods. Finally, if upgrading of pentoses by fermentation into bioethanol is possible, hardwoods seem to be a good raw material, as the presence of C5 sugars is considerably more important than in softwoods.

FROM KRAFT MILL TO FOREST BIOREFINERY: AN ENERGY AND WATER PERSPECTIVE. II. CASE STUDY

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In Canada, the pulp and paper industry, a major contributor to the economy, is facing one of the most severe crises of its history. The biorefinery concept offers an opportunity to revitalize the industry by producing high-value chemicals and biofuels, by developing new technologies and by penetrating new markets. To become successful, the biorefinery should address a number of challenges, associated to feedstock, products, markets, technology and sustainability. This paper is the second part of a work undertaken to evaluate the energy impacts of a Kraft pulp mill conversion into a biorefinery. In Part I, a methodology identifying the interactions between steam and water systems in the Kraft process and their effects on the implementation of energy efficiency measures has been developed. Part II deals with the application of this methodology in the specific Canadian biorefinery context. Hemicellulose extraction from wood chips prior to pulping and its transformation into high-value products is the biorefining technology identified for integration into the existing pulp mills. A Canadian hardwood Kraft pulp mill that has the opportunity to be converted into a dissolving pulp mill was selected as a biorefinery acceptor. Hemicellulose, used as a feedstock for promising products, such as furfural, xylitol and ethanol, has been analyzed. Issues related to the corresponding energy requirements of the biorefinery and to its sustainability have also been investigated.

ANALYSIS OF NON-CARBOHYDRATE BASED LOW-MOLECULAR WEIGHT ORGANIC COMPOUNDS DISSOLVED DURING HOT-WATER EXTRACTION OF SUGAR MAPLE

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The present paper is part of an ongoing study undertaken to evaluate the effect of hot-water extraction on sugar maple (*Acer saccharum*), for extending the scope of ESF biorefinery. The final objective is to assess the contribution of hot-water extracted non-carbohydrate-based organic compounds to generate a stream of platform chemicals. The hot-water extracts (HWEs) were subjected to ultrafiltration to remove the insoluble solids and the clear permeate was extracted with organic solvents, derivatized and analyzed by GC/MS. The organic extracts of the HWEs were composed mainly of phenolics. These compounds were compared to the

extractives obtained from native sugar maple wood. Our results indicate that the aromatic compounds present in the organic extracts of HWE may be extractive-based or products of lignin acidolysis generated primarily by cleavage of the α-O-4 linkages.

MULTIFUNCTIONAL ALKALINE PULPING, DELIGNIFICATION AND HEMICELLULOSE EXTRACTION

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In this study, multifunctional alkaline pulping was suggested to produce different pulp grades at one mill site, ranging from high-yield paper pulp to high-purity dissolving pulp. In all process modifications, sulfur was successfully replaced by anthraquinone. Autohydrolysis and alkaline pre-extraction were applied to *Eucalyptus globulus* wood chips, followed by kraft and soda-AQ pulping. Alkaline pre-extraction prior to soda-AQ pulping largely preserved the pulp yield, while a substantial amount of xylan could be extracted in polymeric form during the pre-treatment. The resulting pulp revealed characteristics indicating an alternate use – as paper pulp and as dissolving pulp – after further purification with cold caustic extraction (CCE). The removal of hemicelluloses from kraft or soda-AQ paper pulps by a CCE post-treatment allowed the production of high yield dissolving pulps. The hemi-rich CCE-lye was recycled to soda-AQ pulping, contributing to yield increase by xylan re-precipitation. Alternatively, the CCE-lye could be purified efficiently by ultrafiltration, by concentrating the rather pure and high molecular weight xylan in the retentate for further use. The results indicated that biorefinery concepts can be realized for alkaline pulping by adopting the proposed modification of multifunctional alkaline pulping.

SECOND GENERATION ETHANOL THROUGH ALKALINE FRACTIONATION OF PINE AND ASPEN WOOD

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Pre-treatment studies on pine and aspen wood with alkaline fractionation were performed, the experimental results obtained being used as input for assessing the conversion of an existing pulp mill to ethanol and lignin production. By the LignoBoost process, the extracted lignin could be used in the lime kiln to replace fuel oil, while the lignin not needed in the lime kiln could be sold as a by-product. In addition to fuel applications, lignin could be used in a wide range of bio-based product applications, which would increase the value of the extracted lignin and increase the total revenues.
A WinGEMS model was used to calculate mass and energy balances, and the results were used for an economic evaluation of the concept. The assessment indicated that the proposed alkaline concept would have

reasonable production costs from both pine and aspen wood, comparable with the bioethanol produced from grain in Northern Europe today, *i.e.* about 0.45 €/L ethanol (~5 SEK/L). The production rate of a typical mill producing 1000 tonnes of pulp per day before conversion would be in the order of 140 000 m3 of ethanol per year, as depending on the raw wood material. The corresponding lignin production would range from 25 000 to 63 000 tonnes per year. The use of alkaline delignification to produce a substrate with low lignin content for the enzymatic hydrolysis builds entirely on known and well-proven technology, yet it needs to be further developed. The process chain from enzymatic hydrolysis to ethanol is very similar to that used today for grain ethanol. Altogether, the technical risk should therefore be low.

THE LIGNOBOOST PROCESS

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A process for lignin removal from alkaline pulping liquors (black liquors) has been developed within the FRAM2 R&D Program (Future Resource Adapted Pulp Mill, part 2). The lignin product (Fig. 1) from a demonstration plant, owned and operated by Innventia (formerly STFI-Packforsk), was characterized and used in different combustion trials with good results – co-firing of lignin and bark in a fluidized bed boiler, o-firing with coal in a PFBC (Pressurized Fluidized Bed Combustion) boiler and firing of lignin in a fullscale lime kiln. The process development and operation of the demonstration plant has displayed good results. Runnability in the demonstration plant and the lignin quality have been both very good. The work done on the investment and operational costs showed great potential for improving the concept of economy, which is very promising.

BIOREFINERY IN A KRAFT PULP MILL: FROM BIOETHANOL TO CELLULOSE NANOCRYSTALS

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Wood, composed of cellulose, lignin and hemicelluloses, is the main raw material used to produce cellulosic fibres. Mills producing cellulosic fibres, also called kraft mills, look very much like a “biorefinery” plant: isolated cellulose is almost pure, and then exploited today mainly as paper; hemicelluloses and lignin are degraded and solubilised during the process as a very complex mixture, called “black liquor”, which is burnt in a recovery boiler. The heat thus produced covers largely the energy needs of the kraft mill, which may then become a net producer of electricity. The aim of this paper is to present two examples of research pathways aiming at enlarging the products portfolio a pulp mill could offer. The first example deals with the definition of hemicelluloses extraction from softwood, prior to its transformation into cellulosic paper pulp by the kraft process. The hemicelluloses

fraction (in the case of softwood species, mainly composed of C6 sugars) should be extracted in a relatively pure form, whereas the cellulose fraction would continue to be obtained as fibres for papermaking. Thus, lignin becomes the main component of the "black liquor" and might continue to be used as fuel for the energy needs of the mill. The extracted hemicelluloses are hydrolysed into hexoses and then fermented into bio-ethanol. This type of second generation bio-ethanol should eventually substitute the first bio-ethanol generation produced today from food raw materials. In the study, softwood chips were submitted to various hydrolysis treatments. Temperature, time and pH were varied so as to optimise the hemicelluloses extraction primarily under the form of sugar monomers. The prehydrolysis liquors were analysed for their total sugar content and submitted to fermentation tests for bioethanol production. Very satisfactory results were obtained in terms of bio-ethanol production, which indicated that no active fermentation inhibitors were present in the selected liquor. The second research pathway deals with cellulose nanocrystals which, in recent years, have attracted the attention of both scientific and industrial communities. It was shown that cellulose nanocrystals reinforced polymer nanocomposites display outstanding mechanical properties and can be used for processing highmodulusthin films.

CHARACTERIZATION OF HARDWOOD-DERIVED CARBOXYMETHYLCELLULOSE BY HIGH pH ANION CHROMATOGRAPHY USING PULSED AMPEROMETRIC DETECTION

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An approach for the quantitative analysis of substituent distribution in carboxymethylcellulose (CMC) is presented. In short, the high-pH anion-exchange chromatography method, coupled to pulsed amperometric detection (PAD), is introduced. Each of the seven derivatives in CMC is presented by a single peak on the PAD trace, thus enabling an easy quantification. New inside information on monomer composition is obtained by this novel method, which is essential for understanding the structure *versus* property relationships in the CMC samples.

