

# CELULOZĂ ȘI HÂRTIE

## VOL.60

## No. 3/2011

### MANAGEMENT BOARD

G. Balogh, M. Botez, Eng. D. Buteică (Chairman), C-tin Chiriac (Vicechairman), G. Crăciun, R. Crăciun, T. Câmpean, B. Dobbelaere, S.T. Eryurek, C. Ferrero, G. Gore, C. Indreica, A. Itu, P.H. Kohler, A.Oncioiu, F. Smaranda, G. Stanciu, D. Tărășenie, A. Vais

### CUPRINS

### CONTENTS

<i>Prof.dr.ing. Constantin Stanciu la a 65 a aniversare</i>	3	<i>Prof.dr.ing. Constantin Stanciu celebrates 65 years</i>	3
DAN BELOSINSCHI, BRUNO CHABOT, FRANCOIS BROUILLETE		DAN BELOSINSCHI, BRUNO CHABOT, FRANCOIS BROUILLETE	
<i>Hârtie antiaderentă: esterii fosfat pot fi o alternativă la compușii siliconici ?</i>	5	<i>Release paper: can phosphate esters be an alternative to silicone ?</i>	5
MARIANA IONESCU, GABRIEL MUSTĂȚEA, VALENTIN IONESCU, GIUSEPPE SPADARO, DANIELA MANEA, CĂTĂLINA TALAȘMAN, ARGENTINA RADU, MARICICA BURLACU		MARIANA IONESCU, GABRIEL MUSTĂȚEA, VALENTIN IONESCU, GIUSEPPE SPADARO, DANIELA MANEA, CĂTĂLINA TALAȘMAN, ARGENTINA RADU, MARICICA BURLACU	
<i>Aspecte privind conformitatea hârtiilor cu proprietăți de barieră îmbunătățite cu reglementările privind siguranța alimentară și protecția mediului</i>	14	<i>Aspects regarding compliance of improved barrier papers with food safety and environment requirements</i>	14
PETRONELA NECHITA, MARICICA BURLACU, NICOLETA MELNICIUC		PETRONELA NECHITA, MARICICA BURLACU, NICOLETA MELNICIUC	
<i>Studii privind influența factorilor endogeni asupra îmbătrânirii hârtiei</i>	20	<i>Studies regarding the influence of some endogenous factors on paper ageing</i>	20
MIHAELA BEGEA, SEVASTIȚA VRACIU, CORINA BERKESY		MIHAELA BEGEA, SEVASTIȚA VRACIU, CORINA BERKESY	
<i>Oportunități pentru dezvoltarea durabilă a sectorului de biomasă din lemn</i>	28	<i>Opportunities for a sustainable development of the wood biomass sector</i>	28
IULIAN ANDREI GÎLCĂ, ADRIAN CĂTĂLIN PUIȚEL, VALENTIN I.POPA		IULIAN ANDREI GÎLCĂ, ADRIAN CĂTĂLIN PUIȚEL, VALENTIN I.POPA	
<i>Posibilități de aplicare a biorafinării în cazul unor produse secundare rezultate din prelucrarea fibrelor liberiene</i>	33	<i>Possibilities of biorefining of some secondary products resulted from bast fibers processing</i>	33
ADINA ELENA PÂNZARIU, TEODOR MĂLUȚAN		ADINA ELENA PÂNZARIU, TEODOR MĂLUȚAN	
<i>Noi posibilități de conversie hidrolitică a materialelor vegetale</i>	39	<i>New perspectives on the hydrolytic conversion of vegetal materials</i>	39

Quarterly journal edited by THE TECHNICAL ASSOCIATION FOR ROMANIAN PULP AND PAPER INDUSTRY and PULP AND PAPER R&D INSTITUTE – SC CEPROHART SA – Brăila, Romania

Sponsored by THE ROMANIAN OWNERSHIP OF PULP AND PAPER INDUSTRY

ISSN: 1220 - 9848

---

## EDITORIAL STAFF

---

**Angels Pelach** - University of Girona, Spain

**Branka Lozo** - Faculty of Graphic Arts, University of Zagreb, Croatia

**Naceur Belgacem** - INP- Pagora Grenoble, France

**Ivo Valchev** - University of Chemical Technology & Metallurgy, Sofia, Bulgaria

**Elena Bobu** - “Gheorghe Asachi” Technical University of Iași, Romania

**Dan Gavrilescu** - “Gheorghe Asachi” Technical University of Iași, Romania (*Editor*)

**Paul Obrocea** - “Gheorghe Asachi” Technical University of Iași, Romania

**Valentin I. Popa** - “Gheorghe Asachi” Technical University of Iași, Romania

**Emanuel Poppel** - “Gheorghe Asachi” Technical University of Iași, Romania

**Teodor Măluțan** - “Gheorghe Asachi” Technical University of Iași, Romania

**Constantin Stanciu** - “Dunărea de Jos” University of Galați, Romania

**Petronela Nechita** - Pulp and Paper Research and Development Institute - SC CEPROHART SA, Brăila, Romania (*Deputy Editor*)

**Daniela Manea** – Pulp and Paper Research and Development Institute - SC CEPROHART SA, Brăila, Romania

**Eva Cristian** – Pulp and Paper Research and Development Institute - SC CEPROHART SA, Brăila, Romania

**Nicoleta Gherghe** – SC VRANCART SA Adjud, Romania

**Mihai Banu** - SC AMBRO SA, Suceava, Romania

---

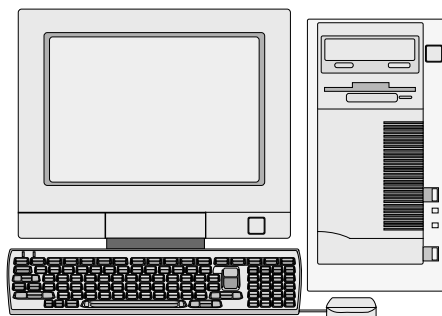
The foreign readers may subscribe by TECHNICAL ASSOCIATION FOR ROMANIAN PULP AND PAPER INDUSTRY, (ATICHR), Walter Mărăcineanu Square no.1-3, Entry 2, Fl. 2, Room 177-178, Land 1, Bucharest, RO-78101, phone: +40 21 315 01 62, +40 21 315 01 75, Fax: +40 21 315 00 27, E-mail: [rompap@pcnet.ro](mailto:rompap@pcnet.ro) ; [rompap@msn.com](mailto:rompap@msn.com)

The articles, information, advertising can be sent on “**CELULOZĂ și HÂRTIE**” editorial office address: A.I.Cuza Blvd, no.3, 810019, Braila, Romania, phone: +40 239 619 741, fax: +40 239 680 280, e-mail: [petronela.nechita@ceprohart.ro](mailto:petronela.nechita@ceprohart.ro), or Walter Mărăcineanu Square, no. 1-3, land 1, Bucharest, phone: +40 21 315 01 62, +40 21 315 01 75

---

Aknowledged in Romania, in the Polymer Materials Sciences field, by the **National Council of the Scientific Research from the Higher Education** (CNCSIS), C group. Indexed in PaperBase Abstracts, PIRA International ([www.paperbase.org](http://www.paperbase.org), [www.piranet.com](http://www.piranet.com))

---



**Prof. dr.ing. CONSTANTIN STANCIU****– 42 de ani de activitate în slujba sectorului de celuloză și hârtie, cercetării și învățământului superior –**

Născut la 25.07.1946 în orașul Botoșani, a absolvit școala elementară și o parte din Liceul Real “George Bacovia” la Bacău. A avut posibilitatea de a cunoaște de mic copil fabrica de hârtie “Steaua Roșie”, care a revenit la numele inițial “Letea” Bacău.

A absolvit liceul real din Buhuși în 1964, ca șef de promoție. În perioada 1964 -1969 este student al Facultății de Chimie Industrială din Iași, fiind absolvent al specializării: Tehnologia Celulozei, Hârtiei și Fibrelor Artificiale. Este repartizat la Combinatul de Celuloză și Hârtie Brăila, unde ocupă diverse funcții cum ar fi: inginer tehnolog, șef secție, șef serviciu tehnic. A fost șeful Serviciului Tehnic al centralelor industriale care au funcționat la Brăila până în anul 1989: Centrala Industrială de Celuloză și Hârtie, Centrala Industrială de Celuloză, Hârtie și Fibre Artificiale. În această postură a coordonat și Serviciul tehnic de protecția muncii-toxicologie și Laboratorul de ambalaje din București. În perioada 1964 – 1989 a avut contribuții notabile la: modernizarea mașinii de carton duplex, a electrofiltrelor și cazanelor de regenerare de la CCH Brăila, la modernizarea instalației de fierbere Kamyr în vederea trecerii de la materia primă stuf la lemn, la valorificarea complexă a prehidrolizatului de la fabricarea celulozei chimice (drojdie furajeră, metanol, furfurool) și mai ales în domeniul dezvoltării producției de hârtii tehnice în România. A contribuit activ la conceperea și realizarea programului de dezvoltare a producției de hârtii și cartoane tehnice (la fabricile de la Letea Bacău, Molidu Vama, Palas Constanța, Comuna din Paris și Reconstrucția Piatra Neamț, Hârtia Bușteni). În calitate de Șef serviciu tehnic a coordonat și activitatea de cercetare uzinală, colaborând foarte bine cu grupele de cercetare de la Reconstrucția Piatra Neamț, Letea Bacău, Palas Constanța, CCH

Turnu Severin, CCH Suceava.

Din 1989 până în 2001 coordonează activitatea de Cercetare și Microproducție a Institutului de Cercetare și Proiectare pentru Celuloză și Hârtie – CEPROHART Brăila. S-a preocupat de realizarea unor teme de cercetare de perspectivă, de îmbunătățirea infrastructurii de cercetare și mai ales de formarea unui nou nucleu de cercetători tineri. În colaborare cu echipa de cercetare a contribuit la implementarea unor noi tehnologii și realizarea unor produse papetare dintre care remarcăm:



- tehnologiile de fabricare a celulozelor papetare din plop necojit, mesteacăn, salcie, kenaf și sorg;
- reducerea conținutului de rășini din celuloze prin utilizarea enzimelor lipazice;
- introducerea procedurii de încleire în mediu neutru pe instalația de hârtii speciale din cadrul CEPROHART (1994) și pe instalația de fabricat hârtie de scris tipar de la SC CELHART DONARIS Brăila (1996);
- introducerea din 1992 a unei noi culturi de drojdie (Candida Scotti) la Celohart Zărnești și Letea Bacău;
- tehnologia de fabricație a hârtiilor speciale pentru marcaje și diverse documente de valoare.

În calitate de coordonator al echipei de cercetare de la Brăila a participat activ la organizarea a numeroase manifestări științifice de profil naționale și internaționale. Activitatea i-a fost recunoscută prin înmânarea în cadru festiv la data de 25.07.2011 la SC CEPROHART SA Brăila a Distincției de Onoare pentru contribuția adusă la promovarea și dezvoltarea activității de cercetare în domeniul celulozei și hârtiei, distincție acordată de Asociația Tehnică pentru Industria Celulozei și Hârtiei din România și Institutul de Cercetare și Proiectare pentru Celuloză și Hârtie SC CEPROHART SA Brăila.

Ca urmare a experienței acumulate în producție și cercetare, din anul 2001 ocupă postul de

conferențiar universitar la Universitatea „Dunărea de Jos” din Galați - Facultatea de Inginerie Brăila, unde susține cursurile aferente specializărilor „Utilaje pentru industria celulozei și hârtiei” și „Ingineria sistemelor biotehnice și ecologice”.

În această perioadă, a avut o activitate didactică și științifică deosebită concretizată în publicarea a 14 cărți și îndrumare de laborator. Este autorul a 168 de lucrări științifice publicate în străinătate și în țară și a 80 de comunicări susținute la simpozioane interne și internaționale. Dintre cărțile și îndrumările publicate remarcăm:

- Proprietăți funcționale și metode specifice de testare a hârtiilor industriale și speciale (2006)
- Utilaje și echipamente pentru fabricarea hârtiilor industriale și speciale (2005)
- Managementul mediului (2 volume) (2005)
- Tehnologii și instalații pentru valorificarea produselor sulfat (2004)
- Materiale simple și complexe pentru ambalarea produselor (2001)
- Biologia și tehnologia drojdiilor (1993)
- Îndrumar de laborator pentru epurarea apelor reziduale (2006)
- Investigații analitice în chimia și tehnologia foliilor celulozice

În anul 2007 devine profesor și conducător de doctorat în domeniul Inginerie Industrială. În această calitate a dezvoltat noi cursuri, pentru licență și masterat dintre care remarcăm: Tehnologia fabricării foliilor celulozice, Tehnologia ambalării produselor alimentare, Procese terțiare pentru epurarea apelor uzate industriale.

Este membru al unor organizații științifice și profesionale internaționale (International Association of Scientific Papermakers – ASPM) și naționale, precum și membru în colectivele redacționale ale revistelor „Celuloză și Hârtie” și „GeoGebra”. Este coautor la 7 invenții dintre care una a fost premiată cu medalia de argint la EUREKA 2009.

În cursul activității a finalizat numeroase teme de cercetare în calitate de director de proiect sau colaborator, dintre care se remarcă tema : „Sistem integrat de securizare a marcajelor și a documentelor de valoare realizat în procesul de obținere și tipărire a hârtiilor suport” pentru care întreg colectivul (condus de Ceprohart Brăila în calitate de coordonator al proiectului) a fost distins cu premiul AGIR 2009 la secțiunea Industrie Chimică.

Această scurtă prezentare cuprinde doar o parte din activitatea colegului nostru care a devenit o personalitate recunoscută în domeniul celulozei și hârtiei.

Atașat de colegi, cu spirit de echipă a reușit să creeze o atmosferă de lucru propice creației.

Cu ocazia împlinirii vârstei de 65 de ani, îi dorim domnului profesor, multă sănătate și putere de muncă în continuare.

*Colegiul de redacție și  
Colaboratorii din Departamentul de Cercetare  
al SC CEPROHART SA Brăila*

## RELEASE PAPER: CAN PHOSPHATE ESTERS BE AN ALTERNATIVE TO SILICONE?

Dan Belosinschi<sup>1</sup>, Bruno Chabot and François Brouillette

*Centre de Recherche sur les Matériaux Lignocellulosiques (CRML), Université du Québec à Trois-Rivières (UQTR)*

*Author correspondence: <sup>1</sup>3351 Boul. Des Forges, C.P. 500, Trois-Rivières, Québec, Canada, G9A5H7, [dbelosinschi@yahoo.com](mailto:dbelosinschi@yahoo.com)*

### Abstract

Release paper is a special paper grade with one or both sides coated with non-sticking materials. Silicone is currently the only material used to produce release paper at the industrial level. Its remarkable properties and availability ensure product quality and sustainability of the industrial production. Meanwhile, the stability of silicone polymers raises serious environmental problems in terms of paper substrate recyclability. Research are currently undertaken to evaluate the ability of phosphate esters as a new class of compounds capable of developing non-adhesive surface properties. This paper presents initial attempts to coat the paper with phosphate esters and to assess phosphate ester / fibrous substrate and phosphate ester / adhesive interactions. The results show that this class of compounds exhibits non-adhesive properties and, coated on paper under certain conditions, can lead to a non-sticking surface. Despite the fact that there is a long way to achieve ester anchoring to the cellulose surface fibres and to control the peeling force from an adhesive tape, preliminary results are encouraging.

**Key words:** *Release paper, Phosphate esters, Silicone polymers, Coating*

### Rezumat

Hârtia antiaderentă este un sortiment special de hârtie cu una sau ambele fețe acoperite cu materiale non-aderente. În prezent, siliconul este singura substanță utilizată pentru a produce hârtia antiaderentă la nivel industrial. Disponibilitatea și proprietățile sale remarcabile garantează calitatea și sustenabilitatea produsului în ceea ce privește producția industrială. Deocamdată, stabilitatea polimerilor siliconici ridică în mod serios probleme mediului înconjurător în ceea ce privește reciclarea hârtiei suport. În mod frecvent sunt efectuate cercetări cu privire la evaluarea capacității esterilor fosfați ca nouă clasă de compuși capabili de dezvoltarea proprietăților antiaderente. Această lucrare prezintă experimente preliminare de acoperire a hârtiei cu esteri fosfați și de evaluare a interacțiunilor reciproce ester fosfat/hârtie suport și ester fosfat/adezivitate. Rezultatele obținute arată că această clasă a compușilor prezintă proprietăți adezive, iar hârtia acoperită în anumite condiții poate avea suprafața antiaderentă. În ciuda faptului că este nevoie de cercetări îndelungate pentru obținerea unei bune ancorări a esterului la suprafața fibrelor celulozice și pentru controlul forței de smulgere a benzii adezive, rezultatele preliminare obținute sunt promițătoare.