DILUTE SULPHURIC ACID AND ETHANOL ORGANOSOLV PRETREATMENT OF *Miscanthus x Giganteus*

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Three processes for the pretreatment of *Miscanthus x Giganteus* were compared, namely, dilute sulphuric acid treatment, an ethanol organosolv treatment and a two-step protocol involving a presoaking step prior to the ethanol organosolv treatment. The pretreatment assays were evaluated and compared on the basis of their Combined Severity factors. It was shown that the organosolv processes permitted an efficient removal of both lignin and hemicelluloses from the solid residue. A presoaking step prior to an organosolv process performed at low severity permitted to enhance the removal of lignin and hemicelluloses and the recovery of hemicellulose sugars.

PYROLYTIC BEHAVIOUR OF CELLULOSE IN A FLUIDIZED BED REACTOR

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The literature devoted to the competitive and sequential kinetics of cellulose pyrolysis is quite controversial, because of the ambiguous relationship established among cellulose molecules, levoglucosan and other products. A fast pyrolysis system composed of a feeding system, a fluidized bed reactor, carbon filter, vapour condensing system and gas storage is created to quantitatively investigate the yield of bio-oil, syngas and char from cellulose pyrolysis, at different temperatures (from 430 to 730 °C) and residence times (from 0.44 to 1.2 s). The products in the bio-oil are characterized by GC-MS, while the gas sample is analyzed by GC. The relationship between levoglucosan and the other main products (5-HMF, FF, HAA and HA) is estimated *versus* the possible routes for primary cracking of the cellulose molecules and the secondary reactions of fragments. CO formation is seen as enhanced at high temperature and residence time, while the yield of CO2 is slightly changed. Further on, an improved kinetic scheme is proposed, to describe the pyrolysis steps of cellulose, showing that levoglucosan acts not only as a product of cellulose cracking, but also as a precursor for the formation of almost all the other products.

CATALYTIC DEOXYGENATION OF CELLULOSE PYROLYSIS VAPOURS OVER MESOPOROUS MATERIALS

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In this paper, catalytic deoxygenation of cellulose pyrolysis vapours over mesoporous materials is investigated. Three different MCM-41 mesoporous materials were employed as catalysts, namely, acidic HMCM- 41-15, H-MCM-41-20 and aluminium-free silica Na-Si-MCM-41, with cellulose beads used as a raw material. Pyrolysis/deoxygenation experiments were carried out in a dual-fluidized bed reactor. Thermal pyrolysis occurred over quartz sand and the vapours formed were upgraded in a consecutive fluidized bed, in
which the mesoporours materials acted as catalysts. Both the yield and chemical composition of the pyrolysis products were affected by the catalysts. More water and CO were formed as a result of catalytic deoxygenation, compared to the non-catalytic experiment. Some of the organic compounds in the catalytic bio-oil had a lower oxygen content than the predominant levoglucosan in the non-catalytic bio-oil.

RELATIONSHIPS BETWEEN CELLULOSE, LIGNIN AND NUTRIENTS IN THE STEMWOOD OF HYBRID ASPEN IN ESTONIAN PLANTATIONS

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Concentrations of cellulose, lignin and nutrients in the stemwood of four clones of 7-year-old hybrid aspen (*Populus tremula* L. x *P. tremuloides* Michx.) were studied on 50 permanent experimental plots established for the afforestation of abandoned agricultural lands in Estonia. Quantitative evaluation of hybrid aspen chemical components indicated a relatively high cellulose and low acid-insoluble lignin concentration, and especially a high C/L ratio, compared to other poplar species. Regression analyses showed strong relationships between stemwood N, P, K, cellulose and lignin concentrations, but no dependence on soil chemical composition was established. Height, diameter and annual increment were strongly dependent on stemwood N, K and P. Based on the results obtained, clones of hybrid aspen appear as economically promising for the afforestation of abandoned agricultural lands, in large-scale, short-rotation commercial plantations, for pulpwood and bioenergy production.

AVAILABILITY OF WOOD BIOMASS FOR BIOREFINING

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Biorefining is an emerging industry that will use increasing volumes of biomass as a raw material. This paper presents the estimates of global forest biomass resources for biorefining, based on the available global forest statistics and literature. The focus is on the large-scale production facilities, such as liquid biofuel production. The raw material sources were divided into three categories, namely, reallocation of current raw material flows to biorefining, mobilization of the existing biomass resources not utilized today, and boosting of biomass production, particularly in plantation forests. By the year 2020, the potential of woody biomass for biorefining will amount to 780 million m3 (327 dry tonnes) annually, corresponding to 147.5 million tonnes of oil in terms of energy content. Assuming that 50% of the energy content of the feedstock can be recovered as liquid biofuel, 73.8 million tonnes (3.1 EJ) of liquid biofuels could be produced, which will represent, in the year 2020, 2.6% of the global forecasted transportation fuel consumption (117 EJ).

EVALUATION OF LIGNOCELLULOSIC BIOMASS UPGRADING ROUTES TO FUELS AND CHEMICALS

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The study evaluates wood and non-wood lignocellulosic conversion into biofuels and renewable intermediate chemical products, on the basis of material efficiency, heat content in final products (lower heating value) and properties of fuel components, as related to their use, existing cars and storage. This type of conversion efficiency analysis can be viewed as a first step in biorefinery route optimization. The upgrading routes considered here include gasification, pyrolysis with subsequent gasification, ethanol, anaerobic acetic acid and ABE-fermentation, digestion and chemical conversion of sugars into fuel. The material efficiency is calculated on the basis of potential yields. In addition, the subsequent conversion of these intermediate products to fuel components through chemical reactions has been considered. Intermediate chemicals, such as ethylene, propylene, ethyl acetate and acetic acid, have also been analyzed. Chemical upgrading of sugars, acetic acid fermentation and gasification converted most of the raw material heat content in the products. The components with good properties containing some oxygen, such as butanol, methyltetrahydrofuran (MTHF) and ethers, appeared as promising from the viewpoint of both fuel properties and biomass conversion.

SO2-ETHANOL-WATER FRACTIONATION OF FOREST BIOMASS AND IMPLICATIONS FOR BIOFUEL PRODUCTION BY ABE FERMENTATION

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The study proposes an economic process for the production of commodity chemicals from forest biomass and recycled fibers. This so-called Bioforest process uses tree tops, limbs, twigs, stumps and recycled paper as feedstock for fermentation to butanol, ethanol and acetone/isopropanol. This mixture of solvents can be sold as chemicals or used to replace gasoline in internal combustion engines. The SO2-ethanol-water fractionation method affords efficient fractionation of forest biomass, under moderate conditions, yielding a high amount of fermentable sugars. Subsequently, sugars are subjected to ABE fermentation. Preliminary trials with conditioned hemicellulose solutions produced by the fractionation process show that they are fermentable by bacteria, such as the *Clostridia* species, but further work is needed to optimize the production of butanol, ethanol and acetone or isopropanol.

EFFECT OF ACID AND ENZYMATIC TREATMENTS OF TCF DISSOLVING PULP ON THE PROPERTIES OF WET SPUN CELLULOSIC FIBRES

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Dissolving-grade softwood pulp was treated with EG-rich enzymes and hot diluted sulphuric acid, to decrease the molecular weight of cellulose. The treated samples were dissolved in aqueous sodium zincate and spun into cellulosic fibres by a wet spinning method. The effects of cellulose concentration in the spinning solution and of cellulose molecular weight on the fibre properties were studied. The molecular weight (Mw) of the treated cellulose decreased by 38 to 63%, depending on the treatment parameters. The falling ball viscosity of the alkaline solution prepared from the differently treated pulps correlated linearly with the Mw of the treated cellulose. At constant Mw of cellulose, the tenacity of the obtained wet spun fibres correlated positively with the cellulose concentration of the spinning solution. However, a higher cellulose concentration could not compensate the lowered Mw as to the fibre properties.