**Cuvinte cheie:** *Hârtie antiaderentă, Esteri fosfați, Polimeri siliconici, Cretare*

## INTRODUCTION

### *Release liner. Release paper*

The release liner is a substrate carrier web material, with one or both sides coated with a non-sticking material, which provides a release effect against any type of tacky materials like adhesives. The substrate can be paper or plastic based while the release agent

consists almost exclusively of silicone material. Among the main uses of these products we can find: pressure sensitive adhesives (PSA) - label stock; tapes; medical and hygiene applications; graphic arts; industrial goods - building and insulation applications. The worldwide production of release liner in 2010 was about 34 billion square meters (more than 2 million tonnes), the PSA-label stock commanding more than 50% of the market share.

The paper remains the main coating substrate - 85% from global market share, compared to 15% for plastic films. The detailed situation of substrate types used in 2010 was as follows: 41% glassine/calendered Kraft papers, 17% polyolefin coated papers, 15% clay coated papers, 15% plastic films, 12% other papers [1].

The release paper is in fact a release liner whose backing is made of paper and since the paper dominates the market today, being also our coating substrate, we will refer to it hereafter. The main functions of release paper, as it is suggested in Figure 1, are to protect the adhesive during transit and storage and, ultimately, easily release the PSA - label during its intended use.

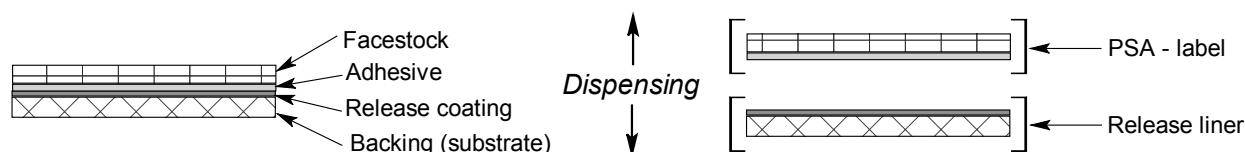


Fig. 1 Structure of a self-adhesive label laminate

**Release agent. Silicone chemistry and properties**

The silicone materials are the universal release agent used to produce release paper nowadays. “Silicone” refers to a general category of synthetic polymers with a siloxane main chain made of repeating silicon to oxygen bond. In addition, each silicon atom is bonded to organic groups, typically two methyl groups in which case the material is called poly(dimethylsiloxane) – PDMS (see Figure 2). The simultaneous presence of organic groups attached to

an inorganic backbone gives silicones a combination of unique properties like high thermal and chemical stability (due to siloxane main chain) associated with strong hydrophobic behaviour and low surface free energy (due to methyl groups), making ideal their use as release agent [2-4]. Besides, the silicone polymers are liquid under normal conditions up to quite high polymerisation degrees and show high wettability to almost all solid surfaces which facilitate the subsequent coating process.

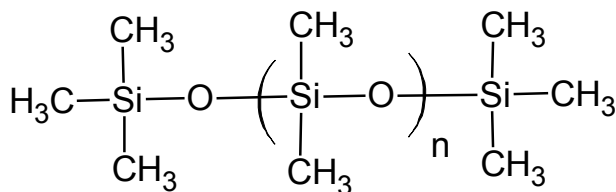


Fig. 2 Chemical structure of poly(dimethylsiloxane) - PDMS

Once coated on the paper substrate, the liquid silicone film must undergo a cross linking reaction, currently named “silicone cure chemistry” that will change the silicone state of matter, from liquid to solid. This process aims to create a network of chemical bonds between silicone polymer chains - to limit the amount of migratory free silicone to adhesive, and between silicone and functional groups present at paper surface - to anchor the silicone film to paper substrate. Usually, the silicone cure chemistry involves the use of catalysts and activation energies and the existence of a small number of reactive functional groups (e.g. silane, vinyl, hydroxyl, epoxy and acrylic) on the PDMS macromolecules coming to replace the inert methyl groups [5]. The silicone cross linking by addition, whose global reaction is presented in Figure 3,

counts for more than 80% of currently available silicone cure mechanisms [6]. Cured silicone films generally have a thickness of 1-2 μm, a basis weight of 1-2 g/m<sup>2</sup> and exhibit anti-tack properties against a wide range of adhesive formulations. The main drawback of using silicone as release agent is that it makes difficult the further recycling of paper substrate, thus losing a significant amount of high quality fibres. Starting from this problem, our research aimed to evaluate the ability of phosphate esters as a new class of compounds capable of developing release properties, allowing the subsequent recycling of paper substrate. This paper presents initial attempts to coat the paper with phosphate esters and to assess phosphate ester / fibrous substrate and phosphate ester / adhesive interactions.

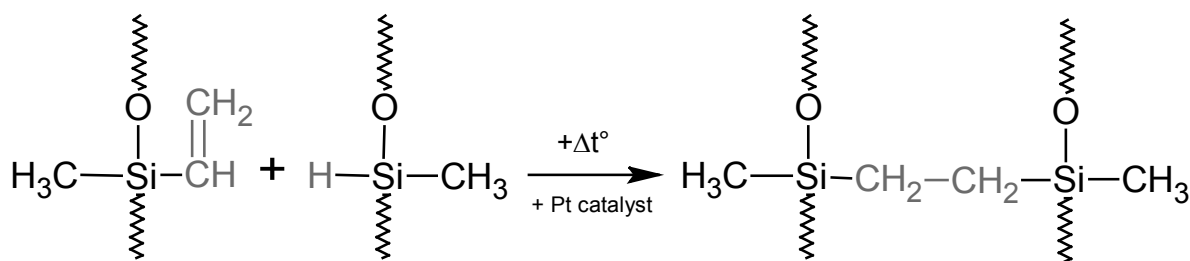


Fig. 3 Silicone thermal addition cure chemistry

## EXPERIMENTAL

### Materials

#### 1. Phosphate esters (PE): Synthesis, analysis and purification.

The phosphoric esters of organic hydroxyl compounds are amphiphilic molecules widely used as cleansing, emulsifying and antistatic agents, rust inhibitors, etc. Especially, salts of phosphate monoesters are useful for articles which are used for direct contact with human bodies, such as shampoo and cleansing agents because they have good water solubility, foaming property and cleansing power, exhibiting low toxicity and low skin irritability [7, 8]. Our research tries to highlight the surfactant nature of these compounds not in the aqueous phase

as we can see above, but in solid phase by coating it on a paper surface.

Two phosphate esters were synthesized by the reaction of phosphoric anhydride and two linear fatty alcohols: 1-octanol (C8) and 1-octadecanol (C18). Stoichiometry mole ratio of the overall reaction showed in Figure 4 was as follows: fatty alcohol/P<sub>2</sub>O<sub>5</sub>/H<sub>2</sub>O = 2/1/1. The reaction conditions were chosen in order to promote the formation of phosphate monoester [7, 8]. Also, the product ratio of mono- and di-ester is closely related to the alkyl chain length of alcohols, increasing with the chain length [9]. Quantitative analysis performed after the esterification reaction showed a ratio of 80% mono- / 20% di-ester for C8 alkyl chain and 100% mono- / 0% di-ester for C18 alkyl chain.

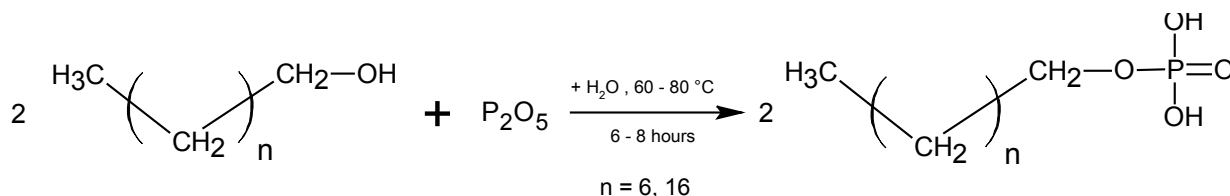


Fig. 4 Phosphate esters synthesis reaction

Inevitably, the final product will consist in a mixture of phosphate esters, unreacted fatty alcohol and phosphoric acid and other by-products. In order to isolate our product, a purification and analysis plan was developed, consisting in three successive water/solvent extractions. The purified product is a white solid compound at room temperature, composed predominantly of phosphate monoester (~100% for C18 and 90% for C8) and whose melting point depends on alkyl chain length: 60-70°C for C18 and 20-30°C for C8.

#### 2. Low porosity paper:

All coating tests were carried out on a special paper substrate made on the CSPP (Centre Spécialisé en

Pâtes et Papiers) pilot paper machine located in Trois-Rivières, Canada. This unsized calendered paper has about 85 g/m<sup>2</sup> basis weight and is made of highly beaten softwood Kraft fibres as the main fibrous furnish component. The papermaking conditions lead to a low porosity paper, as low as 5 ml/min PPS porosity.

#### 3. Polyvinyl alcohol (PVA).

The PVA used was 99% hydrolysed with molecular weight ranging from 85,000 to 124,000. It was solubilised in water at 10% concentration. The addition of PVA to the sheet had two main purposes:

- Coating material: by creating a physical barrier at the paper surface in order to prevent the

penetration of the phosphate ester in the paper structure;

- In a mixture with the phosphate ester: to control the release force vs. adhesive and anchoring force vs. paper substrate.

## Methods

### 1. Paper coating.

The laboratory coating device was composed of a flat worktable on which the substrate to be coated was placed. The active element of coating is a Mayer rod that is inserted in two interconnected pockets driven by a motor simultaneously describing a translation movement parallel to the table. The paper sheet is fixed on the table and the coating sauce is deposited on the sheet at the end where the rod is placed. The sauce is distributed evenly at surface when the bar is driven into motion. The amount of material deposited depends on: the size and number of Mayer rods, the relative distance between the rod and surface to be coated and the coating sauce consistency. Meanwhile, rod speed or sauce viscosity parameters will significantly influence the quality of the coating like sauce surface distribution or structure penetration ability. Frequently, the coating is followed by thermal treatments aimed at evaporating the water from the coating sauce and/or consolidating the coated layer. In our case, the coating delivery system was: 10% solution concentration for PVA, 5% dispersion consistency for phosphate ester C18 and 100% solids for phosphate ester C8 (the compound is liquid at room temperature).

### 2. Surface free energy (SFE) measurement.

SFE characterises the thermodynamics of solid surfaces and is the first and most important parameter which allows the evaluation of the adhesion properties of materials. Usually, the anti-tacking properties are associated to low surface free energy materials, having a major dispersive energy component.

Different approaches are used to determine the energy of solid surfaces, contact angle measurements being the most common method. Starting from Young's equation several variants of this method have been developed. The latest idea presented by van Oss, Chaudhury, and Good is the SFE partition into two independent components - dispersive and polar. The authors divided also the polar component into two other

subsequent components - acid and base, and propose an equation with three unknowns that links all these partitions [10]. Measuring the contact angles of three well known liquids on the same solid surface, a system of three independent linear equations is generated. The mathematical solutions of this system are in fact the SFE and its components.

Contact angle measurements were made with a FTA4000 Microdrop® device manufactured by First Ten Ångströms. The device allows deposition on solid surfaces of very small droplets (as low as picolitre volume) and can capture up to 300 images in less than 5 seconds. All droplet geometry data, including the contact angle, are then determined for each image in part with the FTA32 Video software. Ethylene glycol, formamide and water (as bipolar), and  $\alpha$ -bromonaphthalene (as nonpolar), were used as reference liquids for SFE measurements.

### 3. Peel force measurement.

Peel Test measures the strength required to pull apart bonded surfaces composed of a standard adhesive tape and a coated paper sample. This method was adapted from ASTM F88-99 [11] and is made at a 180° supported separation angle, under controlled conditions: 23°C, 50% relative humidity, 50 mm/min peel speed, 25.4 x 75 mm (width x length) size sample. The double coated adhesive tape is attached on one side to a rigid alignment plate and on the other side to a paper sample. One couch roll - 13 kg weight, is rolled backward and forward 10 times with no supplementary pressure being applied to promote the adhesion between surfaces. This assembly is mounted into an INSTRON device model 4201 with the rigid plate tail held in one grip and the sample tail, folded at 180°, held in the opposing grip while the test is being conducted. At the end of the test, the Bluehill software is used to calculate two important parameters: the peel force - as average of the highest 5 load peaks, and the absorption energy - as integrated area at average load. Besides these measurements, each test is accompanied by a visual evaluation of the peeled surfaces to identify the mode of specimen failure.

### 4. Surface topography analysis.

Optical profilometry is a rapid, non-destructive, and no-contact surface metrology technique. An optical profiler is a type of microscope whose



working principle is based on “white light interferometry”. In its most common application, interferometry is a versatile measurement technology for 3D imaging of surface topography with very high precision [12]. In this study, an optical profiler WYKO NT1100 (Veeco) was used to observe the changes in paper surface micro-geometry as a result of the coating process. The paper roughness is the second parameter which can be measured by the profilometer and usually comes as a further statistical interpretation of surface images.

5. Paper barrier properties.

Barrier properties of the low porosity paper substrate, coated or uncoated with phosphate esters, thermally treated or untreated, was tested as follows [13]:

- Air permeability by PPS (Parker Print Surf) Porosity method (TAPPI T 555 om-99),
- Water permeability by Cobb method (TAPPI T 441 om-98),
- Grease permeability by Castor Oil method (TAPPI T 559 cm-02).

RESULTS AND DISCUSSIONS

Surface free energy

Theoretically, the main idea is to coat the paper with mono phosphate esters and induce a thermal reaction between the two remaining free hydroxyl groups of phosphate function with the corresponding hydroxyl groups of cellulose fibres. In this way we can make sure that the ester anchors at the paper surface, “hiding” the polar phosphate side and exposing the nonpolar alkyl chain side to a future adhesive formulation. First coating attempts were made with phosphate ester - C18. The coated paper exhibited excellent barrier properties (almost a water and greaseproof paper) and low surface free energy, as we can see in Table 1, because of the large size of the alkyl chain. However, the ester proved to be an inert product at the paper surface, easily migrating to the adhesive tape during the peel test. These results have led us to synthesize a second phosphate ester with a much shorter alkyl chain consisting of eight carbon atoms (C8). Although this product is characterized by a high SFE value which can impair the anti-tacking properties, it has at the same time important polar and base SFE components, like PVA and paper, which enhance their reaction compatibility (see Table 1).

Table 1 SFE of different materials measured by Van Oss-Chaudhury-Good method

SFE, mJ/m <sup>2</sup> Material	Total	Dispersive	Polar	Acid	Base
Silicone	25.98	25.98	0	0	0
Phosphate ester (C18)	17.70	16.66	1.046	0.4752	0.5755
Phosphate ester (C8)	38.35	33.73	4.625	0.4061	13.17
Polyvinyl alcohol	39.89	27.15	12.74	1.330	30.49
Low porosity paper	46.27	41.76	4.507	0.1434	35.42

Release properties

The PE (C8) is in liquid state at room temperature and during coating, successfully penetrated even a closed structure like the low porosity paper. Consequently, the coating became rather a paper impregnation process. Despite this, it was interesting to see the sample responses to repeated peel test, given that they were thermally treated for 6 hours at different temperatures (Figure 5). All coated papers

with PE (C8) easily peeled off from the adhesive tape. The release force increased with the number of peel tests. This clearly shows the anti-tacking properties of PE (C8) but also its migratory behavior with repeating peel test. The results from Figure 5 show that thermal treatments bring insignificant changes to the peel force. We can conclude that even at high temperature the “PE (C8) - cellulose fibres” interactions are limited.