HEMICELLULOSES EXTRACTION FROM GIANT BAMBOO PRIOR TO KRAFT AND SODA AQ PULPING TO PRODUCE PAPER PULPS, VALUE-ADDED BIOPOLYMERS AND BIOETHANOL

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Hemicelluloses were pre-extracted from giant bamboo with dilute H2SO4 prior to Kraft and soda AQ pulping. The reaction conditions were selected to convert most of the hemicelluloses into soluble monomeric sugars, leaving almost unaltered the cellulose and lignin from the residual solid phase. A Central Composite Design was used to study four pre-extraction variables: H2SO4 concentration (0.1-0.5% v/v), solid/acid solution ratio (1/3.5-1/5.5 g/mL), temperature (80-140 °C) and time (10-50 min). Temperature had a dominant influence on the hydrolysis process. A maximum xylose yield – of 83.4% – (based on oven dry raw material mass) was obtained at a 0.4% v/v H2SO4 concentration, a solid/solution ratio of 1/4 (g/mL), at 140 °C and an extraction time of 40 min. The bamboo, from which 2.4% hemicellulose had been extracted, was subsequently pulped by both Kraft and soda AQ pulping methods. Soda AQ pulping gave the best results in terms of pulp yield, viscosity and kappa number, compared to the non-extracted bamboo, pulped under similar conditions.

USE OF IONIC LIQUIDS IN THE PRETREATMENT OF FOREST AND AGRICULTURAL RESIDUES FOR THE PRODUCTION OF BIOETHANOL

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Pretreatment of lignocellulosic materials is an important step to achieve higher amounts of simple sugars, mono- and disaccharides, for obtaining ethanol as a biofuel, *via* enzymatic hydrolysis. The study introduces a concept that utilizes ionic liquids (ILs) as solvents in the pretreatment step, before enzymatic saccharification, for both forest residues (Eucalyptus *(Eucalyptus globulus* Labill.) and Lenga (*Nothofagus pumilio* (POEPP. EX. ENDL.) KRASSER) and for agricultural residues (wheat and corn). The procedure was evaluated at four different temperatures (80, 121, 150 and 170 °C) for 30 and 60 min, respectively, with 1-ethyl-3-methylimidazolium chloride ([EMIM+][Cl-]). Subsequent enzymatic

hydrolysis of these materials was carried out at 47 ºC, for 72 h, with commercial cellulases. The results demonstrated that the best experimental conditions found for wheat, corn and Eucalyptus residues were the following: 150 °C, for 60 min, yielding a total of 46, 48 and 30% sugars, respectively; in the case of Lenga residues, the optimum conditions were: 150 °C for 30 min, yielding a total of 40% sugars after saccharification. Finally, an analysis of the solid material after ionic liquid pretreatment is required, to determine the changes related to lignin, cellulose and hemicellulose composition.

WOOD HYDROLYSIS INDUSTRY IN THE SOVIET UNION AND RUSSIA: A MINI-REVIEW

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Dedicated to the memory of Vassily I. Sharkov,founder of the Soviet hydrolysis industry

The main objectives, feedstock, processes and spectra of products (commodities, specialties, fine chemicals, including pharmaceuticals as by-products of lignin) manufactured by the Soviet and Russian hydrolysis industry for over 75 years are briefly overviewed. The limitations and the difficulties that might have affected this type of industry are also considered. The history of the Soviet/Russian hydrolysis industry clearly shows that, without state subsidies, the production of commodities, such as ethanol or fodder yeast, from lignocellulosic raw materials, can survive only if it also involves the production of heat and electric power from lignin and value-added products, which requires special techniques and equipment, along with a pre-developed market niche.

TOWARDS IONIC LIQUID FRACTIONATION OF LIGNOCELLULOSICS FOR FERMENTABLE SUGARS

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The present study investigates wood fractionation through ionic liquid (IL) mediated pretreatment, for obtaining simple fermentable sugars, namely oligo- and monosaccharides, and in particular hexoses (and pentoses). The study focuses on softwood, Scots Pine (*Pinus sylvestris*) and Norway Spruce (*Picea abies*), exposed to ionic liquid 1-ethyl-3-methylimidazolium chloride (EmimCl). Since both EmimCl and the monosaccharides are water-soluble and dissolve readily in similar solvents, the separation of this hydrophilic IL from sugars is difficult. Moreover, the analytics of monosaccharides released from lignocellulosics with the help of EmimCl is challenging. Sufficiently diluted samples, with low enough EmimCl concentrations, tolerated by GC sugar columns, can be also analyzed by GC. The results obtained suggest that some IL-tolerating HPLC columns can be utilized for a quantitative determination of monosaccharides. However, frequently, these columns have low separation ability for monosaccharides and, consequently, the retention time values are very close to each other. So far, the best results on HPLC

utilization were obtained with isocratic elution, using a refractive index detector and a diode array UV detector in series.

ULTRAPYROLYSIS OF WOOD BIOMASS FOR PRODUCTION OF ECOLOGICALLY CLEAN BOILER FUELS AND MOTOR FUELS

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A formed-layer based pyrolytic reactor, incorporating the counter flow of heated gas and the particles of raw waste wood, has been designed and constructed on a mobile platform. The basis of the design is a computer model (POLY.TERM 2), which calculates the gas and particle temperatures as they proceed from the pposing ends of the reactor, as a function of particle size and flow rates. The time of residence in the reactor, necessary to optimize the yields of biopetroleum (BPT) and fine charcoal (FCC), may be evaluated accordingly. Typical data are presented, based on preliminary results with wood chip fuel, a comparison between the theoretical and the experimental values being performed. The results of some early thermoliquefaction experiments are also included.

LEVOGLUCOSAN TRANSFORMATION OVER ALUMINOSILICATES

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Catalytic transformation of levoglucosan (1-6-anhydro-β-D-glucopyranose) was carried out in the liquid phase in the batch mode, at 20 bar and 150 °C, and in the continuous mode, at 300 °C and at atmospheric pressure over aluminum silicates. Proton forms of Beta-25 zeolite and MCM-48 mesoporous material were tested as catalysts, while quartz sand was used as a reference material in non-catalytic transformation experiments. Levoglucosan conversion varied with residence time and catalyst. A variety of products was detected with HPLC, GC and GC-MS. The yields of the main products, *e.g.* different oxygenated species (glucose, glycolaldehyde, formaldehyde, acetaldehyde and acetic acid) varied, as a function of conversion, residence time and zeolite structure.

PHYSICS OF CELLULOSE XANTHATE DISSOLUTION IN SODIUM HYDROXIDE–WATER MIXTURES: A RHEO-OPTICAL STUDY

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The way cellulose xanthate (viscose) fibres dissolve in sodium hydroxide–water mixtures is studied *in situ*, under flow, using a counter rotating optical rheometer. When a bunch of viscose fibres is placed in a solvent, a visco-elastic shell is formed, slowing down the diffusion of the solvent to non-dissolved fibres. It forms a highly concentrated, visco-elastic phase that disperses slowly through a pulling mechanism sucking this visco-elastic solution into the solvent. Due to this mechanism, dispersion and distribution of cellulose xanthate into the solvent is very slow.

A POLYMER-DRUG SYSTEM BASED ON REGENERATED CELLULOSE USED IN TEXTILE INDUSTRY

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Biocompatible absorptive materials with porous structure, formed by cavities with different sizes, have many medical applications, such as drug carriers, base for cell regeneration, implants for tissue regeneration. The immobilization of synthesized indazole derivatives with germicidal, aseptic and anti-inflammatory activity, by diffusion into a regenerated cellulose matrix is studied. The rheological properties of the new composite material are studied, considering the mechanical properties of the materials with potential use in shoe manufacturing for diabetic foot diseases. The immobilization of indazole derivatives onto the cellulose matrix is influenced by certain parameters, like the derivatives/cellulose ratio and cavity structure of the cellulose matrix. New polymer-drug blend systems with medical benefits were obtained and the most important physicomechanical properties of the new composite, such as water retention and tensile strength, were studied.

A COMPARATIVE RHEOLOGICAL STUDY OF SEVERAL COLLOIDAL SYSTEMS BASED ON CELLULOSE DERIVATIVES

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Aiming at diversifying the range of thickening products used in textile printing, several cellulosic ethers (methylcellulose, methylhydroxypropylcellulose and hydroxyethylcellulose) were tested. IR spectroscopy confirmed the chemical structures and the substitution degree of the commercial products Benecel, Benecel M and Tubicoat HEC. Rheological measurements were performed for systems with different concentrations, at temperatures in the normal working range and shear rates ranging from 1 s-1 to 243 s-1. The rheological models elaborated on the basis of the resulted rheograms, allowed to calculate the viscosity of parameters' experimental domains. The present study leads to the conclusion that the colloidal systems consisting of 2% methylhydroxypropylcellulose and hydroxyethylcellulose have sufficient consistency to form pastes with adequate properties for textile printing.

SODA-ANTHRAQUINONE PULPING OF RESIDUES FROM OIL PALM INDUSTRY

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The main objective of the present work is to evaluate the suitability of soda-AQ process for pulping EFB (empty fruit bunches), viewed as an alternative raw material for pulp and paper production. To this end, a central composite design was used to study the influence of various operational variables – temperature (155-185 ºC), cooking time (30-90 min), soda concentration (10-20%), anthraquinone concentration (0-1%) and liquid/solid ratio (6:8) – during soda-anthraquinone cooking of EFB, on the pulp and paper sheet properties obtained. The equations relating the dependent variables (pulp and paper sheet properties, yield, Kappa number, viscosity, beating degree, tensile index, stretch, burst index, tear index and brightness) to the independent ones (temperature, cooking time, soda concentration, anthraquinone concentration and liquid/solid ratio) were established, with errors below 15%, in all cases. The Kappa number range (10.8-74.3), viscosity (282-849 mL/g) and brightness (44.7-65.6%) of these cellulosic pulp materials are not appropriate for highbrightness printing papers. Instead, the physical properties (28.65 kN/g, 2.84%, 1.98 kPam2/g, 0.54 mNm2/g for tensile index, stretch, burst index and tear index, respectively) recommend the cellulosic pulp obtained from the soda-AQ process for strengthening the virgin fibre in recycled papers and also for developing certain types of packaging.

RELATIONSHIP BETWEEN FIBRE CHARACTERISTICS AND TENSILE STRENGTH OF HARDWOOD AND SOFTWOOD KRAFT PULPS

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Fibre characteristics of kraft softwood and hardwood unbleached and bleached pulps, namely FS number – indicating fibre strength, L number – indicating fibre length and B number – indicating fibre bonding ability, were determined by the PULMAC zero-span tester. A higher tensile index of softwood pulp and unbleached pulps is related to a higher FS and L number and, consequently, to higher strength and length of fibres. On the contrary, hardwood pulps have, at an equal tensile index, a higher B number than softwood pulps. At an equal tensile index, the B number of bleached pulp is higher than that of unbleached pulp.

HIGHLY REACTIVE COTTON LINTERS FROM REFINING OF PREHYDROLYSED AQ-SODA PULP

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Prehydrolysed cotton linters were subjected to soda- and soda-AQ pulping, followed by hot and cold refining. The presence of AQ in different concentrations during soda pulping resulted in a more open and accessible fine structure, especially with 0.1% AQ concentration; compared to hot refining, cold refining was more efficient. Further improvement in cotton linter characteristics was observed when AQ was added through the acid prehydrolysis step, preserving soda pulping, especially with cold alkali refining.

KRAFT PULP OXIDATION AND ITS INFLUENCE ON RECYCLING CHARACTERISTICS OF FIBRES

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The work examines the effects of TEMPO-mediated 2,2,6,6-tetramethyl-1-piperidinyloxy (4-acetmido- TEMPO) oxidation on the characteristics of fibres and the recycling behaviour of oxidized fibres. Oxidation had a significant impact on fibre and paper properties, being dependent on the degree of oxidation. Generally, high-level oxidation had a negative effect on the beating degree of pulp, sheet density, folding endurance of paper and fibre bonding. However, pre-oxidation of once-dried fibres prior to secondary recycling could minimize the adverse influence of hornification.

EFFICIENCY AND EFFLUENT CHARACTERISTICS FROM Mg(OH)2-BASED PEROXIDE BLEACHING OF HIGH-YIELD PULPS AND DEINKED PULP

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The present research project, devoted to peroxide bleaching, evaluated magnesium hydroxide [Mg(OH)2] as a substitute of sodium hydroxide [NaOH] for different mechanical pulps and deinked pulp. The analysis of the results obtained on both TMP and CTMP showed that the use of Mg(OH)2 as a substitute of NaOH in peroxide bleaching allowed a reduction in both magnesium hydroxide and sodium silicate concentration, and a higher concentration of residual peroxide, which could be recirculated in the process. In deinked pulp, a significant reduction in Mg(OH)2 concentration was also achieved. The yield of the bleaching process was improved by 1 to 2%, yet the final brightness level was slightly lower. Other benefits related to the effluent were observed, such as a significant reduction of the cationic demand and a decrease of some environmental parameters, *e.g.* the biochemical oxygen demand (BOD), the chemical oxygen demand (COD), the dissolved solids (DS) and the total organic carbon (TOC).

EFFECTS OF FENTON SYSTEM ON RECYCLED UNBLEACHED PULP IN ABSENCE AND PRESENCE OF *p*-HYDROXYBENZOIC ACID

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The effects of the Fenton reagent on recycled unbleached pulp in the absence and presence of a model chemical contaminant, the *p*-hydroxybenzoic acid (HBA), were studied. In the absence of HBA, the Fenton system clearly modified the chemical and papermaking properties of the pulp. The kappa number was reduced and the specific light absorption coefficient was increased, indicating lignin modification. The amount of total acid groups increased, suggesting lignin or carbohydrate oxidation. Pulp freeness and wet tensile strength were significantly improved, while short compressive strength was slightly increased. Nevertheless, dry tensile strength decreased. In the presence of HBA, the chemical and papermaking properties of the pulp were less modified. When a higher ferrous ion charge was applied, half of the HBA present in pulp was eliminated while, at a lower ferrous ion charge, a lower reduction in HBA was produced,
pulp strength being nevertheless preserved.

APPLICATION OF COMPUTER IMAGE ANALYSIS FOR CHARACTERIZATION OF VARIOUS PAPERMAKING PULPS

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Laboratory-prepared bleached kraft pulps, made from wood of different tree species, and industrial neutral sulphite semichemical (NSSC), chemithermomechanical (CTMP) and groundwood pulps were studied by the computer image analysis method. The number of fibres in a mass unit of pulp, the relative content of fines and also the morphological fibre properties were determined. The obtained results were discussed and compared.

HYDROLYSIS OF *TILIA JAPONICA* WOOD FOR PRODUCTION OF A FERMENTABLE SUBSTRATE

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To prepare a substrate for microbial conversion of xylose into xylitol, *Tilia japonica* wood was hydrolyzed with dilute sulfuric acid. When the reaction temperature was fixed at 121 °C, an optimum yield of xylose was obtained by treatment with 3% sulfuric acid, for 60 min. Both an increase in the sulfuric acid concentration and a prolonged residence time resulted in a decrease in the xylose yield. A fermentable substrate with a relatively high xylose concentration (57.0 g L-1) was obtained by hydrolysis with 3% sulfuric acid, at a liquid-to-solid ratio of 3 g g-1. During hydrolysis at elevated temperatures, certain undesired by-products were also generated, such as degradation products of solubilized sugars and lignin, which are potential inhibitors of microbial metabolism. These compounds were, however, successfully removed from the hydrolyzate by treatment with activated char.

SUPERIORITY OF LITHIUM BROMIDE OVER LITHIUM CHLORIDE USED AS FLAME-RETARDANTS ON COTTON SUBSTRATES

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The effect of lithium bromide as compared to lithium chloride, as non-durable finishes, on the flammability of 100% cotton fabric (woven construction, weighing 151 g/m2) has been investigated in the present article. The laundered, bone-dried, weighed specimens were impregnated with suitable concentrations of aqueous lithium bromide and/or lithium chloride solutions by means of squeeze rolls and then dried at 110 °C for 30 min. Afterwards they were cooled in a desiccator, re-weighed with an analytical balance and kept under ordinary conditions before carrying out the vertical flame test. The optimum add-on values conferring flame retardancy, expressed in g anhydrous lithium bromide and lithium chloride per 100 g fabrics, were found to be about 3.85% and 7.5%, respectively. The thermogravimetric analysis (TGA) of pure cotton and of the fabrics supported by salts at optimum additions was performed and the thermograms were then compared and commented. The results obtained proved the superiority of lithium bromide in imparting flame retardancy as compared to lithium chloride. Overall, the additions comply with *Free radical theory* in explaining flame-retardancy. The results may provide some beneficial data and assessments to be put into practice for commercial purposes, such as in the dope of insulators, plastics and polymers.