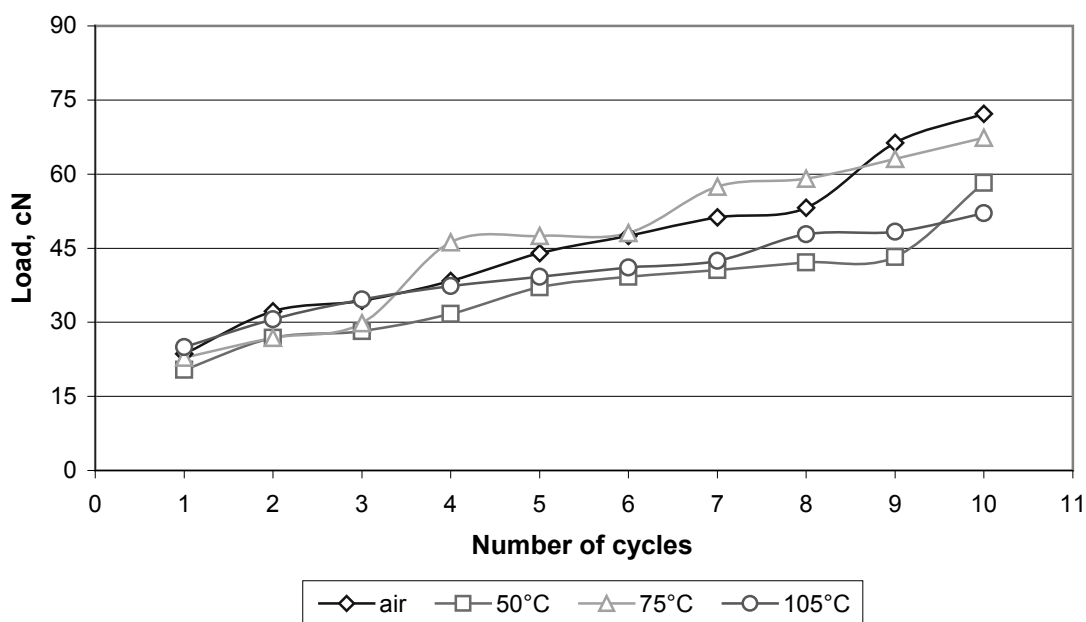


Fig. 5 Influence of thermal treatments and number of peel tests on the peel force value

Two solutions were proposed to limit the PE (C8) penetration into the paper structure. The first attempt was to apply a PVA barrier layer at the paper surface before the PE coating (PVA/EP) and the second was to use a viscous mixture of PVA and PE as coating sauce (PVA+PE). The peel test results of these samples are presented in Table 2. As expected, the adhesive tape causes the sample break (tearing) for uncoated paper and PVA coated paper. The paper coated with 30%PVA+70%PE mixture sauce showed release properties for the first

peel cycle but the coated layer was removed and the paper structure delaminated starting with the second peel cycle. Small fibres picking appeared on the PE coated paper surface after a quite important number of peel cycles. The PVA/PE double layer coated paper was the only sample that is easily peeled off, the release force remained fairly constant and its surface intact after more than 20 peel test cycles. These properties are closest to those of the reference release paper - silicone coated paper.

Table 2 Peel test behaviour of coated paper samples

Paper coated with	Coat basis weight, g/m <sup>2</sup>	Average peel force, cN	Absorption energy, mJ	Number of peel cycles	Notes:
PVA	2	3095	1512	1	Sample rupture
PVA + PE (C8)	4-8	360	140	2	Sample delaminating
PE (C8)	10-12	72	31	>10	Small picking
PVA / PE (C8)	2/--	66	15	>20	Intact surface
Silicone	1	190	97	1	Intact surface

Surface topography

The topographic images (from Figures 6-8) and the corresponding roughness (Figure 9) confirm in fact the results reported for peel tests. Rough surfaces with high density of asperities, like uncoated paper or PVA and PVA+PE coated papers, promoted the adhesion by a mechanical interlock mechanism while the hydroxyl polar groups of these materials lead to an adsorption adhesion mechanism as a result of secondary intermolecular forces at the interface. Instead,

the adhesive bonding is quite limited for PE and PVA/PE coated papers due to much smoother surfaces and nonpolar alkyl chain exposure at the interface. The surface topography and roughness value of PVA/PE and silicone coated papers looked very similar but these papers are quite different in terms of peel force. The silicone release paper provided some residual adhesion that keeps the adhesive “bonded” while the PVA/PE coated paper had almost “no bonds” to it.

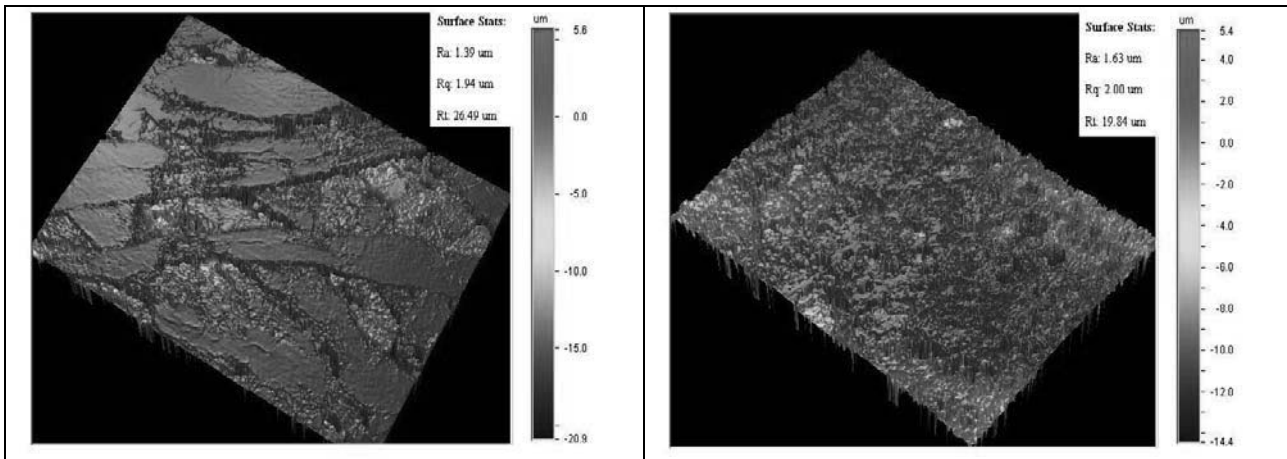


Fig. 6 Surface topography of paper (left) and paper coated with PVA+PE mixture (right)

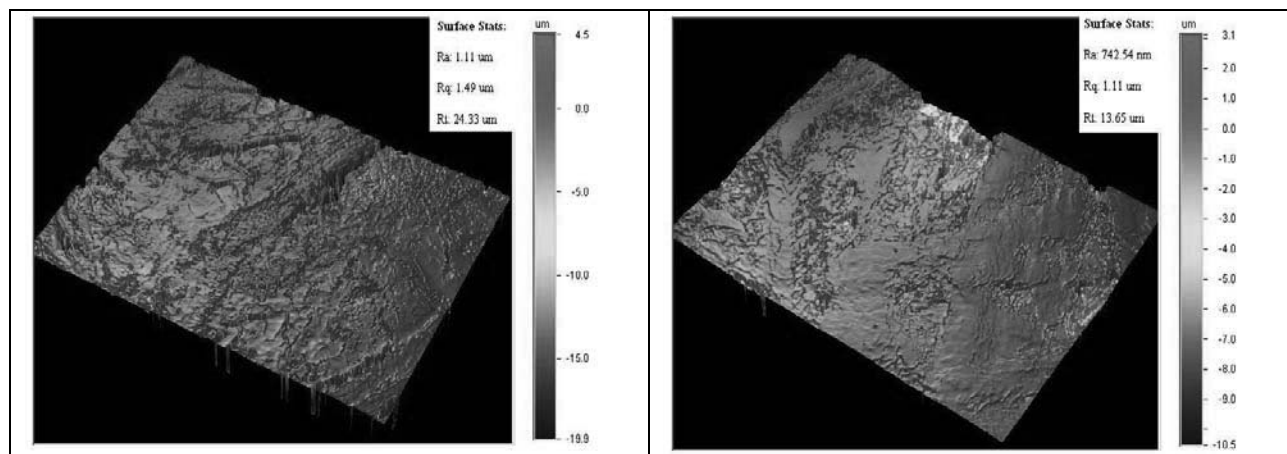


Fig. 7 Surface topography of paper coated with PVA (left) and PE-C8 (right)

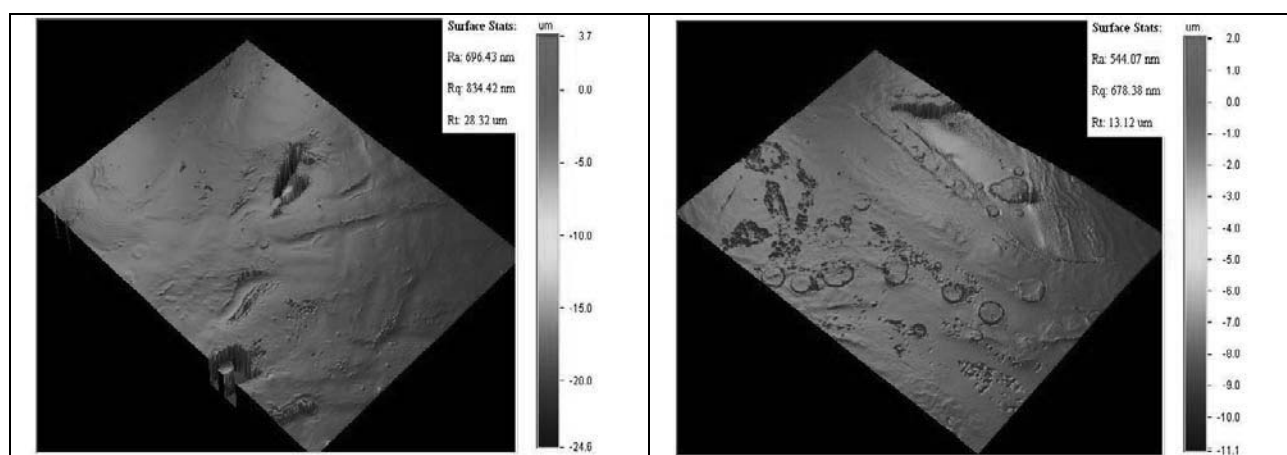


Fig. 8 Surface topography of paper coated with PVA/PE-C8 (left) and silicone (right)

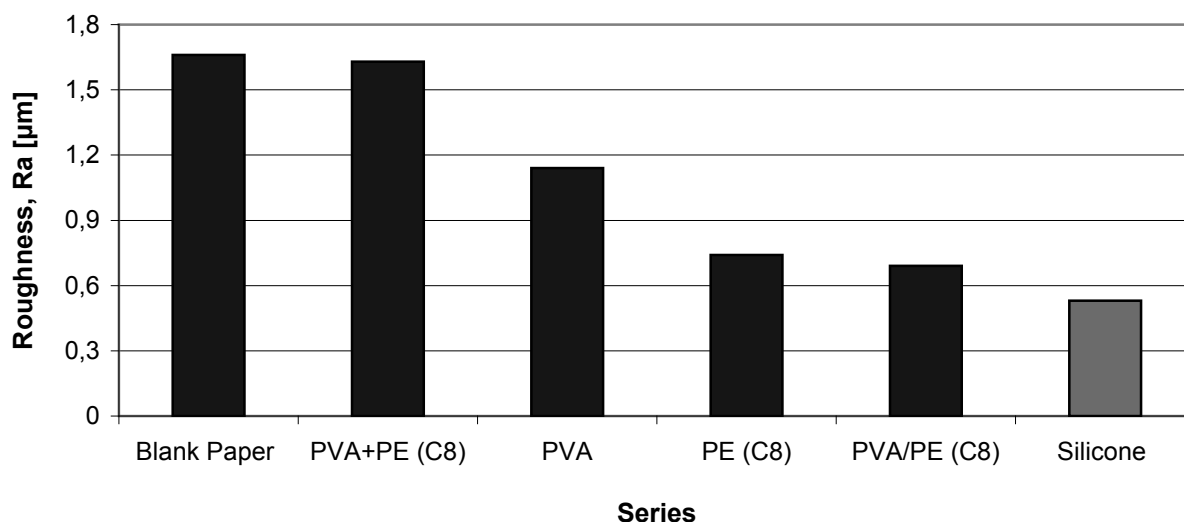


Fig. 9 Changes in paper surface roughness as result of the coating process

## CONCLUSIONS

The phosphate esters of fatty alcohols are compounds which exhibit anti-tacking properties as proven by peel tests and surface free energy measurements. The interaction of the phosphate ester layer with the paper surface is quite limited, leading often to a mass transfer when the adhesive tape is peeled off. However, it seems that anchoring occurs when esters and coating surfaces present similarities in term of SFE (like total energy level and/or energy component distribution). Despite the fact that it is not yet possible to control the anchor and release processes as with silicone polymers, these first results are encouraging.

## FUTURE STUDIES

- Continue to evaluate the anti-tacking properties of other phosphate esters or poly (phosphate esters);
- Determine the conditions that lead to optimal ester/substrate anchoring and controlled ester/adhesive release;
- Study the interface phenomena and quantify the migratory behavior of phosphate esters.

## ACKNOWLEDGEMENTS

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for their financial support and Centre Spécialisé en Pâtes et Papiers (CSPP), Cégep de Trois Rivières team for their technical and scientific support.

## REFERENCES

1. Spaulding, M., What the global release-liner market will look like in 2015, The Converting Curmudgeon, <http://convertingcurmudgeon.com/2011/03/31/what-the-global-release-liner-market-will-look-like-in-2015>.
2. Bondurant, S., Ernster, V., Herdman, R., Silicone Chemistry (chapter), Safety of Silicone Breast Implants (book) - 1999, <http://www.nap.edu/catalog/9602.html>.
3. Colas, A., Introduction / Silicones in Industrial Applications (chapter), Inorganic Polymers (book), Nova Science Publishers - 2007.
4. Colas, A., Curtis, J., Silicones Biomaterials: History and Chemistry (p. 80-86) & Medical Applications of Silicones (p. 697-707), Biomaterials Science: An Introduction to Materials in Medicine - Second Edition, Elsevier Academic Press - 2004.
5. Cray, S., Silicone Release Coatings for the Pressure Sensitive Adhesive Industry / Silicones in Industrial Applications (chapter), Inorganic Polymers (book), Nova Science Publishers - 2007.
6. Holwell, J., A., Global Release Liner Industry Conference 2008; Platinum Metals Review, 52 (4): 243–246, 2008.

7. Tsuyutani et al., Process for preparing phosphoric ester, United States Patent US 6,710,199 B2, March 23, 2004.
8. Kurosaki et al., Method for producing a phosphoric monoester, United States Patent 4,350,645, September 21, 1982.
9. Hadj-Bouazza, A., Brouillette, F., Synthesis of phosphate mono esters and study of their effect on the reduction of the linting propensity of paper, TAPPSA Journal, 2 : 34-37, 2010.
10. Żenkiewicz, M., Methods for the calculation of surface free energy of solids, Journal AMME, 24 (1): 137-145, 2007.
11. ASTM F88-99, Standard Test Method for Seal Strength of Flexible Barrier Material, Annual Book of ASTM Standards, 1999.
12. Optical Profilometry, <http://www.mri.psu.edu/facilities/mcl/techniques/optProfilometry.asp>.
13. TAPPI Test Methods: T 555 om-99, TAPPI T 441 om-98, TAPPI T 559 cm-02.

## ASPECTS REGARDING COMPLIANCE OF IMPROVED BARRIER PAPERS WITH FOOD SAFETY AND ENVIRONMENT REQUIREMENTS

Mariana Ionescu<sup>1</sup>, Gabriel Mustățea<sup>1</sup>, Valentin Ionescu<sup>1</sup>, Giuseppe Spadaro<sup>1</sup>, Daniela Manea<sup>2</sup>, Catalina Talasman<sup>2</sup>, Argentina Radu<sup>2</sup>, Maricica Burlacu<sup>2</sup>

<sup>1</sup>National Institute of R&D for Food Bioresources – IBA Bucharest, Romania

<sup>2</sup>Pulp and Paper Research and Development Institute, Ceprohart SA Braila, Romania

*Author correspondence:* <sup>1</sup>National Institute of R&D for Food Bioresources – IBA Bucharest, Romania, email: [mariana.ionescu@bioresurse.ro](mailto:mariana.ionescu@bioresurse.ro)

### Abstract

New types of packages containing cellulose fibers used for food with fat and oil content were analyzed and characterized to assess their compliance with food safety requirements: Regulation (EC) No 1935/2004 and GD No. 1197/2002 with subsequent changes.

Methods of analysis for global migration in fat medium (olive oil or alternative testing simulants: isooctane and 95% ethanol) followed standards of analysis for materials intended for food contact. Presence and transfer of substances from paper and board, causing strong smell (off-flavor), depend on the fibers composition, added chemical compounds, type of contact (dry, wet, fatty foods) and contact conditions (time and temperature). Thus, several methods, some of them standardized were applied: organoleptic testing of different paper varieties and the specific migration of heavy metals (Pb, Cd, and Cr). To assess compliance with environmental requirements: GD no. 621/2005 and Directive 94/62/EC the content of heavy metals (Pb, Cd, Cr, Hg) and ash (EN 13431:2005) were analyzed.