OPTIMIZATION OF HEMP YARN GRAFTING DEGREE FOR MEDICAL TEXTILES DURING SIMULTANEOUS WET SPINNINGGRAFTING

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The present paper studies the way the reactive derivative monochlorotriazinyl-β-cyclodextrin can be grafted on bast fibres simultaneously with their wet spinning. Process modelling involved simultaneous mechanical and chemical processing, at different parameters of wet spinning-grafting (concentration of monochlorotriazinyl-β-cyclodextrin and speed of the material in the impregnation stage). The mathematical methods of dispersion analysis and regression were applied to obtain optimum values of the process parameters. To attain physico-mechanical characteristics adequate for a 100% hemp yarn and an optimum grafting degree for subsequent inclusion operations, a soaking time of 23.7 sec and a solution concentration of 55 g/L monochlorotriazinyl-β-cyclodextrin are required for simultaneous wet spinning-grafting.

LIGNIN RECOVERY FROM SPENT LIQUORS FROM ETHANOLWATER FRACTIONATION OF SUGAR CANE BAGASSE

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The aim of the present work was to find the most adequate method of lignin recovery from two spent liquors from ethanol-water fractionations catalyzed with sulfuric acid. Different methodologies to separate lignin from liquors were assessed, based on the dilution and/or evaporation of the solvent. The carbohydrates, organic acids, ethanol and degradation products content of the spent liquors were analyzed by liquid chromatography. The yield of lignin recovery was quantified. The laboratory system, represented at an industrial scale by the reduction of ethanol concentration in the spent liquors through evaporation in a flash tank to 30% v/v, dilution 1:1 at 40 ºC and centrifugation, appeared as the best alternative for lignin recovery (45% of precipitate with a purity of 94%, yielding 42% pure lignin). The second feasible procedure involved lignin precipitation and recovery from the spent liquors by dilution with water, at room temperature. This method yielded 41% pure lignin, from a precipitate of 48% with 87% purity (much more contaminated, mainly with carbohydrates).

A METHOD FOR MEASURING PULPING LIQUOR PENETRATION INTO WOOD STRUCTURE

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The paper describes the development and operation of an instrument that can measure the flow rate of penetrants through the capillary structure of wood. The instrument was tested with aspen wood (sapwood and heartwood) and several surfactants, either individually or in blends. The results of the penetration measurements, precise and repeatable, showed that only the slower penetration of aspen heartwood could be improved with selected blends of surfactants, as surfactants could not improve the already fast penetration of the black spruce wood and aspen sapwood. Experiments in a pulping pilot-plant strongly supported the results obtained by the penetration instrument.

CHEMICAL AND THERMOGRAVIMETRIC ANALYSIS AND SODA AND ORGANOSOLV PULPING OF *HESPERALOE FUNIFERA*

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The *Hesperaloe funifera* plant was characterized in terms of its major components (cellulose, hemicellulose, lignin and extractives), hot water solubles, 1% NaOH solubles and ash, by using conventional chemical methods and thermogravimetric analysis. The contents in lignin, α-cellulose, holocellulose, hemicellulose, ethanol–benzene extractives, hot water solubles, 1% NaOH solubles and ash of *Hesperaloe funifera* were of 7.3, 40.9, 76.5, 35.6, 4.0, 13.5, 29.5 and 5.9%, respectively. By its chemical composition, *Hesperaloe funifera* provides an effective source of cellulose for producing pulp and paper, with some advantages over other non-wood raw materials including kenaf, bagasse, cotton stalks, wheat straw, paulownia and sunflower stalks. The application of soda and organosolv (ethyleneglycol, diethyleneglycol, ethanolamine and diethanolamine) processes to *Hesperaloe funifera* determined a very good performance of the pulp samples, especially of those obtained by 10% soda and 1% anthraquinone at 155 ° C, for 30 min. In fact, the resulting soda–anthraquinone pulp exhibits good yield (48.3%), Kappa number (15.2), viscosity (737 mL/g) and beating degree (65.1 ºSR), the paper sheets obtained from it evidencing good tensile index (83.6 Nm/g), stretch (3.8%), burst index (7.34 KN/g) and tear index (3.20 mNm2/g) values.

ANALYTICAL PYROLYSIS CHARACTERISTICS OF ENZYMATIC/MILD ACIDOLYSIS LIGNIN FROM SUGARCANE BAGASSE

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The pyrolysis characteristics of enzymatic/mild acidolysis lignin (EMAL) isolated from sugarcane bagasse were investigated by thermogravimetry Fourier transform infrared spectroscopy (TG-FTIR) and pyrolysis gas chromatography mass spectrometry (Py-GC/MS). During thermal analysis, the decomposition of EMAL was found to occur over a wide temperature range, from approximately 150 to 800 °C, while the generated solid residue was of 29% at 900 °C. Two weight loss peaks were recorded at 294 and 385 °C, respectively. The release of gaseous products and of some organic compounds from EMAL pyrolysis, detected on-line using FTIR, occurred mainly between 200 and 500 °C, corresponding quite well with the degradation curves measured by TG. The evolution of CO2 and organic compounds containing functional groups of C=O and C–O–C marked release peaks mainly at about 300 °C, while the formation of methane, methanol and phenols usually reached the maximum peak at about 400 °C. The phenols can be further divided into G, S and H type derivatives with various substituents, as based on Py-GC/MS results. The basic understanding and insights into lignin pyrolysis and product characteristics will help design the production processes of biofuels.

ELECTROSPUN NANOFIBER PROCESS CONTROL

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Fiber diameter is an important structural characteristic for electrospinning, due to its direct influence on the properties of the produced webs. In this paper, an image analysis-based method, called *direct tracking*, for measuring the electrospun fiber diameter, has been developed. The results obtained by direct tracking significantly excelled distance transformation, indicating that the method could be used for measuring electrospun fiber diameter.

THERMAL DEGRADATION OF LIGNIN – A REVIEW

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The review describes recent knowledge acquired in the thermal degradation of lignin as an approach to obtaining valuable chemicals or hydrocarbon fuel. Information on the temperature range, kinetics and mechanism of thermal degradation, as well as on the type of degradation products and on the methods proposed to obtain valuable chemicals is presented.

CELLULOSE/CHONDROITIN SULFATE HYDROGELS: SYNTHESIS, DRUG LOADING/RELEASE PROPERTIES AND BIOCOMPATIBILITY

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The present study investigates some hydrogels, based on natural, biodegradable and biocompatible polysaccharides, such as cellulose (C) and chondroitin sulfate (CS), as sustained release carriers, and evaluates their biocompatibility. Investigations were performed on cellulose/chondroitin sulfate (C/CS) hydrogels, in different mixing ratios. Swelling and drug delivery studies were conducted in a phosphate buffer solution (pH = 7.4) that simulates the pH of the intestinal fluid, at 37 °C. Natural-based hydrogels were evaluated for the release of paracetamol and theophylline. The release profiles of the drugs from C/CS hydrogels depend on the CS content: for paracetamol, a decrease of the percent released and, for theophylline, a percentual increase with the increase of the CS content. The results showed good biocompatibility with the tested formulations.

IN-SITU CELLULOSE FIBRES LOADING WITH CALCIUM CARBONATE PRECIPITATED BY DIFFERENT METHODS

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In-situ loading of cellulose fibres is meant at maximizing filler retention, which is one of the most difficult problems in the production of printing papers with high filler content. Three methods for *in-situ* precipitation of calcium carbonate [CaCO3] into the lumen and in the wall of the cellulose fibres were investigated ISPCC): a) calcium hydroxide [Ca(OH)2] formation by the reaction of calcium chloride [CaCl2] and sodium hydroxide [NaOH] in a fibre suspension, followed by CaCO3 precipitation with carbon dioxide [CO2] – carbonation; b) CaCO3 precipitation by a double-exchange reaction between CaCl2 and sodium carbonate [Na2CO3] in a fibre suspension; c) CaCO3 precipitation through cellulose fibre saturation with a Ca(OH)2 solution, followed by a carbonation reaction. The effectiveness of the *in-situ* precipitation methods was evaluated on pulp filter pads and paper handsheets, obtained on a standard lab former, by various analyses and investigations: calcium carbonate content, X-ray diffraction, SEM images, optical and mechanical properties of the paper sheets. The analyses proved that, whichever *in-situ* precipitation method was used, calcium carbonate precipitated both into the lumen and wall pores of fibres, particulates presenting a typical calcite diffraction pattern. However, significant differences were noticed among the *in-situ* precipitation methods concerning the yield of calcium carbonate precipitated into the fibre structure and particle sizes, and their distribution in the fibre wall and lumen, which influence the optical and mechanical properties of paper.