**Key words:** *Food contact packaging, Food safety, Global migration, Paper packaging*

### Rezumat

Noi tipuri de ambalaje pe bază de fibre celulozice destinate produselor alimentare cu conținut de uleiuri și grăsimi au fost analizate și caracterizate în conformitate cu condițiile și reglementările privind siguranța alimentară: Directiva (EC) Nr. 1935/2004 și GD Nr. 1197/2002 cu modificările ulterioare.

Metodele de cercetare utilizate privind migrarea totală într-un mediu cu conținut ridicat de grăsimi (ulei de măsline sau testele alternative cu izooctan și etanol 95%) sunt însoțite de standardele și buletinele de analiză a substanțelor care vin în contact cu produsele alimentare. Prezența și transferul substanțelor din hârtie și carton produc un miros puternic înțepător (fără aromă), în funcție de compoziția fibrelor, aditivii chimici prezenți în hârtie, tipul contactului (alimente uscate/deshidratate, lichide, uleioase/grase) și condițiile de contact (timp și temperatură). Astfel, doar câteva metode din cele standardizate au fost aplicate și anume: cercetarea organoleptică a diferitelor tipuri de mostre de hârtie și migrarea specifică a metalelor grele (Plumb, Cadmiu și Crom). Pentru stabilirea conformității cu cerințele privind protecția mediului au fost studiate următoarele reglementări: GD nr.621/2005 și Directiva 94/62 EC privind conținutul de metale grele (Plumb, Cadmiu, Crom, Mercur) și cenușă (EN 13431:2005).

**Cuvinte cheie:** *Ambalaje pentru produse alimentare, Siguranța alimentară, Migrare globală, Ambalaje din hârtie*

□

## INTRODUCTION

New types of primary cellulosic fiber packages for food containing oil and fats are an important area of the packaging market; they must be integrated into the food quality assurance system from its packaging to its entry into consumption. Therefore, analyzing and assessing their compliance with food safety requirements as well as environmental requirements become absolutely necessary.

Paper and board used for food contact should not release substances used as processing aids, which have potential toxicity on food; they also must be microbiologically suitable, taking into account the final use of the material.

Currently, there is no global or regional legislation on paper and board used for food contact. In fact, many countries including Romania don't have their own specific legislation for paper and board used for food contact. Therefore, many of these countries adapt their regulations with those of other countries, such as FDA American Regulations and BgVV German Regulations. FDA regulations are more general than the German BgVV regulations which are listed more like European References.

CoE ResAp Resolution (2002) version 3, regarding paper and board says that "using chemical or toxicological screening tests for possible unknown toxic substances must be assessed and recommended in the future". Analysis methods to be applied are set either in CoE ResAp Resolution (2002) or in standards of analysis for paper and board intended for food contact.

Basic rules necessary for testing the migration, including simulants, were recently changed, as specified by EC Regulation No.10/2011 on plastics. EU official methods states the use of food simulants typically of all types of food and temperatures that relate to use conditions: 10% ethanol solution (A), 3% acetic acid solution (B), 20% ethanol solution (C), 50% ethanol solution (D1), olive oil (D2) and MMPO (modified poly-phenylene-oxide) (E).

However, testing alternatives for olive oil have been studied since 1980 because of difficulties related to the use of olive oil. The strongest testing simulants include isooctane and 95% ethanol solution. In 1997 was published the Commission Directive 97/48/EC which introduced volatile simulants mentioned above and MMPO (modified poly-phenylene-oxide) as an alternative to fatty food simulants. Alternative used simulants were 94% ethanol solution and isooctane.

The migration tests at high temperatures should be made only using MMPO as test stimulant

and using the contact temperature provided in the EC Regulation no.10/2011. Testing must take into account the possible degradation products formed at high temperatures.

There are currently testing standardized methods of overall migration using Tenax (MMPO) and olive oil, but only for plastic materials. However, currently, Tenax is not commercially available.

## MATERIALS AND METHODS

New types of paper have been analyzed and characterized to assess their compliance with general rules: Regulation (EC) no. 1935/2004 and G.D. no.1197/2002 and ulterior changes, regarding materials and articles intended for food contact, and to assess their compliance with environmental requirements: G.D. no.621/2005 and Directive 94/62/EC.

Materials used for obtaining papers with barrier properties by applying mass waterproofing treatments and surface treatments:

- Waterproofing fluorescent agents;
- Chitosan
- Zeolite
- Charcoal

Testing methodology used in the laboratory includes:

- Analysis of overall migration from food packages in: olive oil and isooctane;
- Organoleptic testing of paper materials inertia;
- Analysis of heavy metals content.

## RESULTS AND EXPERIMENTS

### 1. Overall migration tests in olive oil

Test conditions for analyzed materials followed the standard SR EN 1186-2/2003: Materials and articles in contact with foodstuffs - Plastics - Part 2: Test methods for overall migration into olive oil by total immersion.

#### *Principle method*

Overall migration from a material sample is determined as the loss of mass per unit area intended to come into contact with food. Test conditions are chosen depending on use conditions, according to SR EN 1186-1:2002.

Samples with known mass are immersed in olive oil during 24 hours exposure time at 40 Celsius

degrees, then withdraw from the olive oil, dried by blotting in order to remove the oil adhering to the sides and then re-weigh.

Generally, samples retain olive oil by absorption, oil being extracted with an extraction solvent.

Migration in olive oil is calculated by subtracting the mass of oil retained by the sample weight after the extraction of olive oil then decreases the mass of the initial sample mass.

Overall migration is expressed in lost mg per dm<sup>2</sup> surface of the sample intended to come into contact with food. Calculate with the following formula:

$$M = \frac{[m_a - (m_b - m_c)] \cdot 1000}{S}, \text{ where:}$$

- M overall migration in olive oil of the sample intended to come into contact with food, (mg/dm<sup>2</sup> surface);
- m<sub>a</sub> initial sample mass before contact with olive oil (grams);
- m<sub>b</sub> sample mass after olive oil contact (grams);
- m<sub>c</sub> absorbed olive oil mass (grams);
- S sample area (dm<sup>2</sup>).

Table 1 Results of overall migration in olive oil

No.	Sample name	m <sub>a</sub>	m <sub>b</sub>	m <sub>c</sub>	M (mg/dm <sup>2</sup> )
1.	S <sub>1a</sub>	0.2908	0.5034	0.2241	11,5
2.	S <sub>1b</sub>	0.2942	0.3950	0.1112	10,4
3.	S <sub>1c</sub>	0.2841	0.3758	0.0966	4,9
4.	S <sub>2a</sub>	0.2528	0.4374	0.1877	3,1
5.	S <sub>2b</sub>	0.2701	0.3708	0.1084	7,7
6.	S <sub>2c</sub>	0.2898	0.3870	0.1101	12,9
7.	S <sub>3a</sub>	0.2468	0.4021	0.1662	10,9
8.	S <sub>3b</sub>	0.2577	0.3411	0.0840	0,6
9.	S <sub>3c</sub>	0.2501	0.3264	0.0850	8,7
10.	S <sub>4a</sub>	0.2622	0.4313	0.1695	0,4
11.	S <sub>4b</sub>	0.2540	0.3460	0.0924	0,4
12.	S <sub>4c</sub>	0.2888	0.3813	0.0939	1,4
13.	S <sub>1bz<sub>2</sub></sub>	0.3114	0.3950	0.0927	9,1
14.	S <sub>1cz<sub>2</sub></sub>	0.2906	0.3629	0.0843	12,0
15.	S <sub>3bz<sub>2</sub></sub>	0.3138	0.3977	0.0846	0,7
16.	S <sub>3cz<sub>2</sub></sub>	0.3006	0.3697	0.0703	1,2

Samples (surface of 50 cm<sup>2</sup>) were immersed in olive oil (extraction ratio 2:1) and maintained for 24 hours at de 40<sup>0</sup> C

## 2. Overall migration test in fatty food simulants by rapid extraction into isooctane

Test conditions for analyzed materials followed the standard SR EN 1186-15/2003: Materials and articles in contact with foodstuffs - Plastics - Part 15: Alternative test methods to migration into fatty food simulants by rapid extraction into isooctane and/or 95 % ethanol.

### Principle method

To simulate real conditions from practice, the extraction ratio (sample surface reported to extraction liquid volume) was estimated at 2:1 (cm<sup>2</sup>: cm<sup>3</sup>).

Samples with known weight were immersed in isooctane for 24 hours at 40 °C. In parallel were also performed control samples (simulants in which have not been immersed samples). All extractions were

carried out under the same conditions. Released substances mass from the sample into simulant, was gravimetrically determined by evaporation of the stimulant and weighing the residue. Results were expressed as mg/dm<sup>2</sup> or mg/kg (ppm).

Calculation:

$$M = (m - m_1) / V * 1000, \text{ where:}$$

- M = overall migration (mg/L);
- m = mass released by sample (mg);
- m<sub>1</sub> = mass released by control sample (mg);
- V = extraction liquid volume evaporated (mL).

Results of overall migration are expressed in mg/dm<sup>2</sup>.



Table 2 Results of overall migration in isooctane

No.	Sample	Overall migration (mg/dm <sup>2</sup> )
1.	S <sub>1</sub> a	1,0
2.	S <sub>1</sub> b	1,16
3.	S <sub>1</sub> c	0,83
4.	S <sub>2</sub> a	0,75
5.	S <sub>2</sub> b	1,0
6.	S <sub>2</sub> c	1,16
7.	S <sub>3</sub> a	1,66
8.	S <sub>3</sub> b	0,92
9.	S <sub>3</sub> c	1,25
10.	S <sub>4</sub> a	0,92
11.	S <sub>4</sub> b	1,16
12.	S <sub>4</sub> c	1,33
13.	S <sub>1</sub> bz <sub>2</sub>	0,83
14.	S <sub>1</sub> cz <sub>2</sub>	0,66
15.	S <sub>3</sub> bz <sub>2</sub>	1,83
16.	S <sub>3</sub> cz <sub>2</sub>	1,50

Overall migration limit imposed by current regulations, respectively G.D. no.1197/2002 for approving the Norms regarding materials and objects intended to come into contact with food, is 10 mg/dm<sup>2</sup> or 60 ppm (mg of released compounds/kg of food); analytical tolerance is +3 mg/dm<sup>2</sup>.

The values of overall migration into olive oil stand at a higher level in the S1, S2, S3 and S1bz series. The lowest values are observed for samples S3b, S4a, S4b, S3bz and s3cz.

The values of overall migration into isooctane are not significantly different, all values obtained being at a level lower than 2.0 mg/dm<sup>2</sup>.

Most values of overall migration into olive oil are higher than those obtained into isooctane. These can be explained by the high capacity of petroleum ether extraction (Soxlet extractor).

In conclusion, overall migration values into fatty simulants, for all paper samples analyzed are below the limit of 10 mg/dm<sup>2</sup> (+ 3 mg/dm<sup>2</sup> analytical tolerance).

### 3. Organoleptic testing of paper samples

Test conditions for analyzed materials followed the standard SR EN 1230-1/2010 Paper and board intended to come into contact with foodstuffs. Sensory analysis. Part 1: Odor.

#### Principle method

Samples of tested material are preserved in glass jars for 20 up to 24 hours at room temperature (23 °C ± 2 °C), in the dark. Odor of the air is estimated by a panel of selected evaluators. Odor intensity is assessed on a scale of 0 to 4.

Organoleptic tests didn't show any odor modifications for all tested paper samples.

### 4. Analyzing the compliance of the papers with environmental requirements

Determination of lead, cadmium, mercury and total chromium content from final products included:

- Mineralization of the paper sample in the microwave oven (65% HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>);
- Analysis of the metals by atomic absorption spectrometry.

For the analysis of lead, cadmium and total chromium was used an atomic absorption spectrometer with graphite furnace "AAAnalyst 600".

For the analysis of mercury was used an atomic absorption spectrometer equipped with a cold vapors generation MSH system.

The results of heavy metals content (lead, cadmium, total chromium and mercury) and also the ash content are shown in Table 3.

Table 3 Results of heavy metals content analysis and ash content

No.	Sample	Heavy metals content								Ash content (%)
		Pb		Cd		Cr (total)		Hg		
		mg/dm <sup>2</sup>	ppm	mg/dm <sup>2</sup>	ppm	mg/dm <sup>2</sup>	ppm	mg/dm <sup>2</sup>	ppm	
1.	S <sub>1</sub> a	0.0007	0.979	0.3•10 <sup>-5</sup>	0.004	<LOD *	<LOD*	<LOD *	<LOD*	0.413
2.	S <sub>1</sub> b	0.0021	2.840	1.58•10 <sup>-5</sup>	0.021	0.0018	2.469	<LOD *	<LOD*	0.530
3.	S <sub>1</sub> c	0.0029	3.850	0.9•10 <sup>-5</sup>	0.012	0.0048	6.377	0.67•10 <sup>-5</sup>	0.009	0.854
4.	S <sub>2</sub> a	0.0013	1.764	5.25•10 <sup>-6</sup>	0.007	6.68•10 <sup>-5</sup>	0.089	<LOD *	<LOD*	0.459
5.	S <sub>2</sub> b	0.0023	3.039	6.6•10 <sup>-5</sup>	0.088	0.0014	1.883	0.45•10 <sup>-5</sup>	0.006	0.753
6.	S <sub>2</sub> c	0.0020	2.667	3.75•10 <sup>-6</sup>	0.005	<LOD *	<LOD*	1.06•10 <sup>-4</sup>	0.142	0.752
7.	S <sub>3</sub> a	0.0011	1.508	7.5•10 <sup>-7</sup>	0.001	<LOD *	<LOD*	<LOD *	<LOD*	0.346
8.	S <sub>3</sub> b	0.0018	2.503	1.5•10 <sup>-5</sup>	0.020	0.0011	1.483	6.22•10 <sup>-5</sup>	0.083	0.705
9.	S <sub>3</sub> c	0.0030	4.205	4.05•10 <sup>-5</sup>	0.054	0.0032	4.239	3.37•10 <sup>-5</sup>	0.045	1.330
10.	S <sub>4</sub> a	0.0022	2.923	4.5•10 <sup>-6</sup>	0.006	0.0004	0.606	2.4•10 <sup>-5</sup>	0.032	0.452
11.	S <sub>4</sub> b	0.0048	6.434	2.25•10 <sup>-6</sup>	0.003	0.0036	4.887	2.7•10 <sup>-5</sup>	0.037	0.717

Table 3 (continuation)

12.	S <sub>4</sub> c	0.0037	4.972	<LOD *	<LOD*	0.0029	3.924	1.25•10 <sup>-4</sup>	0.167	0.647
13.	S <sub>1</sub> bz <sub>2</sub>	0.0021	2.737	0.6•10 <sup>-5</sup>	0.008	0.0031	4.203	6.07•10 <sup>-5</sup>	0.081	1.820
14.	S <sub>1</sub> cz <sub>2</sub>	0.0041	5.531	1.9•10 <sup>-4</sup>	0.256	0.0061	8.116	7.8•10 <sup>-5</sup>	0.105	1.758
15.	S <sub>3</sub> bz <sub>2</sub>	0.0016	2.201	8.25•10 <sup>-6</sup>	0.011	0.0027	3.676	2.77•10 <sup>-5</sup>	0.037	2.502
16.	S <sub>3</sub> cz <sub>2</sub>	0.0013	1.806	0.9•10 <sup>-5</sup>	0.012	0.0012	1.610	1.29•10 <sup>-4</sup>	0.172	1.765

\*LOD – Detection limit for: Cd – 0.2 ppb; Cr – 1.3 ppb; Hg – 4.0 ppb

Evaluation of the results can be made referring to:

- SR CR 13695-1: 2002 Standard, Annex D3; for the maximum content of the 4 heavy metals in the final product the standard specify the following limits: Pb < 50 ppm; Cd < 0.4 ppm ; Cr (total) <10 ppm ; Hg< 0.5 ppm;
- G.D. no. 621/2005 and Directive 94/62/CE with amendments; the sum of the 4 heavy metals content is 100ppm.

Ash content was analyzed following SR ISO 1171:1994 (calcinations 1 hour at 525 °C). Very small values showed in Table 3 indicate that organic materials content is higher than 50 %, which means a good energy recovery potential according to SR EN 13431:2005.

Also, heavy metals content can be reported to the QM values (Table 4) established in CoE Res AP (2002) 1 - TD 2. QM is relevant to the restriction for food contact approval from EFSA, BfR XXXVI Recommendation and FDA.