EFFECT OF VELOCITY GRADIENT ON PAPERMAKING PROPERTIES

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The influence of velocity gradient on the anisotropy of tensile stiffness index, tensile energy absorbance, tensile index, tear strength, tensile stiffness orientation, formation and curl of MG paper, as well as on the anisotropy of coating raw paper, was investigated. The maximum strength of MG paper was achieved in the 0.93-1.05 range of the jet-to-wire speed ratio. The best formation and the lowest curl with fibre orientation ±1.7° was achieved at a jet-to-wire speed ratio around 1.0, while CMT and SCT of fluting from a mixture of semi-chemical pulp and recovered fibres produced at a constant speed difference of the jet and wire are influenced by basis weight and semi-chemical pulp content.

EVALUATION OF COATED PAPER QUALITY USING A PLACKETT-BURMAN STATISTICAL DESIGN

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Paper is pigment-coated to produce a more uniform and more receptive surface for printing ink, thus assuring better graphic reproduction. A large number of variables, involved in coating processes, interact with each other. To perform coating experiments on indigenous base papers in a most systematic way, with many variables, statistically designed experiments – based on a Plackett-Burman design – have been carried out to examine the effects of different process variables. The variables considered were the following: dosages of china clay, talc, natural and precipitated calcium carbonate, binder, as well as total solids of coating color and thickener dosage (water retention chemicals). Based on such experiments, the effects of the above process variables on different properties of coated paper were identified.

FACTORS INFLUENCING A HIGHER USE OF RECOVERED PAPER IN THE EUROPEAN PAPER INDUSTRY

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Europe is one of the global leaders in paper recycling. Recovered paper is an indispensable raw material (around 50% of the fibrous raw material is recovered paper), which contributes to the sustainability of the sector. However, certain factors do have a limiting influence on the possibility of an extended use of recovered paper, such as the quality of the recovered paper, the poor sorting activities, the price for recovered paper, the acceptance/demand of recovered paper-containing products by the consumers, the recyclability of the paper products, etc. Against this background, the COST Action E48 – "The limits of paper recycling" – has analyzed the issues that predominantly influence the competitiveness of the paper and board recycling industry, and detected potentials for an extended use of recovered paper in the European paper industry. The analysis has been carried out on the basis of a detailed and comprehensive questionnaire aiming at collecting experiences and opinions on the situation of the different European countries, related to paper recycling.

ENVIRONMENTAL AWARENESS AND PAPER RECYCLING

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The collection and utilization of recovered paper has increased over the past decades all over the world and this trend will continue. However, paper recycling is limited by the availability of resources, as well as by their recovery and quality. The paper describes how environmental awareness plays an important role in overcoming these limits. Firstly, the works carried out within the framework of COST Action E48 – "The limits of paper recycling" – are presented. These works have analysed the most important driving forces for extending the collection of recovered paper in Europe and established that environmental awareness is a key factor. Secondly, different initiatives for the development of environmental awareness and promotion of paper recycling – mainly based on information and educational campaigns, with special emphasis on child education – are presented.

QUALITY REQUIREMENTS IN GRAPHIC PAPER RECYCLING

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Paper recycling has a long history. The use of recovered paper in white grades received a boost since the 1970s, with the introduction and spreading of flotation deinking. The paper analyzes two main aspects related to the quality of recovered paper for deinking: one is related to the characteristics of delivery, in terms of contamination, moisture and composition, and the other to the recyclability of the paper products in delivery. The first aspect is in close connection with the collection system, handling and storage of the recovered paper. It is essential for the paper industry that paper and board should be collected separately from other recyclables. The deinking process is designed to remove inks, but not to whiten unbleached fibres. Therefore, the deinking industry favours a separate collection of graphic papers from households, for reducing the contamination with non-deinkable paper and board. The content of brown packaging papers and boards is therefore one of the most important parameters in the entry inspection of recovered paper deliveries. INGEDE, the International Association of the Deinking Industry, has developed methods for entry inspection and runs a database for its members. Deinkability mainly depends on the characteristics of the inks and, therefore, on the printing process. Flotation deinking, the dominant process, developed to remove letterpress and rotogravure inks, works well on mineral-based offset inks and dry toners. Flexographic and inkjet ink particles are too hydrophilic and too small for an efficient flotation. Cured systems and some toners, particularly liquid toners, form agglomerates, which are too big to float. The acknowledged assessment scheme for deinkability, the removal ability of inks, uses INGEDE Method 11 for testing. The results are converted into "deinkability scores". The second product-related quality aspect is the ability to remove adhesive applications. This depends not only on the chemical characteristics of the adhesive, but also on its type of application. INGEDE's database on the recyclability behaviour of

adhesive applications is considerably smaller than the one on deinkability. The tests focused on glued spines and labels. Glued spines often show sufficient recyclability, if they are made with hot-melt adhesives. Of them, polyurethane glues are generally the best option. Labels are much more critical; one of the reasons is the low film thickness. Not enough is known yet on the way feasible chemical nature can compensate for this disadvantage. In order to find out more about how adhesive applications can improve their recyclability, INGEDE with some co-sponsors launched a survey on the recycling behaviour of about 200 printed products containing adhesive applications.

POTENTIAL BENEFITS OF RECOVERED PAPER SORTING BY ADVANCED TECHNOLOGY

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Quality is the major prerequisite for extending the use of recovered paper (RP) as a raw material for paper and board manufacturing. Several studies related to furnish quality focus on recovered paper from household collection, which is the main source with potential for further increasing the recycling rates. The first part of the paper analyses the role of household collection for future development of paper recycling and trends of RP quality in Europe. Many studies have demonstrated that an extended household collection is always detrimental to RP quality. Without the adequate actions of all actors from the recycling chain, quality decrease could jeopardize the sustainability of paper recycling. In this context, many researches on the improvement of recovered paper quality are being carried out in Europe. A representative example for this research field is FP7 project – SORT IT (Recovered Paper **SORT**ing with **I**nnovative **T**echnologies), whose objectives of RP quality improvement and expected benefits are analysed briefly in the second part of this paper.

MORPHOLOGICAL CHARACTERIZATION OF PULPS TO CONTROL PAPER PROPERTIES

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Recovered paper quality is a key issue for papermakers that intend to maintain the quality of their final products at a high and constant level, for meeting the consumer demands. However, since paper recovery is increasing, the quality of recovered paper is decreasing and, what is even worse, it varies along the time. The physical properties of recycled pulp fibres have a strong influence on most of the paper properties and, therefore, they play an important role in the establishment of the optimal papermaking conditions. These properties are directly related to the morphology of fibres and to pulp composition. In recent years, several new fibre and pulp morphological analyzers have been developed and released on the market. The use of online optical fibre analyzers allows papermakers to know the variations in pulp quality, enabling them to adjust the process and to maintain constant the quality of the paper produced. However, most of these devices are optimized for virgin fibres, their application for recovered paper being still limited. The present

paper describes the modifications carried out in the programs of a fibre and pulp morphological analyzer (Morfi V7.9.13.E) to optimize its performance for the characterization of recycled pulps. The three programs (VESSELS, FIBRES and SHIVES) that the device includes by default have been considered and validated in a paper mill, producing different grades of newsprint and light-weight coated papers. The results show that, with the modified program, the device appears as a very promising tool to control and improve the final quality of recycled paper.