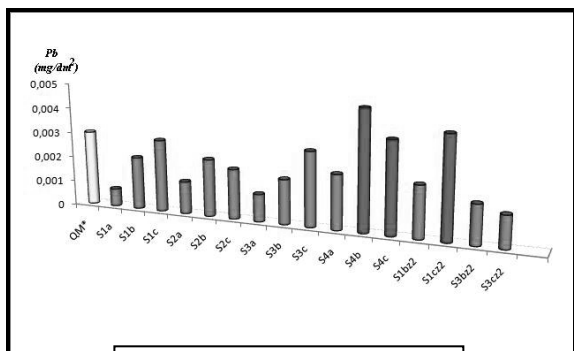


Fig. 1 Lead content

Table 4 Restriction limits (QM) for Cd, Pb and Hg

Metal	Restriction limit in paper and board (mg/dm <sup>2</sup> )
Cadmium (Cd)	0.002
Lead (Pb)	0.003
Mercury (Hg)	0.002

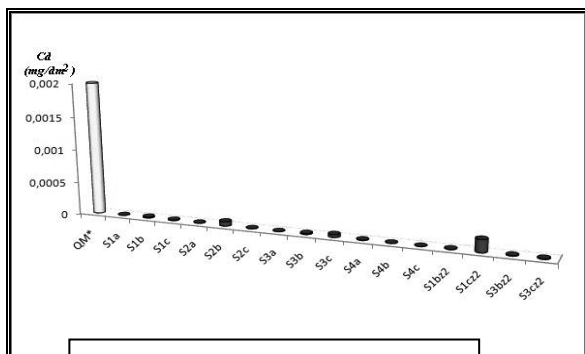


Fig. 2 Cadmium content

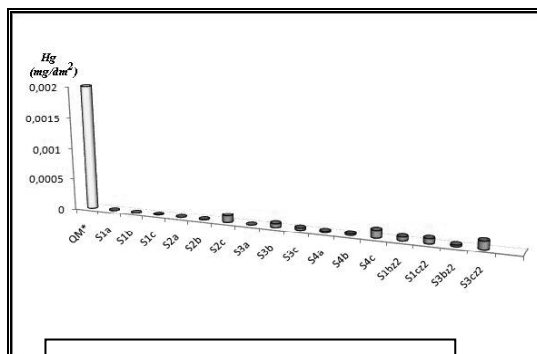


Fig.3 Mercury content

## CONCLUSIONS

- Given the destination of greaseproof papers was analyzed the overall migration into fatty food simulants and was observed for all samples that overall migration is bellow the limit of 10 mg/dm<sup>2</sup> (+ 3 mg/dm<sup>2</sup> analytical tolerance), according to G.D. no. 1197/2002.
- According to CoE Res AP (2002) 1- TD 2, the content of the 3 heavy metals are bellow QM limits, excepting lead (3 values slightly exceed the limit of 0.003 mg/dm<sup>2</sup>).
- The values of heavy metals content and ash content of analyzed paper samples satisfy the requirements of these regulations, ensuring a high level of environment protection

## ACKNOWLEDGEMENTS

The financial support of “ Partnerships in priority areas” Program 4, by means of project no. 52-169/2008 for achieving this contribution is gratefully acknowledged.

## REFERENCES

- [1] Birgit A.. Migration of substances from paper and board food packaging materials. *Academic dissertation*. Helsinki. 2001.
- [2] \*\*\* Alternatives to manufacture packaging for compliance with European requirements. *Final Report*. 2006.
- [3] \*\*\* Paper and Board Food Contact Materials. TemaNord 2008:515 © Nordic Council of Ministers. Copenhagen. 2008.
- [4] \*\*\* Technical document No. 2 Testing conditions and methods of analysis for paper and board intended to come into contact with foodstuffs. 9.3.2001 available in www-form: [URL:http://www.coe.fr/soc-sp/sante/pack/pres.htm](http://www.coe.fr/soc-sp/sante/pack/pres.htm)

## STUDIES REGARDING THE INFLUENCE OF SOME ENDOGENOUS FACTORS ON PAPER AGEING

Petronela Nechita<sup>1</sup>, Maricica Burlacu<sup>1</sup>, Nicoleta Melniciuc<sup>2</sup>

<sup>1</sup>*Pulp and Paper Research and Development Institute – CEPROHART SA Brăila, Romania*

<sup>2</sup>*Alexandru Ioan Cuza University of Iași, Romania*

*Author correspondence: Pulp and Paper Research and Development Institute – CEPROHART SA Brăila, Romania, tel: +40239 619741, email: [petronela.nechita@ceprohart.ro](mailto:petronela.nechita@ceprohart.ro)*

### Abstract

The problem of documents restoration has a high importance for conservation and preservation of cultural heritage. Durability of organic media documents especially of those based on cellulose structures is a complex area, the inherent paper instability leading to very serious effects from a historical and documentary perspective, regarding the book collections and documents, manuscripts or printed.

The objective of this paper was to investigate the effect of endogenous factors (fillers, sizing, surface treatments of paper using various additives) on paper ageing in different conditions. The experiments were accomplished on laboratory samples, for paper ageing evaluation being used the following methods: dry heat treatment at 105°C (24, 48 and 72 hours) according with SR ISO 5630 – 1 and treatment on sulphur dioxide vapors (10 mg/m<sup>3</sup>) for 24, 48, 72 and 96 hours. The obtained results have revealed that: the papers neutral-alkaline sized present the better stability on pollutants used in the experimental programme; using the polyamidamineepichlorhidryne resin as retention agent in paper composition has a slight effect on increasing of paper stability subjected on heat treatments; the surface treatment of paper with different additives has a protective effect against the action of polluting factors, the coating layer structure preventing the diffusion of polluted gases into paper structure, both by closing of surface pores and acidity neutralizing reactions. Based on registered results can be concluded that these treatments can be used in the consolidation and restoration of documents based on cellulose fibres.

**Key words:** *Paper ageing, Endogenous factors, Fillers, Sizing, Surface treatments*

### Rezumat

Problema restaurării documentelor este de importanță primordială pentru conservarea și păstrarea patrimoniului cultural. Durabilitatea documentelor pe suporturi de natură organică și în particular a celor pe structuri celulozice reprezintă un domeniu complex, instabilitatea inerentă a hârtiei conducând la efecte deosebit de grave din perspectivă istorică și documentară, la nivel de colecții de carte și documente, manuscrise sau tipărite. Cercetările efectuate în această lucrare au avut ca obiectiv evaluarea efectului factorilor endogeni (materiale de umplere, grad de înclieiere tratamente la suprafață cu diverși aditivi) asupra rezistenței la îmbătrânire a hârtiei. Experimentele s-au realizat pe probe de laborator, iar pentru evaluarea rezistenței la îmbătrânire a hârtiei s-au folosit următoarele metode: tratament cu căldură uscată la 105°C (24, 48, 72 ore), cf. SR ISO 5630 – 1 și tratamente în atmosferă de vapori de dioxid de sulf 10 mg/m<sup>3</sup> timp de 24, 48, 72, 96, ore. Rezultatele obținute au evidențiat faptul că tratarea hârtiei la suprafață cu diverși aditivi are efect protectiv față de acțiunea factorilor poluanți, structura stratului de acoperire împiedicând difuzia vaporilor gazelor poluante în structura foii, atât prin închiderea porilor de la suprafață în primă fază, cât și prin reacții de neutralizare a acidității. Aceste tratamente pot fi utilizate în procesul de consolidare și restaurare a documentelor pe bază de fibre celulozice.

**Cuvinte cheie:** *Îmbătrânirea hârtiei, Factori endogeni, Materiale de umplere, Înclieiere, Tratamente la suprafață*

### INTRODUCTION

Any grade of paper is subjected to the natural ageing process, but the degradation degree have large variations, depending on the causes and influences that determine this phenomenon. In addition to the cellulose fibres ageing, during development of this process act positively and negatively some factors that can be divided into two main groups: *endogenous or internal* factors that are determined mainly by the raw materials type, additives and manufacturing conditions, and *exogenous or external* factors that are determined by outside influences of paper. [1]

The paper is inevitably subject to a degradation process, the important being its development speed. To increase of papers life is well known the influence factors, both internal and external, in order to take the measures to limit their negative action. [2]

### EXPERIMENTAL

The experimental program carried out aimed to evaluate the effect of fillers, sizing agents and surface treatments with various additives on paper durability.

Tests have been carried out on paper samples with different compositions obtained in laboratory. [3]

#### Materials and methods

Paper samples with different charges of filler and sizing agent have been obtained as hand sheets with a basis weight of 80 g/m<sup>2</sup>, on the Rapid Kothen sheet former according to the provisions of STAS 6095/3:1990.

For surface treatments the hand sheets obtained as above have been surface treated with solutions of oxidized starch, carboxymethylcellulose, polyvinyl alcohol and chitosan.

#### - papers with different charges of filler

Composition	RF0	RF5	RF10	RF15	RF 20
Bleached softwood kraft pulp (28 – 30°SR)	70	70	70	70	70
Bleached hardwood kraft pulp (32 – 34°SR)	30	30	30	30	30
Retention agent, Kymene 611, p.c.	1,5	1,5	1,5	1,5	1,5
Filler, CaCO <sub>3</sub> (GCC)	0	5	10	15	20

#### - papers with different charge of sizing agent

Composition	Ref.	RFAq 5	RFAq 10	RFAq 15	RFAq 20
Bleached hardwood kraft pulp (28 – 30°SR)	70	70	70	70	70
Bleached softwood kraft pulp (32 – 34°SR)	30	30	30	30	30
Retention agent, Kymene 611, p.c.	1,5	1,5	1,5	1,5	1,5
Filler, CaCO <sub>3</sub> (GCC)	15	15	15	15	15
Sizing agent, Aquapel 610 D (alkyl dimer ketene)	0	0,5	1,0	1,5	2,0

#### - surface treated papers with different additives

Sample	Bleached softwood kraft pulp (28–30°SR)	Bleached hardwood kraft pulp (32–34°SR)	Retention aid, Kymene 611	Filler, ground CaCO <sub>3</sub>	Sizing aid, Aquapel 610 D (alkyl dimer ketene)
Base paper RF	70	30	-	-	-
Base paper RFAq15	70	30	1,5	15	1,5
RFAM	Surface treatment with sol.6% of oxidized starch (2 – 4 g/m <sup>2</sup> )				
RFCCM	Surface treatment with carboxymethylcellulose CMC (Blanose 7M1) Sol. 10% (2 – 4 g/m <sup>2</sup> )				
RFPVA	Surface treatment with polyvinyl alcohol, Sol. 10% (2 – 4 g/m <sup>2</sup> )				
RFCh	Surface treatment with chitosan , sol.6% (2 – 4 g/m <sup>2</sup> )				

#### Methods of degradation

For paper samples obtained in laboratory the following treatments have been applied:

**- dry heat treatment at 105°C (24, 48, 72 hours), according to SR ISO 5630 – 1, Paper and board – Part 1: Dry heat treatment at 105°C**

Before and after each series of treatments the physical-mechanical and chemical characteristics of tested paper samples have been evaluated, as follows:

- Tensile strength /breaking length according to SR ISO 1924-2:1996
- Double folding strength according to SR ISO 5626:1996

**- maintaining in sulphur dioxide atmosphere (10 mg/m<sup>3</sup>) for 72 and 96 hours**

Before and after each series of treatments physical-mechanical and chemical characteristics of the tested paper samples, as follows:

- Tensile strength/breaking length, according to SR ISO 1924-2:1996
- Double folding strength according to SR ISO 5626:1996
- Water absorption, Cobb60, according to SR EN 20535:1996

## RESULTS AND DISCUSSIONS

### 1. Papers with different charges of filler

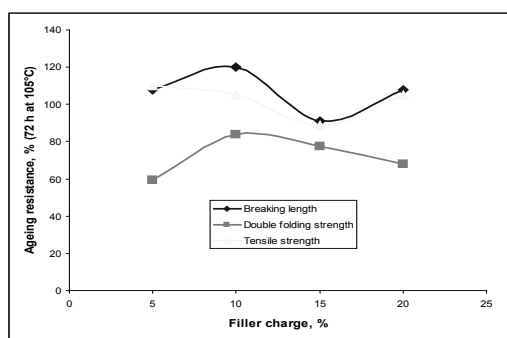
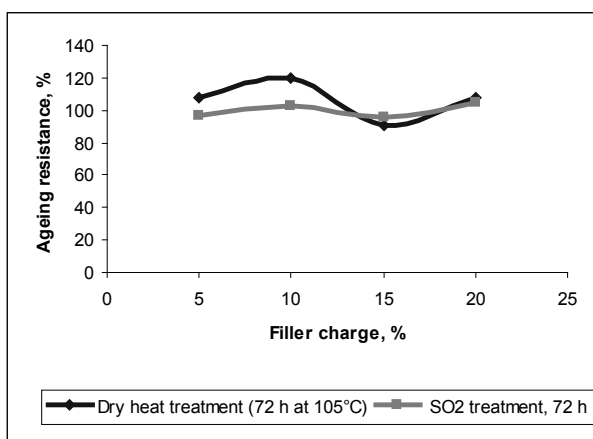


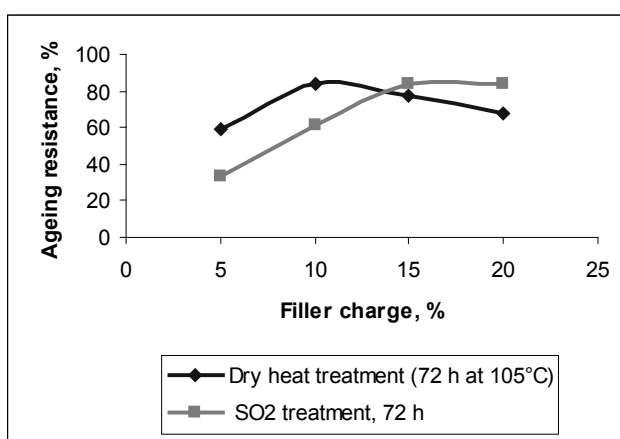
Fig. 1 Ageing resistance (72 h at 105°C) of paper samples obtained as hand sheets versus GCC charge

As is presented in figure 1, can be observed the positive effect of addition of GCC on the paper durability. After keeping of 72 hours at 105°C, some characteristics of mechanical strength (tensile strength and breaking length) have greater values than reference sample (RF 20). This behaviour may be due to the presence in the samples paper composition of polyamidamineepichlorhidryne resin which have cross linking effect on this temperature (105°C). This behaviour leads to paper „maturation” and to obtain better strength properties.

Regarding the influence of filler charge on paper durability under pollutants gases action, in figure 2 a) and b) is presented a comparison between the results obtained after treatments of paper samples under sulphur dioxide atmosphere and after heat treatments.



a)



b)

Fig. 2 The evolution of ageing resistance of paper samples under different conditions versus filler charge: a) Breaking length, b) Double folding strength

Can be observed from these graphics, on the one hand the action of pollutant gases on paper degradation is more pronounced than the heat treatment, on the other hand the presence of fillers

in paper samples composition gives it the better stability under attack of exogenous factors.

Analyzing the evolution of pH can be observed that the sulfur dioxide treatment is without significant reduction in pH value, maintaining its value in the range of 8.8 – 9.14. This behavior leads to the conclusion that the paper containing filler base on GCC has a better stability under the influence of environmental factors.

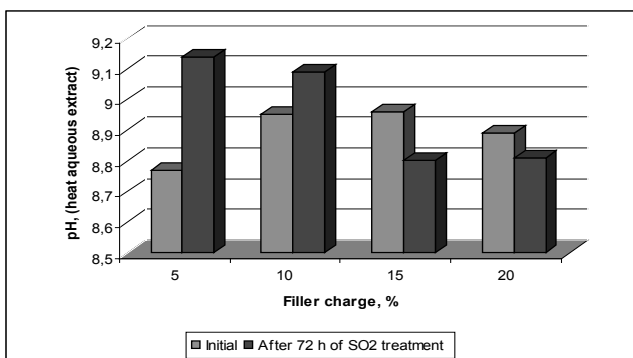


Fig. 3 The pH evolution of paper samples subjected on pollutant gases attack versus filler charge

### 2. Papers with different charge of sizing agent

It is noticed that the dry heat treatment has the most pronounced effect on the double folding strength, that registered the highest decrease at 48 h maintaining at 105°C, regardless sizing agent charge. (figure 4)

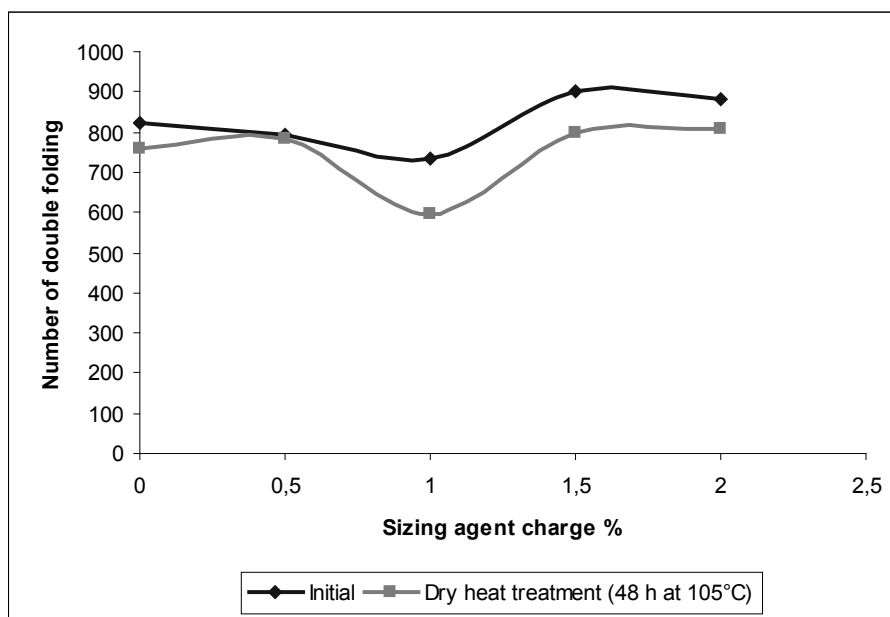


Fig.4 The evolution of double folding strength versus sizing agent charges of paper samples subjected on dry heat treatment

Analyzing the overall influence of sizing agent addition on the paper samples durability, can be seen that used sizing system (neutral – slightly alkaline) offers a good stability of papers under the action of degradation factors.

Using the polyamidamineepichlorhidryne resin in paper samples composition, (Kymene 611), resulted in the higher stability of papers subjected to accelerated ageing. This behaviour

can be explained (as above mentioned) by that the resin takes the destructive action of heat treatment, having a protective role.

Figures 5 and 6 present the results of pH and water absorption characteristics of paper samples exposed to sulphur dioxide treatment for 24, 48 and 72 hours.

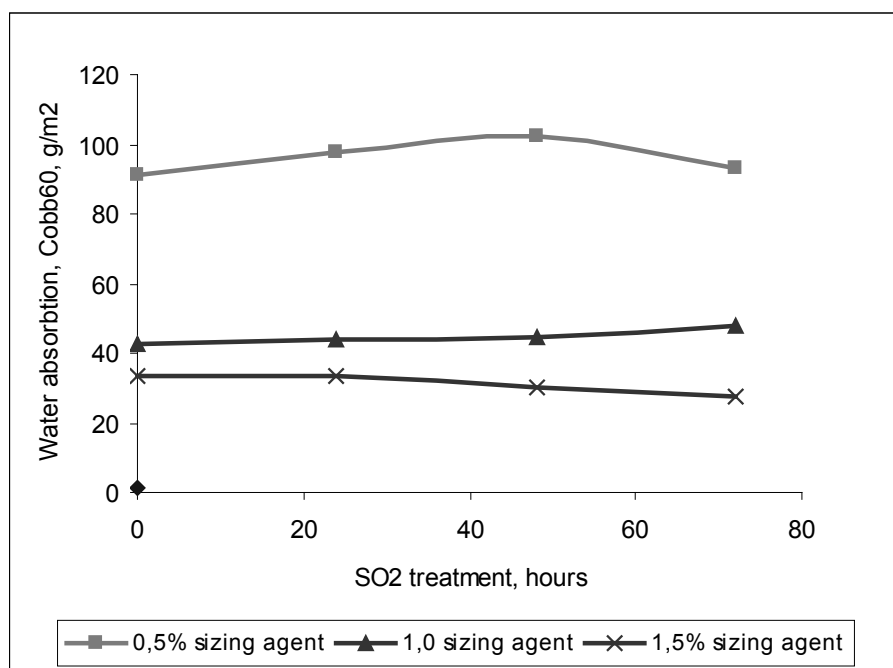


Fig.5 The influence of SO<sub>2</sub> treatment on the sizing degree of paper

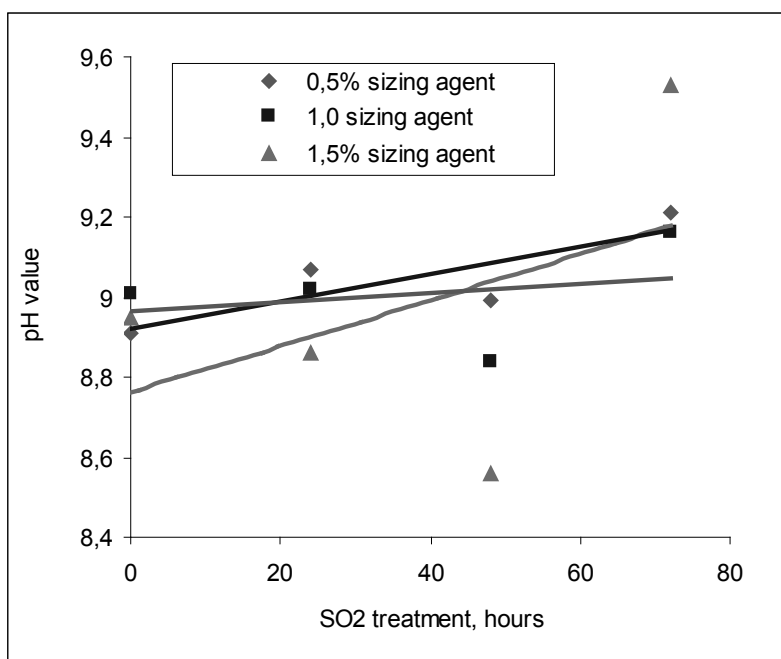


Fig.6 pH evolution of paper samples subjected on SO<sub>2</sub> treatment

Generally, the paper samples subjected to different treatments of accelerated ageing, register a decrease of sizing degree and pH. Besides the nature of pollutants, these phenomena are influenced by the pH of papermaking process. In our case, the paper samples were obtained under neutral alkaline pH, making them more stable under pollutants action, as shown in figures 5 and 6.

Regarding the influence of sizing agent

addition on the mechanical strength of paper samples subjected on SO<sub>2</sub> treatment, is illustrated in figure 7 that the breaking length of tested paper samples is not greatly affected after 72 hours of treatment with SO<sub>2</sub>. The addition of 0,5% and 1,0% of sizing agent, has as result a slight increase of this parameter. This fact is due to the presence of polyamidamineepichlorhidryne resin in paper samples composition.

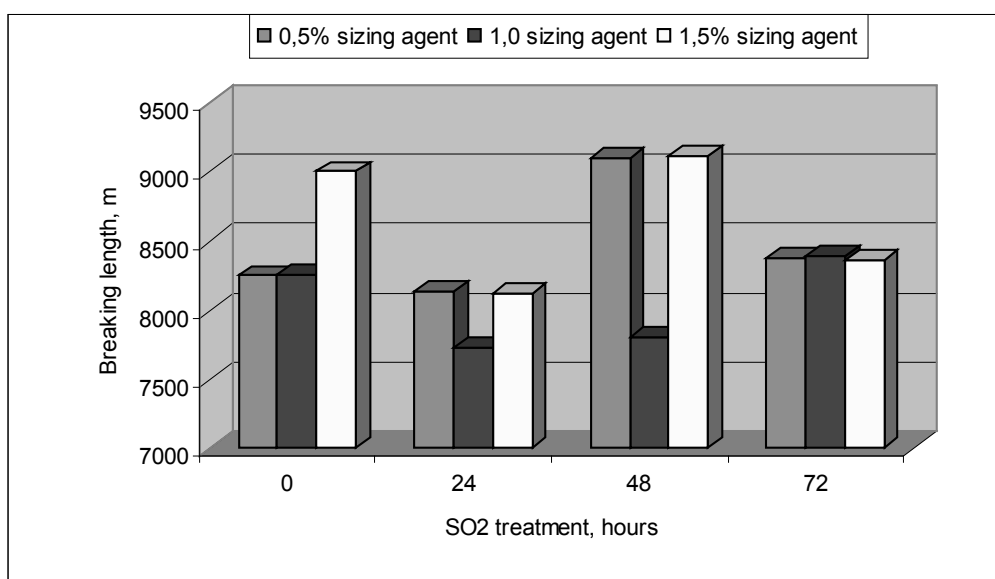


Fig.7 Breaking length evolution versus sizing agent addition and duration of SO<sub>2</sub> treatment



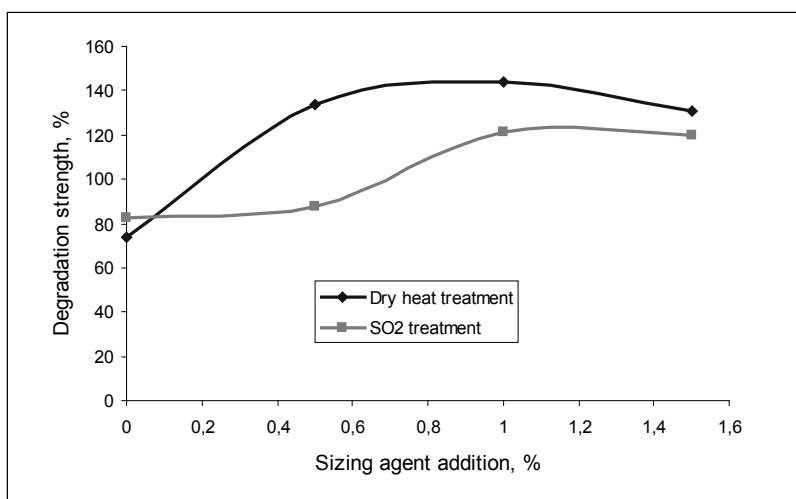


Fig. 8 The influence of ageing treatment on the paper degradation (double folding strength)

Analyzing the influence of different ageing treatments on paper samples with different levels of sizing, it appears that the treatment with SO<sub>2</sub> has a more pronounced influence on the paper degradation.

### 3. Surface treated papers with different additives

#### Accelerated ageing by dry heat treatment

Analyzing the results presented in figures 9 and 10, it is noticed that paper surface treatments provide a slight improvement of durability as the strength characteristics of samples subject to accelerated ageing treatments by dry heating register higher values than treatment free samples.

Can be emphasized that the surface treatments of paper with CMC and chitosan additives are efficient for improving of paper stability on heating processes (especially in case of number folding preservation). But, it is important to underline that properties of the initial base paper – paper sized in neutral-alkaline medium, containing calcium carbonate as a filler and alkyl-dimer-ketene as a sizing aid - provided a higher ageing strength, a better efficiency of surface treatments, respectively. [4]

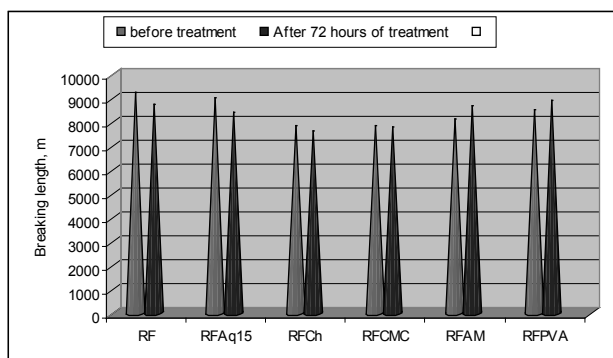


Fig. 9 Influence of heat process on breaking length of paper samples surface treated with various additives

#### Accelerated ageing by SO<sub>2</sub> pollution

Sulphur dioxide is an acid gas that is transformed on water vapors and time in H<sub>2</sub>SO<sub>4</sub> – the strong acid that has negative effects on archive documents.

The surface treated samples and references were subjected on sulphur dioxide atmosphere for 72, and 96 of hours.

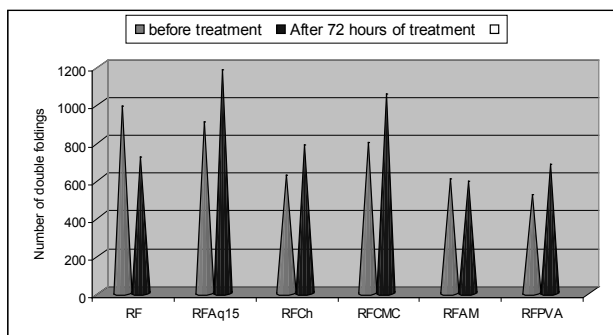


Fig. 10 Influence of heat process on double folding of paper samples surface treated with various additives

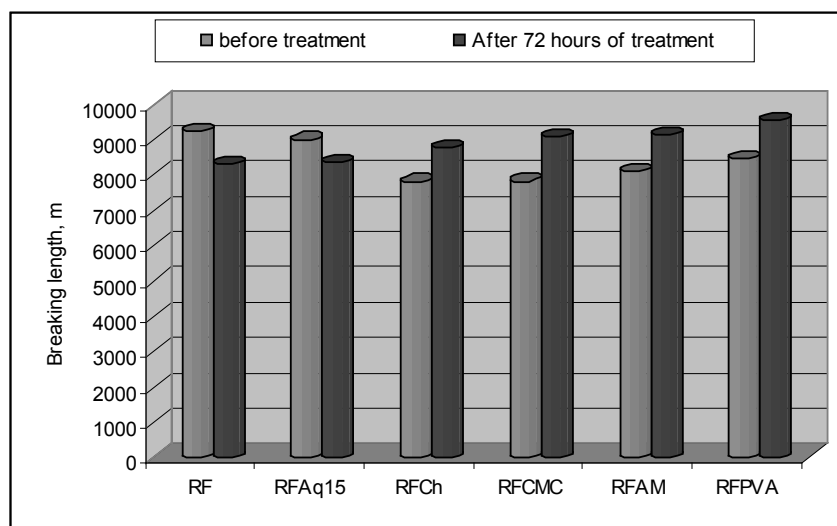


Fig.11 Influence of sulphur dioxide treatment on breaking length of paper samples surface treated with various additives

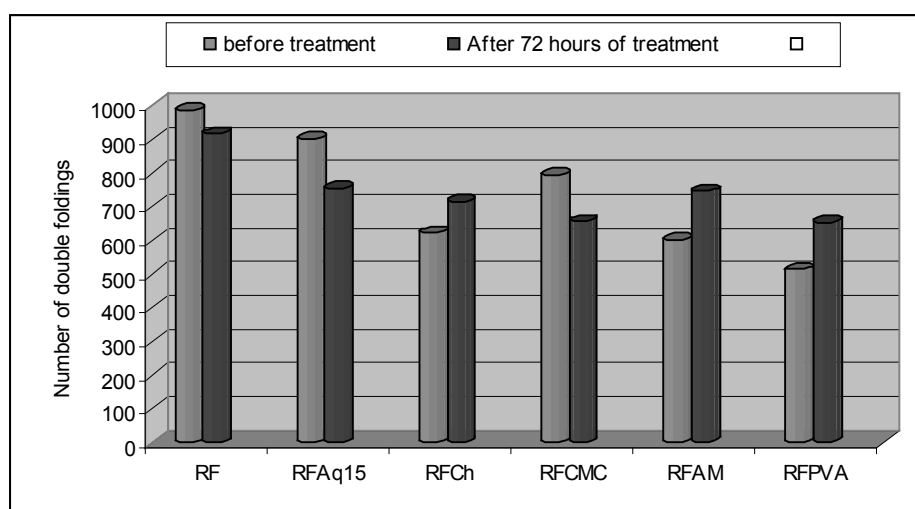


Fig.12 Influence of sulphur dioxide treatment on double folding of paper samples surface treated with various additives

It is noticed that, sulphur dioxide atmosphere ageing less affected the mechanical strength properties of surface treated paper samples. If the ageing resistance of references is about 90 - 93%, for all the samples surface treated, the ageing resistance is 98 ÷ 120%. (figure 11 and figure 12).

The results suggest that the surface treatments have a protective effect versus pollutant action of sulphur dioxide vapors. Therefore the coating layer structure is affected by acidity (the water absorption is increased – figure13), the coating layer preventing the vapors diffusion in the sheet structure, both by closing the surface pores in the first stage and by the neutralization reactions of acidity.