DEINKING FLOTATION OF RECYCLED LINERBOARD FOR FOOD PACKAGING APPLICATIONS

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Brown packaging linerboard, made entirely from recovered pulp, was subjected to deinking flotation for evaluating the possible improvements in its chemical, optical and mechanical properties. The increase in the rate of recovered paper utilisation, along with the tendency towards lower basis weights, in the packaging paper production, has created a growing need for the utilisation of secondary fibers of improved quality. To attain better quality fibers, flotation deinking of brown grades is being considered, along with the addition of primary fibers to recovered paper furnish. Numerous conducted studies, in which the flotation technology was used in the treatment of brown grades, support this idea. Most of them show that the quality of fibers is improved after flotation deinking, resulting in higher mechanical properties of the deinked handsheets and in lower amounts of chemical contaminants. As to food and human health safety, packaging paper has to meet specific requirements, to be classified as suitable for its direct contact with foods. Recycled paper and board may contain many potential contaminants, which, especially in the case of direct food contact, may migrate from packaging materials into foodstuffs. In this work, the linerboard sample selected for deinking was made from recycled fibers not submitted previously to chemical deinking flotation. Therefore, the original sample contained many noncellulosic components, as well as the residues of printing inks. The studied linerboard sample was a type of packaging paper used for contact with food products that are usually peeled before use, *e.g.* fruits and vegetables. The decrease in the amount of chemical contaminants, after conducting deinking flotation, was evaluated, along with the changes in the mechanical and optical properties of the deinked handsheets. Food contact analysis was done on both the original paper samples and the filter pads and handsheets made before and after deinking flotation. Food contact analysis consisted of migration tests of brightening agents, colorants, PCPs, formaldehydes and metals. Microbiological tests were also performed to determine the possible transfer of antimicrobial constituents.

IMPROVING THE COST-EFFECTIVENESS OF WHITE TOP LINERBOARD BASED ON RECYCLED PULP

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The objective of this research project was to minimise the costs of producing white top linerboard. On the one hand, this was achieved by tapping cost-effective recovered paper grades so far rarely or never used as fibrous raw materials for white top testliner. On the other hand, production costs have been reduced, while the fibrous raw materials remained at a constant level, by implementing a concept for controlling the grammages of the individual plies. In a first stage, several recovered paper grades were extensively treated at a laboratory and pilot scale, the treatment being specific for each and every recovered paper quality. The obtained results were used to calculate the requirements for the individual layers and for the entire testliner sheet, by using a simulation tool developed by PTS. This means that simulation allows testing of the different recovered paper grades and determining of their possible utilization as a fibrous raw material in the production of white top linerboard. This tool also permits to create combinations for pulp blends for the top liner and undertop ply in the testliner, which comply with the required quality parameters on the optical and strength properties.

EFFECTS OF PULPING TEMPERATURE AND ACCELERATED AGEING ON OPTICAL PROPERTIES OF DIGITAL DUPLICATOR PRINT HANDSHEETS

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Deinking efficiency and optical stability of digital duplicator print handsheets have been examined. During chemical deinking through washing, fatty alcohol ethoxylate C 13-15 with 7 EO groups has been used as a surfactant. The pulping temperatures were changed, while the other washing process conditions, including surfactant concentration, pulping and homogenization time, were carefully chosen and kept constant. Deinking efficiency was monitored through the optical properties of the laboratory handsheets in the visible part of the electromagnetic radiation. The best optical performance of a handsheet was achieved at the lowest disintegration temperature. The optical stability of the handsheets obtained at different disintegration temperatures was tested by accelerated ageing. The changes in the values of relative reflectance and scattering and absorption coefficients, due to the interaction of UV and visible electromagnetic radiation with the samples, were monitored. The results obtained point out that optimal deinking efficiency and optical stability are achieved under energy-saving (low disintegration temperature, which is unusual for common deinking) and environmentally friendly (only surfactant – without other deinking chemicals – has been used) process conditions.

INFLUENCE OF LAYER COMPOSITION ON PROPERTIES OF RECYCLED BOARDS

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In the present study, three types of recycled boards with different top layer composition have been analysed. The quality of coated boards with different fibrous composition has been evaluated by determining their structural, mechanical, optical and surface properties. The slight increase in virgin fibre content in the top layer, from 10 to 20%, has been found to improve the surface, the optical and mechanical properties of coated recycled boards. A greater influence on the mechanical properties is exerted by the addition of a higher percentage of chemical pulp in the top layer of the three-layered structure of recycled boards, rather than by the addition of a forth layer from recovered paper and board. Additionally, the investigation aimed at determining the viscoelastic properties of the boards and assessing the influence of a 90% relative humidity on their tensile properties. Besides lowering tensile strength, humidity has even a more significant influence on the viscoelastic properties. Of the coated recycled boards under study, the influence of humidity has been found as less pronounced in the boards containing higher amounts of chemical pulp in the top layer.

INFLUENCE OF RECOVERED PAPER QUALITY ON RECYCLED PULP PROPERTIES

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Statistical data show that a further increase of recovered paper (RP) supply to European paper mills could come mainly from increasing and improving household collection. However, it is generally accepted that an extended collection from households is always detrimental to RP quality. The low quality of recovered paper is determined by the high content of unusable materials consisting of non-paper components and unwanted paper and board (paper and board that does not conform to RP grade definition). In this study, the effects of unwanted paper and board (p&b) on recycled pulp properties are analysed for RP grades 1.11 and 1.04, originated from household collection. In the case of deinking RP grade 1.11, it was shown that even a low content (3-5%) of brown packaging p&b strongly affects the optical properties of deinked pulp, by decreasing brightness and by increasing the number and size of specks, due to brown fibre flakes. In the case
of packaging RP grade 1.04, the increasing content of graphic paper results in lower freeness, higher ash and
short fibre contents and lower mechanical strength of recycled pulp.

ENERGY MANAGEMENT GUIDELINES IN PULP AND PAPER PRODUCTION

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Forest products industry is one of the major industrial consumers of energy. Worldwide, the final energy use in the pulp and paper industry amounted to 6 ExaJoules in 2003 (*i.e.* 6% of the total industrial energy use). In Europe, the total primary energy consumption attained the level of 1.3 ExaJoules in 2003. The pulp and paper industry, including recycling processes, also produces energy, as well as by-products that can be used for energy generation. It already generates enough to cover approximately 50% of its own energy needs. A significant share of this energy is renewable CO2 neutral biomass. Energy costs, energy supply and climate change are other important issues impacting the future of the forest based industry. They will have impacts on the manufacturing costs, as well as on the allocation of investments around the globe. It seems, however, that at an industrial level crucial knowledge on the state-of-the-art is still missing. The chain of the energetic sector very often lacks a correct management strategy and, therefore, it is not optimally efficient. Climate change mitigation policy will add extra force to all these developments and the companies (not only from the papermaking sector) will move forward towards the application of modern, conscious management strategies.

TAPPI JOURNAL 2010 ABSTRACTS

BIORAFINĂRIE

Preextracţia în mediu neutru a hemicelulozei şi obţinerea ulterioară a celulozei sulfat din foioase sudice în amestec

Sung-Hoon Yoon, Mehment Sefik Tunc, Adriaan van Heinigen

În acest studiu, tocătura din foioase sudice în amestec a fost extrasă cu soluţii alcaline la diferite adaosuri de chimicale, durate diferite (45-110 min.) şi temperaturi diferite (125ºC- 160 ºC). La adaosuri ridicate de alcalii (10% şi 20% hidroxid de sodiu NaOH) sub formă de oxid de sodiu (Na_2O), extractul a avut un puternic caracter alcalin (pH de circa 13) şi 17%-40% din lemn s-a dizolvat. Fierberea sulfat ulterioară a tocăturii supuse procesului de extracţie a avut un randament de 5%-7% mai puţină celuloză decât acela al celulozelor sulfat de referinţă. Totuşi, la un adaos mai mic de alcalii dar suficient pentru neutralizarea aproximativă a acizilor rezultaţi în timpul procesului de pre-extracţie, randamentul în celuloză (faţă de lemnul iniţial) după procesul sulfat ulterior, nu a fost afectat. În acest caz, circa 5%-10% din substanţa lemnoasă se elimină în timpul procesului de pre-extracţie cu 3% NaOH sau 3% leşie verde (+ 0,05% antrachinonă) la 140ºC şi 160ºC pentru 60, 90 şi 110 min. Extractul de leşie verde obţinut după 110 min. La 160ºC conţinutul de zaharuri a fost de 2,1% (gramaj a.u.), 2,1% acid acetic şi 1,6% lignină care reprezintă 64% din reducerea greutăţii lemnului.

Fierberea sulfat a tocăturii din lemn supusă procesului de pre-extracţie s-a realizat la un adaos real de alcalii de 12% şi a indicat viteze de delignificare mult îmbunătăţite cu aproximativ acelaşi randament sau unul puţin mai mare decât celuloza sulfat de referinţă la un adaos real de alcalii de 15%. Celulozele sulfat supuse procesului de pre-extracţie alcalină cu leşie verde + antrachinonă au indicat un grad de măcinare mai mic dar o rezistenţă mai ridicată la rupere şi rezistenţă la tracţiune similară comparativ cu celulozele sulfat de referinţă. Rezultatele acestui studiu ar putea ajuta planificatorii din cadrul industriei în eforturile acestora de integrare a conceptului de biorafinare a procesului de pre-extracţie a hemicelulozei în producţia de celuloză existentă.

CHIMISMUL PROCESULUI

Identificarea compuşilor de colmatare a filtrului, insolubili în acizi şi procedurile optime de spălare cu acid pentru filtrele tubulare de presiune cu impuls de întoarcere

Kevin Taylor, Rich Adderly, Gavin Baxter

În timp, performanţa filtrelor tubulare de presiune cu impuls de întoarcere din fabricile de celuloză sulfat a scăzut chiar şi în cazul spălării regulate cu acid. Înlocuirea neprogramată a filtrului din cauza rezultatelor colmatării filtrului care implică costuri semnificative poate avea ca rezultat oprirea fabricii. Cercetătorii au identificat materialele de colmatare a filtrului, insolubile în acizi, prin scanarea cu microscop electronic/ spectroscopie cu raze X şi dispersie a energiei (SEM/EDS) şi analiza prin difracţie cu raze X, atât la filtrele din polipropilenă cât şi la filtrele cu membrană Gore-Tex™. Componentele majore de colmatare ale filtrului au fost sulfatul de calciu (gips), fosfatul de calciu (hidroxilapatita) caoline de aluminosilicat, sulfuri metalice şi carbon. Cercetătorii au efectuat analiza de prelevare detaliată atât pentru procedura standard de spălare cu acid cât şi pentru o procedură modificată. Se pare că procesul de colmatare a filtrului cu gips şi sulfuri metalice are loc ca urmare a procesului de spălare cu acid. Formarea gipsului pe filtru a rezultat din hidroliza semnificativă a soluţiei de acid sulfamic la temperaturi mai mari de 130ºF. Modificarea procedurii de spălare cu acid a redus în mare măsură cantitatea de gips şi adaosul de agent tensioactiv la o durată de spălare mai mică şi a antrenat o parte a carbonului din filtru. Cu agentul tensioactiv, spălarea cu acid a fost completă în proporţie de 95% după 40 min.

Prin modificarea procedurilor de spălare cu acid, inginerii tehnologi pot reduce costurile funcţionării filtrului sub presiune prin creşterea duratei dintre spălările cu acid şi reducerea înlocuirii neprogramate a filtrului datorită colmatării.

REGENERAREA CHIMICĂ

Influența clorului şi a potasiului asupra funcționării şi proiectării echipamentelor de regenerare chimică

Marcelo Hamaguchi, Esa K. Vakkilainen

Principalul obiectiv al acestui studiu este evaluarea efectului clorului (Cl) şi al potasiului (K) asupra funcționării şi proiectării echipamentelor din circuitul de regenerare chimică. Datorită reglementarilor de mediu mai severe, închiderile circuitelor la nivelul fabricii tind să crească ducând la acumularea elementelor nedorite cum ar fi Cl şi K în circuitul leşiei sulfat. Conținutul total de solide anorganice din leşiile de la fierbere creşte în prezența Cl şi a K ceea ce afectează funcționarea echipamentelor de regenerare chimică. Obiectivul acestui studiu este acela de a indica mărimea acestor impacturi şi de a estima diferențele de cost operaționale prin folosirea unor conținuturi diferite de Cl şi K în leşii. Bilanțul de materiale şi energetic al fabricii de celuloză sunt folosite în acest caz iar o fabrică de celuloză braziliană a servit ca model de caz. Rezultatele studiului au arătat că pentru un domeniu specific, conținutul de solide din leşia neagră poate fi cu 6,6% mai ridicat prin creşterea procentului masic de Cl şi K din leşia neagră. Această diferență reduce cu 6,2% valoarea mai mare a entalpiei leşiei negre şi creşte cantitatea de substanță uscată destinată arderii în cazanul de regenerare, de asemenea cu 6,6%. Încărcarea la evaporare creşte cu consumul de abur. Acesta scade producția de energie totală cu până la 1,6 MW datorită fluxului redus la treapta de condensație a turbinei cu abur. De asemenea bilanțurile demonstrează faptul că o parte din costurile de pompare pot fi cu 12% mai mari când funcționarea se desfăşoară de la o concentrație mică la una ridicată de Cl şi K în leşia neagră. Rezultatele acestui studiu indică importanța eliminării elementelor necondensabile (NPEs) cum ar fi Cl şi K, din circuitul leşiei. Nu numai costurile coroziunii cresc în acelaşi timp cu nivelurile crescute ale Cl şi K dar costurile de exploatare ale fabricii de celuloză sunt semnificativ mai mari. Folosind această cercetare, fabricile de celuloză pot estima mai bine magnitudinea impacturilor provenite la Cl şi K asupra proceselor de regenerare şi determină cele mai bune niveluri ale acestor elemente necondensabile din activitățile lor.

ALBIRE

Albirea eficientă în raport cu costurile a pastei termomecanice obținută din pin

Thomas Q. Hu, Carmen Margetts, Krista Morrow, Michelle Zhao, Surjit Johal, Bernard Yuen

Cercetătorii au pus la punct o metodă de albire eficientă în raport cu costurile pentru depăşirea plafonării gradului de alb al pastei termo-mecanice (TMP) obținută din tocătura fabricii care conține îndeosebi pin. Metoda implică albirea sinergetică a pastei termocanice în rafinor cu hidrosulfit (Y) şi acid dietilentriaminpentaacetic (DTPA) ca agent de chelatizare. Agentul care asigură sinergia, în rafinorul Y, la care se adaugă albirea în prezența agentului de chelatizare, când este urmată de treapta din post-rafinorul Y sau albirea cu peroxid pot avea ca rezultat o creştere a gradului de alb sau un cost mai mic al agentului de albire pentru Y sau în cazul pastei termo-mecanice albite cu peroxid. Pasta termo-mecanică se obține din tocătura fabricii. Economiile estimate ale costurilor pentru albirea Y la un grad de alb de 60%, şi albirea cu peroxid la un grad de alb de 74,3% sunt de 5,2 U.S.$/ tona de celuloză şi respectiv 5,2-6,2 US$/ tona de celuloză. Fabricile de pastă termo-mecanică care folosesc pin şi tocătură din pin pot albi celuloze astfel încâ obținerea gradului de alb să se realizeze la costuri mai mici, cu ajutorul unui adaos de hidrosulfit de sodiu şi a agentului de chelatizare, DTPA la rafinor şi prin reducerea dozelor de chimicale adăugate în turnurile de albire sau în rezervoarele de stocare post-rafinor.

FIBRA RECICLATĂ

Utilizarea materialului hibrid silice anorganică/alcool polivinilic sol-gel pentru îmbunătățirea rezistenței la suprafață a plăcilor din fibră reciclată

Yi-ding Shen, Yan-na Zhao, Xiao-rui Li

Cercetătorii au creat cu succes un material hibrid care cuprinde alcool polivinilic organic (PVA) şi silice anorganică, cu ajutorul unei reacții sol-gel cu tetraetilorosilicat (TEOS). Materialul hibrid a fost caracterizat cu ajutorul FT-IR. Rezultatele chimice au indicat că au existat legături chimice între SiO_2 şi PVA (alcool polivinilic organic). Testarea foilor de laborator a indicat faptul că rezistența la pliere, rezistența la tracțiune, rezistența la sfâşiere şi viteza de smulgere au crescut cu 22,3%, 35%, 26% şi respectiv 26% când s-a folosit materialul hibrid la gramaj al acoperirii de 61 g/m^2. Mai mult, evoluția rezistenței hibridului arată că aceasta creşte prin utilizarea unui amidon oxidat la un raport de adaos de 3:1. Fabricile pot beneficia de rezultatele acestei cercetări încercând să combine avantajele materialelor organice şi anorganice pentru obținerea unui compozit cu proprietăți superioare care îndeplineşte standardele industriale şi pentru care, actualmente, cererea este mare.