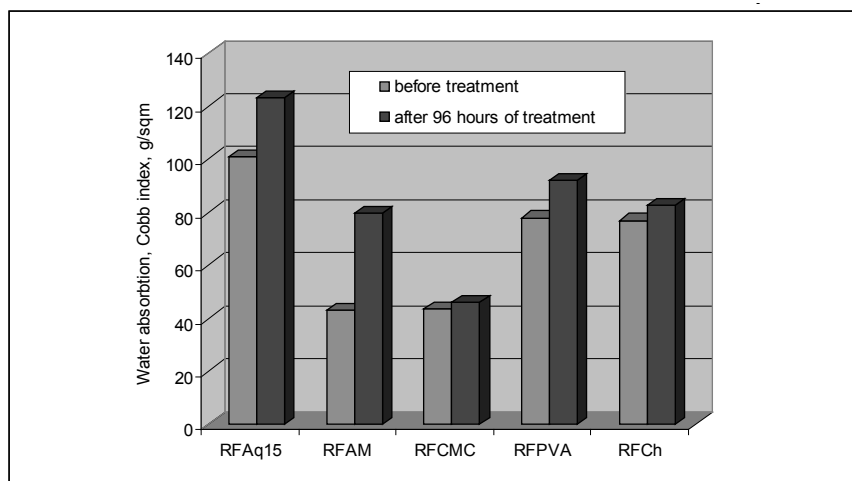


Fig.13 Development of sizing degree concerning paper samples surface treated with various additives in line with the time of maintaining in sulphur dioxide atmosphere

### CONCLUSIONS

- Paper durability is influenced directly by the technological parameters of manufacturing process (fibrous material, pH, additives etc.)
- The neutral/alkaline sized papers (that contain GCC as filler and AKD as sizing agent) have a better stability under the action of pollutants that were studied within the experimental program;
- Use of polyamidamineepichlorhidryne resin as retention agent have a slight effect of increasing the paper stability under dry heat treatment.
- Paper ageing processes have been lead to decreasing of strength characteristics of references samples (without surface treatments- RF and RFAq15 samples) and moderate changes of these characteristics in case of surface treated samples; an efficient surface treatment for paper ageing is surface treatment with chitosan (natural polymer, biodegradable, bioactive and biocompatible);
- Paper surface treatments with various additives have a protective effect in relation to the action of pollutant factors, the coating layer structure preventing the diffusion of pollutant gas vapors in the sheet structure, both in closing the surface pores in the first stage, and through the neutralization reactions of acidity;

### REFERENCES

- [1] Dessauer, G. - Das Papier, 32 (10A) : V32-V38 (1978)
- [2] Poppel, E., Ciobanu, D. - Celuloză și Hârtie, 31 (3) : 46-49 (1982)
- [3] Nechita P., - *Report of PapRest - Research project* (contract no.9277/2008) – stage 3/2010, p. 22- 25.
- [4] Ardelean E., Asandei, D., Tanase M., Bobu E., - *Study on some resizing and consolidation methods of old papers support* – European Journal of Science and Theology, vol.3, no.3, (2007), p.53-61

## OPPORTUNITIES FOR A SUSTAINABLE DEVELOPMENT OF THE WOOD BIOMASS SECTOR

Mihaela Begea<sup>1</sup>, Sevastita Vraciu, Corina Berkesy

*ICPE Bistrița SA*

*Author correspondence: <sup>1</sup> ICPE Bistrița SA Strada Parcului 7, Bistrița, Romania, [ela\\_begea@yahoo.com](mailto:ela_begea@yahoo.com)*

### Abstract

Pathway to succeeding 2020 target to produce 20% of the energy from renewable sources depends on SMEs and potential investors that need a clear vision regarding the future of renewable energy sector. Apart from reduction of administration burden and stable support schemes, awareness raising activities and introduction of innovative business models will increase the number of successful projects in the field of production of energy from renewable sources. The paper presents the solutions proposed by the consortium of BiomassTradeCenter2 project in order to support the development of common European biomass market and development of strong bio-based industry and energy supply through market orientated actions for target groups along biomass production chains. Mobilising more wood is a general effort, which requires the cooperation of all relevant actors – forest services, forest owner groups, forest industry, energy producers, market actors and decisions makers.

**Key words:** *Renewable resources, Sustainable development, Biomass*

### Rezumat

Căile pentru reușita obiectivelor 2020 propuse, de producere a 20% din energie din surse regenerabile, depind în mare măsură de IMM-uri și potențialii investitori, care trebuie să aibă o viziune clară privind viitorul sectorului energiei regenerabile. În afară de simplificarea demersurilor administrative și de schemele de sprijin stabile, activitățile de conștientizare și de sensibilizare în favoarea introducerii unor modele de afaceri inovatoare pot contribui la creșterea numărului de proiecte de succes în domeniul producției de energie din surse regenerabile.

În ciuda volumului semnificativ de activitate depusă la nivel politic referitoare la mobilizarea sectorului de biomasă din lemn la nivel european, precum și la nivel național, există în continuare provocări care trebuie abordate pentru o mobilizare de succes. Cele mai importante provocări sunt: procedurile administrative greoaie, lipsa informațiilor adecvate și sprijinul de specialitate pentru potențialii investitori în domeniul producției de biomasă, furnizarea nesigură de biomasă produsă la nivel local și regional și la conștientizarea slabă a consumatorilor de energie cu privire la beneficiile utilizării energiei din surse regenerabile.

Lucrarea prezintă soluțiile propuse de consorțiul proiectului BiomassTradeCenter2 în scopul de a sprijini dezvoltarea pieței comune europene de biomasă din lemn și dezvoltarea puternică a industriei bazate pe biotehnologie și furnizarea de energie pe piață, prin acțiuni orientate pentru diferite grupuri țintă de-a lungul lanțurilor de producție de biomasă.

Mobilizarea lemnului ar trebui să reprezinte un efort general, care necesită cooperarea tuturor actorilor relevanți - servicii forestiere, grupuri proprietar forestiere, industria forestieră, producătorii de energie, actorii de pe piață și factorii de decizie.

**Cuvinte cheie:** *Resurse regenerabile, Dezvoltare durabilă, Biomasă*

## INTRODUCTION

In spite all the significant work done at the policy level related to wood biomass mobilization on European level, as well as at the national level, there are still challenges to be addressed for a successful wood biomass mobilization.

Potential biomass is regionally distributed over Romania. Fuelwood and wood waste is mostly found in the Carpathians and Subcarpathians, while agricultural waste is available in the South Plain and Moldavia, and biogas in the South and Western plains. In the Renewable Energy Resource Assessment for Romania, the European Bank for Reconstruction and Development (EBRD) estimates the South Plain region most promising for the utilization of agricultural waste, and the Carpathian and Subcarpathian mountains as most promising for the development of district-heating plants from firewood and wood waste in a range of 1-6 MWth [1].

The most important challenges in the field of biomass utilization are the burdensome administration procedures, the lack of appropriate information and expert support for potential investors in the field of biomass production, the unsecure supply of biomass produce at the local and regional level, and low awareness of the energy users regarding the benefits of the use of energy from renewable sources.

The idea of BiomassTradeCenters2 project - Development of biomass trade and logistics centres for sustainable mobilisation of local wood biomass resources (IEE/10/115/SI2.591387) -was to improve the professional organization of wood fuels supply along wood biomass production chain from private forests and connecting stakeholders from the supply and demand sides.

The project will further develop the idea of its predecessor, the BiomassTradeCenters project. The main lesson learned from this project is that apart from a concept of trade and logistics centres, quality assurance and quality control (QA/QC) are decisive for a greater consumption of energy from biomass on the market. Given this, it also aims to implement biomass quality standards in biomass business, which will encourage the consumption and boost the biomass market.

The project addresses stakeholders along firewood and chips supply chain at regional scale and promote new biomass trade and logistics centres through market oriented activities like workshops, match-making events, study tours to

show cases, catalogue of regional wood producers and feasibility studies. Important new issues that will be addresses are quality assurance standards, sustainability criteria and their implementation in practice.

The project targets especially those that may find their business opportunity in wood biomass production, e.g. small forest owners and those already involved in biomass production, to further explore their market opportunities, e.g. move from mere biomass products to the organised distribution within the framework of trade centres or find their opportunity in energy contracting sector. Our target groups are fundamental subjects in order to mobilise wood biomass potentials, to bring quality biomass to the market and to balance supply and demand sides.

The BiomassTradeCenters2 project was to encourage quality in biomass use by building a simplified quality assurance and quality control (QA/QC) system for small wood biomass business and to create a proposal for labelling wood biomass to create awareness of the quality and efficiency of a local or regional biomass pathway (sustainability). In this respect, the project objective is to create a network of wood biomass laboratories that will help biomass producers and users to check wood biomass quality. In this respect an overview on needed steps for establishment of new biomass laboratories and first ideas about standard operation procedures for wood biomass quality measurements based on EU CEN technical specifications will be performed.

Finally, project partnership aims to elaborate an integrated solution for the whole chain in the biomass production – from biomass production, logistics and distribution of biomass products to energy contracting and ensuring quality control.

## TECHNOLOGICAL IMPLICATIONS

At present, the forest as a resource is not yet fully exploited. The growing enthusiasm for biomass must be combined with a determination to ensure that in future the forests continue to be cultivated in a sustainable manner and that wood as a raw material is used efficiently. Standards and regulations should continue to safeguard the quality standards of biomass products on the European level and the quality requirements are essential for ensuring that wood as an energy resource is used as efficiently as possible.

Romania is covered by 40% of agricultural land and 27% of forest and has great biomass potential, which is estimated at 88.000 GWh per year. In 2004, for example, about 43% of the biomass potential in the country was exploited and the entirety of that biomass potential went to the production of heat. Heat generated from wood biomass was approximately 54% and heat generated by agricultural biomass was about 46% [1].

The data from the Romanian Forestry Service ROMSILVA in 2010 are the following:

- the area managed - 3.69 million ha of forests, of which:
  - 3.26 million ha – public property;
  - 0.43 million ha – private property.
- the potential for exploitation for forest of public property is 10.8 mil. m<sup>3</sup>;
- the volume for exploitation – 9.3 mil. m<sup>3</sup>;
- the percentage of firewood is 38%;
- the percentage of small wood (branches etc.) is 6.4% .

Firewood and agricultural waste account for about 80% of the total waste. About 66% of the firewood and wood waste is located in the Carpathians and Sub-Carpathians, and about 58% of agricultural waste is located in the South Plain, West Plain, and Moldavia. Approximately 63700 square km of Romania is covered by forests, which is approximately 27% of the total land. The exploitable potential of the Romanian forests is estimated at 20000 cubic meters [2].

Large amounts of small-sized wood is obtained in wood industry, but utilization of this wood for energy purposes is insufficient due to difficulties related to gathering, processing and transportation. Studies show that these wood wastes are economically viable resources.

Plant debris and residues from wood processing could provide over 60% of alternative energy produced in Romania. Biomass energy potential, estimated at 7.6 million tons / year or 318000 TJ / year, representing about 19% of the total consumption of primary sources in Romania. [3]

Currently, biomass is used only for heating purposes, direct burning for cooking and hot water preparation. About 95% of the biomass currently used is firewood and agricultural waste, the rest is wood waste from industrial processes. The average installed capacity in sawmills is 3.3 MWth [1].

The use of biomass energy in Romania is presented below [4]:

- the entire amount was used to produce heat;
- 54% comes from biomass and 46% comes from agricultural waste;
- 89% with traditional combustion technologies in more than 14 million individual household stoves and ovens and 11% in relatively modern equipment;
- more than 550 industrial boilers and steam hot water with capacities between 0.7 to 7 MW (45 MW total);
- 7 urban locations for the production of woody biomass-based heat (38.9 MW);
- the possible development of biomass use at 140 PJ (3.35 million toe / year) at present to 112 PJ (2.675 million toe / year) in 2020.

As regards the Romanian legislation, the national authority in charge to implement the legislative package „Energy - climate change” is the Ministry of Economy, Trade and Business. The main tasks of this body are the following:

- to develop the strategy for recovery and promotion of renewable energy;
- to develop the national action plan in the field of renewable energy in the form established by the European Commission.

The main Romanian legislation as regards the renewable energy sources are the following:

- the Governmental decision 1884/2005 regarding the promotion of biofuels and other renewable fuels for transport (amended and supplemented);
- the Law 220/2008 regarding the system for promotion of energy production from renewable energy sources, as amended by Law No. 139 / July 7, 2010.

At European level, European standards for solid fuels are managed by Technical Committee CEN / TC 335, established in 2001. There are already developed or are at various stages of voting for standard projects and documents for all forms of solid fuel use in Europe, including wood chips, pellets and briquettes, logs, sawdust and straw bales. The standards developed describe the properties of fuel and moisture content, ash content, calorific value, size distribution, bulk density, mechanical strength of pellets and briquettes made of wood, carbon, hydrogen and nitrogen, sulphur and chlorine, etc. [3]

In Romania, within the Standards Association of Romania (ASRO) works the Technical Committee *TC 360 Characterization of waste and sludge*. In July 2010 the European Standard *EN 14 961 - Solid biofuels. Fuel specifications and classes*,

*first part - General requirements*, was approved. The following parts, which are currently being planned by the committee, will be most likely published at the end of this year and shall refer to wood pellets for use non-industrial (Part 2), wood briquettes for non-industrial use (Part 3), non-industrial use of wood chips (part 4), firewood for non-industrial use (Part 5), materials other than wood pellets for non-industrial use (Part 6). [3]

At present the Romanian producers of briquettes and pellets certify products qualitatively using German standards DIN 51731 (Testing of solid fuels - wood and bark compacted in its natural state - Pellets and briquettes - Requirements and test specifications) and DIN plus (Wood pellets used for small heating systems) or Austrian standard ÖNORM M 7135 (Densified wood and bark compacted in its natural state - Pellets and briquettes - Requirements and test specifications).

In meantime, the requirements for approval of Romanian certification bodies will be settled and the sustainability criteria and origin of biofuels and bioliquids will be designate during the third quarter of this year. In this respect, the referential Directive (CE) 28/2009 and the series of drafts of standard prEN 16214 (1-4) are translated, namely:

- EN 16214-1 - Sustainably produced biomass for energy applications — Principles, criteria, indicators and verifiers for biofuels and bioliquids — Part 1: Terminology;
- EN 16214-2 - Sustainably produced biomass for energy applications — Principles, criteria, indicators and verifiers for biofuels and bioliquids — Part 2: Conformity assessment including chain of custody and mass balance;
- EN 16214-3 - Sustainably produced biomass for energy applications — Principles, criteria, indicators and verifiers for biofuels and bioliquids — Part 3: Biodiversity and environmental aspects;
- EN 16214-4 - Sustainably produced biomass for energy applications. Principles, criteria, indicators and verifiers for biofuels and bioliquids. Calculation of the GHG emission balance associated with sustainable biofuels and bioliquids using a lifecycle approach.

The main goal of BiomassTradeCenters2 project in this direction is to prepare a system that will help to guarantee the solid biofuel quality through the whole supply chain, from the origin to the delivery of the solid biofuel and provide adequate confidence. With a proper quality assurance procedure and specification of origin and source

(i.e. kind of biofuel) in the whole production chain, it is possible to reduce or eliminate the parameters that need analyzing.

The EU CEN standards to be considered are the following:

- A. Regarding specifications and classes of the wood fuels
  - a. EN 14961-1:2010, Solid biofuels – Fuel specification and classes – Part 1: General requirements;
  - b. EN 14961-2:2011, Solid biofuels – Fuel specification and classes – Part 2: Wood pellets for non-industrial use;
  - c. EN 14961-3:2011, Solid biofuels – Fuel specification and classes – Part 3: Wood briquettes for non-industrial use;
  - d. EN 14961-4:2011, Solid biofuels – Fuel specification and classes – Part 4: Wood chips for non-industrial use;
  - e. EN 14961-5:2011, Solid biofuels – Fuel specification and classes – Part 5: Firewood for non-industrial use.
- A. Regarding the fuels quality assurance:
  - a. prEN 15234-1, Solid biofuels – Fuel quality assurance – Part 1: General requirements;
  - b. prEN 15234-2, Solid biofuels – Fuel quality assurance – Part 2: Wood pellets for non-industrial use;
  - c. prEN 15234-3, Solid biofuels – Fuel quality assurance – Part 3: Wood briquettes for non-industrial use;
  - d. prEN 15234-4, Solid biofuels – Fuel quality assurance – Part 4: Wood chips for non-industrial use;
  - e. prEN 15234-5, Solid biofuels – Fuel quality assurance – Part 5: Firewood for non-industrial use;
  - f. CEN/TR 15569:2009 - Solid biofuels - A guide for a quality assurance system.

Regarding the analysis on carbon foot prints, the calculations of CO<sub>2</sub> storage in wood fuels and estimation of emissions will be based on internationally agreed methodologies (e.g. PAS 2050, IPCC Good practice guidelines), and knowledge from the national project “The importance of forest based production chain for mitigation and adaptation to climate change” will be used.

Wood heating system manufactures, particularly those who produce small to medium scale devices, need that the wood fuels available on

the market meet the quality standards to which the heating appliances developed have been tested and certified.

## CONCLUSIONS AND FUTURE PROSPECTS

The main motivation for starting the BiomassTradeCenters2 project was the predicted future impact that promotion of new business opportunities in the field of wood biomass can have on the production and use of energy from renewable sources.

Apart from the concept of trade and logistics centres, quality assurance and quality control (QA/QC) are decisive for a greater consumption of energy from biomass on the market. Given this, it is important to implement biomass quality standards in biomass business, which will encourage the consumption and boost the biomass market. This will be also supported by the creation of a network of wood biomass laboratories that will help biomass producers and users to check wood biomass quality.

In the framework of the BiomassTradeCenters2 project a certification system will be established and promoted throughout European countries. By supporting establishment of new biomass trade centres – companies, established by (small) forest owners for distribution of their own biomass products, the use of locally and regionally produced biomass will be encouraged.

Additionally, more studies of alternative sources of wood biomass like forest residues, short rotation plantations, and small diameter wood from thinning operations should be carried out.

## ACKNOWLEDGEMENTS

This paper presents the results of the project BiomassTradeCentre2 “Development of biomass trade and logistics centres for sustainable mobilisation of local wood biomass resources” (Contract IEE/10/115/SI2.591387). The project is co-funded by the EU in the framework of Intelligent Energy – Europe Programme.

## REFERENCES

1. European Bank for Reconstruction and Development (EBRD) Renewable Development Initiative – Romania country profile. Available online at: <http://ebrdrenewables.com/sites/renew/countries/Romania/default.aspx>.
2. Intelligent Energy Europe - Report on the Perspectives to the Development of the Biomass Potential. Accelerated Penetration of Small-Scale Biomass and Solar Technologies, 2005.
3. Iorga, Diana (2010). *Solid biofuels. Review Standardizarea*, March 2011, 34.
4. Solovastru, Valerian (2010). *Biomass for 2<sup>nd</sup> and 3<sup>rd</sup> generations. Guidelines on certification and standardization of biomass*. The 3<sup>rd</sup> International Conference Bioenergy in Romania, RENEXPO, Bucharest 24 November 2010. Available online at: [www.renexpo-bucharest.com](http://www.renexpo-bucharest.com).
5. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.



## POSSIBILITIES OF BIOREFINING OF SOME SECONDARY PRODUCTS RESULTED FROM BAST FIBERS PROCESSING

Iulian-Andrei Gîlcă<sup>1</sup>, Adrian-Cătălin Puițel<sup>1</sup>, Valentin I. Popa<sup>1</sup>

<sup>1</sup> *Universitatea Tehnică „Ghorghe Asachi” din Iași, România, Facultatea de Inginerie Chimică și Protecția Mediului*

*Author correspondence: <sup>1</sup> Facultatea de Inginerie Chimică și Protecția Mediului, Iași, vipopa@ch.tuiasi.ro*

### Abstract

It is well known that byproducts resulted from bast fiber (flax, hemp, jute) processing are used in energy production. Taking into account their chemical composition bast fiber processing waste could be processed step by step (biorefining) to recover some components. The paper presents some preliminary results obtained in glycerol organosolv fractionation of hemp processing waste. Glycerol is also a byproduct of biodiesel production from vegetable oil. By using this treatment it is possible to recover cellulosic fiber and lignin. The obtained pulp was analyzed to determine the delignification degree and the papermaking potential. The lignin, which is susceptible for hydroxymethylation and epoxidation to obtain nanoparticles, was recovered from the residual pulping liquor and subjected to analytic and spectral characterization.

**Key words:** *Bast fibers, Biorefining, Residual liquor, Biodiesel*

### Rezumat

Se știe că în prelucrarea fibrelor liberiene (cânepa și inul), pușderiile care rezultă ca produse secundare se utilizează în scopuri energetice. Având în vedere însă compoziția lor chimică, pușderiile ar putea fi supuse unui proces de prelucrare în trepte (biorafinare) care să permită recuperarea componentelor. În lucrare sunt prezentate unele rezultate preliminare privind fracționarea pușderiilor de cânepă printr-un procedeu organosolv bazat pe utilizarea glicerinei. Aceasta rezultă la rândul său la fabricarea biodieselului din uleiul unor plante oleaginoase. Prin aplicarea acestui tratament a fost posibilă recuperarea fibrelor celulozice și a ligninei. Celuloza obținută a fost caracterizată prin gradul de delignificare și în ceea ce privește potențialul sau papetar. Lignina recuperată din soluția reziduală de la dezincrustare cu posibilități de utilizare în reacții de hidroximetilare și epoxidare pentru obținerea de nanoparticule, a fost supusa investigațiilor analitice și spectrale.

**Cuvinte cheie:** *Fibre liberiene, Biorafinare, Leșie reziduală, Biodiesel*

## INTRODUCTION

Alkaline kraft pulping is the dominant chemical pulping process today, accounting for more than 80% of pulp production, but it has some serious shortcomings consisting in air, water pollution and high investment costs (Murinnen, 2000). Lower environmental impact, possibility of lignin and sugar recovery, easier solvent recovery and possibility of using a wide variety of organic solvents are considered advantages of organosolv

pulping processes over conventional ones (Saberikhan *et al.*, 2010; Wang *et al.*, 2010).

During hemp and flax processing about 70-80% of the initial raw material is removed as waste woody core (shives). The hemp woody core waste is generally used as fuel, building material manufacturing (gypsum and cement fiber board), animal bedding in agriculture, composting or landfilling (Dutta *et al.*, 2008).

Pulp and paper industry utilizes wood as pulping raw material. The interest towards using alternative fiber sources has increased as the paper demand is continuously increasing its production (Dandg *et al*, 2006).

The secondary product of pulping industry is the lignin contained by the black liquor. The black liquor is usually concentrated and burned in the recovery boiler for energy and chemical recovery. However, more and more applications are employed for the black liquor recovered lignin (Anvar *et al*, 2010).

At present, hemp woody core is not used by the pulp and industry because of the following inconvenients:

- Difficulty of delignification as consequence of higher wood or bast fiber lignin content in cell wall;
- Unbleached pulp obtained from flax and hemp by using conventional pulping processes (soda and Kraft) have lower yields and higher Kappa numbers than pulps obtained from hardwood pulping;
- Fibers obtained from hemp and flax woody core are two by three times shorter than fiber obtained from wood;
- Pulp trend to have lower papermaking properties;
- Chemical recovery is difficult due to high silica content;

All these factors contribute to a lower usage of the conventional pulping methods for hemp woody core pulping. Some of these mentioned difficulties might be overcome if non-conventional pulping processes such as organosolv are applied.

The aim of this work was to investigate the possibilities of integrating the hemp woody core (fibrous waste material) into the production of non wood pulp and lignin recovery by using glycerol organosolv pulping method, according

to the biorefinery concepts. Using the organosolv processes for delignification of hemp woody core is environmentally friendly because the residual liquor may be easily recycled after lignin recovery. The recovered lignin may be used as raw material in synthesis as well as for biocide systems based on lignin nanoparticles (Gîlcă *et al*, 2011).

## EXPERIMENTAL

The hemp woody core (30-60 mm) have been introduced into an autoclave type reactor together with the glycerol and alkali. Heating to the desired cooking temperature took place in 60 minutes. The established cooking time at the temperature of 170°C was 120 minutes at a liquid to solid ratio of 6:1. Alkali charge was varied in order to establish the effect of this parameter on the delignification process. Kappa number of pulps was determined according to standard ISO 302:2004.

A rapid glycerol recovery control method is performed by measuring the viscosity of glycerol solution and establishing its concentration by the dependence on the viscosity. An interesting aspect would be the exact influence of dissolved on the viscosity of the recovered glycerol solution.

Beatability was studied by beating the pulp in Yokro mill at different numbers of revolutions per minute. After beating paper hand sheets were obtained by using a Rapid Koethen laboratory sheet former.

Lignin was separated by precipitation to pH 4, using hydrochloric acid (5%) (Lyn, 1992).

The obtained lignins were vacuum dried at 40°C and after were further characterized by UV-VIS spectroscopy - a Jasco V550 UV-VIS spectrometer was used. FTIR spectroscopy was performed by using KBr technique on Digilab Scimitar FTS2000 at 64 scans at a resolution of 4 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

The yield, rejects and kappa number (which is an indication of the residual lignin

in the obtained pulp) values – are presented in table 1.

Table 1 Values of kappa number, yield and rejects as a function of alkali charge

Alkali charge, % , Na <sub>2</sub> O on o.d. material	Kappa number	Yield %	Rejects, %
6.87	61	56.0	19.6
13.75	44	40.0	1.37
20.63	24	37.0	0
16.21 (NaOH si Na <sub>2</sub> S)	56	51.0	14.4

The experimental data on yield, rejects and kappa number show the possibility of obtaining good results on glycerol pulping by using less or similar alkali charges that those used in conventional Kraft

pulping. The delignification degree increases with the increase in the alkali charge. The mechanical characteristics of the obtained pulps are comparable with those of wood pulps.

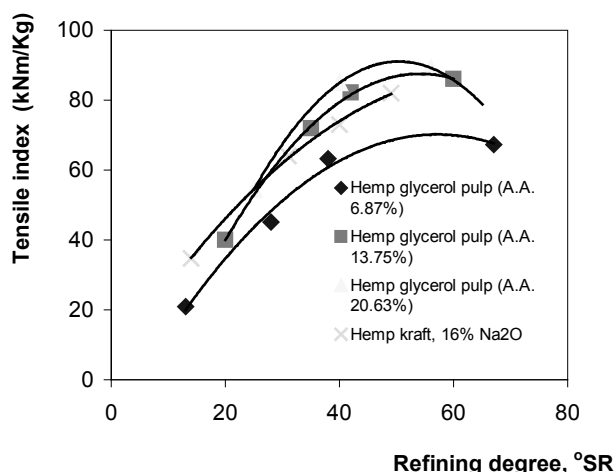
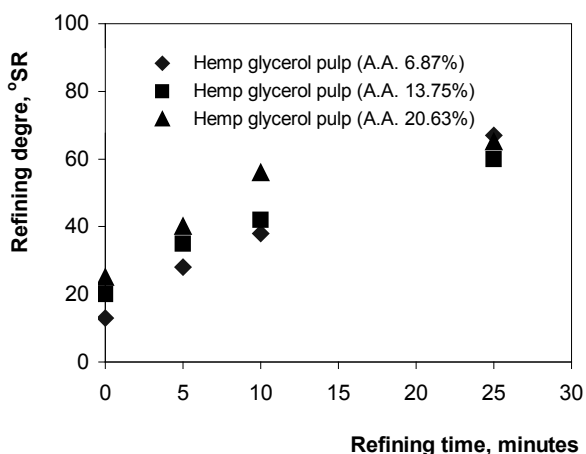


Fig. 1 a) Evolution of refining degree as a function of time b) Evolution of tensile index as function of refining degree

Figure 1 shows a rapid evolution of refining degree during refining. Good mechanical properties can be achieved at a refining degree between 35...40 °SR. It is well known that the paper properties depend on an optimal refining degree. Refining

rate is also important due to energy consumption problems. Refining rates is comparable to that of hardwood pulp, but somehow with higher values (Stoica *et al*, 2010).

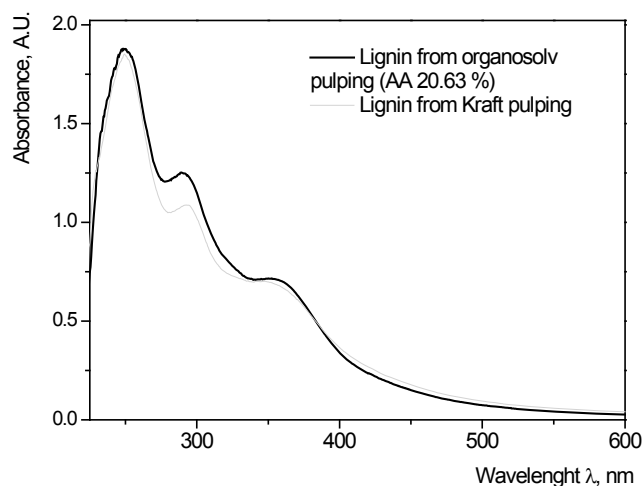


Fig. 2 UV-VIS diferential ionization spectra for glycerol hemp woody core lignin and kraft hemp woody core lignin

UV-VIS spectra of lignin samples obtained by different pulping liquors consist of a maximum at 250 nm, shoulders at 290 and 295 nm and 355 nm. In general, kraft lignins exhibit higher absorbances due to the presence of stilbene,  $\alpha$ -carbonyl and

other conjugated groups formed during the pulping process (Lyn, 1992). The same characteristics seem to be present in glycerol lignin spectra but with a slight shift to 290 nm of the secondary absorption band.

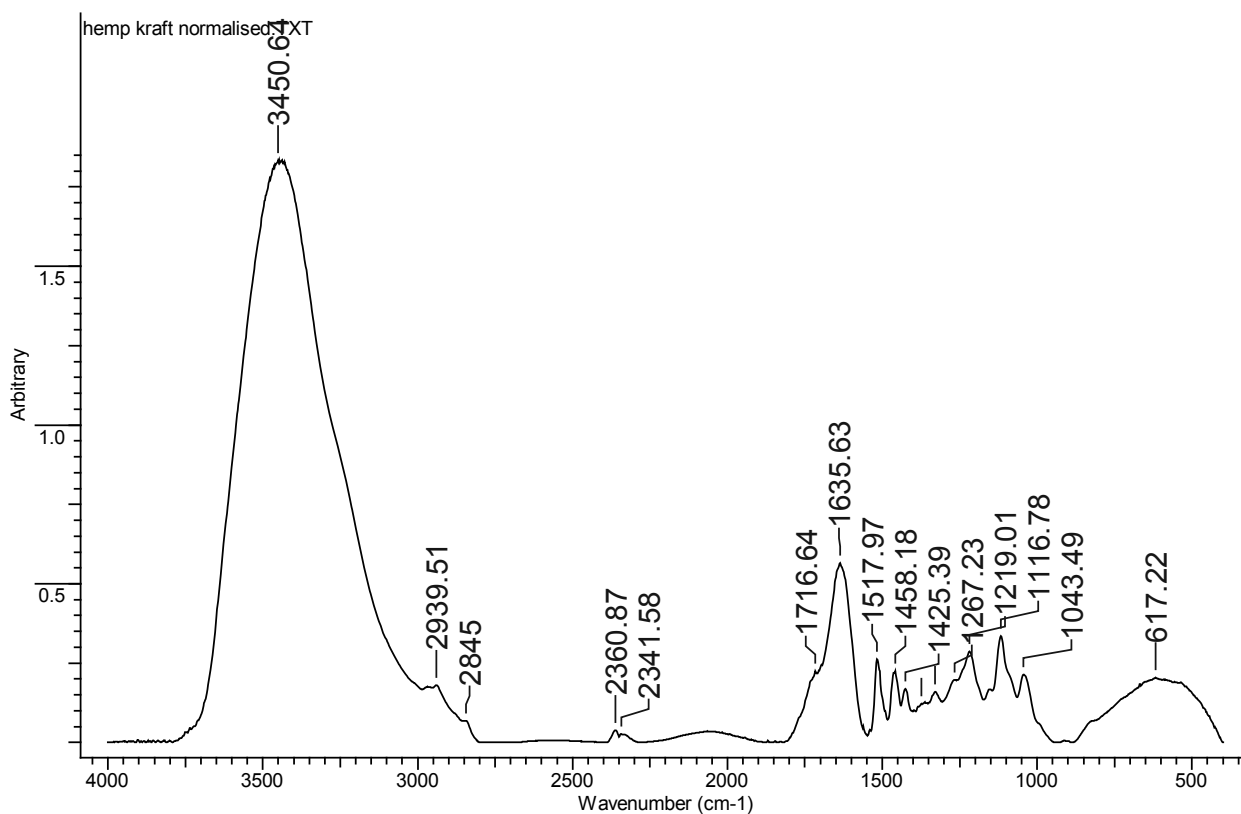


Fig. 3 Hemp woody core kraft lignin FTIR spectra

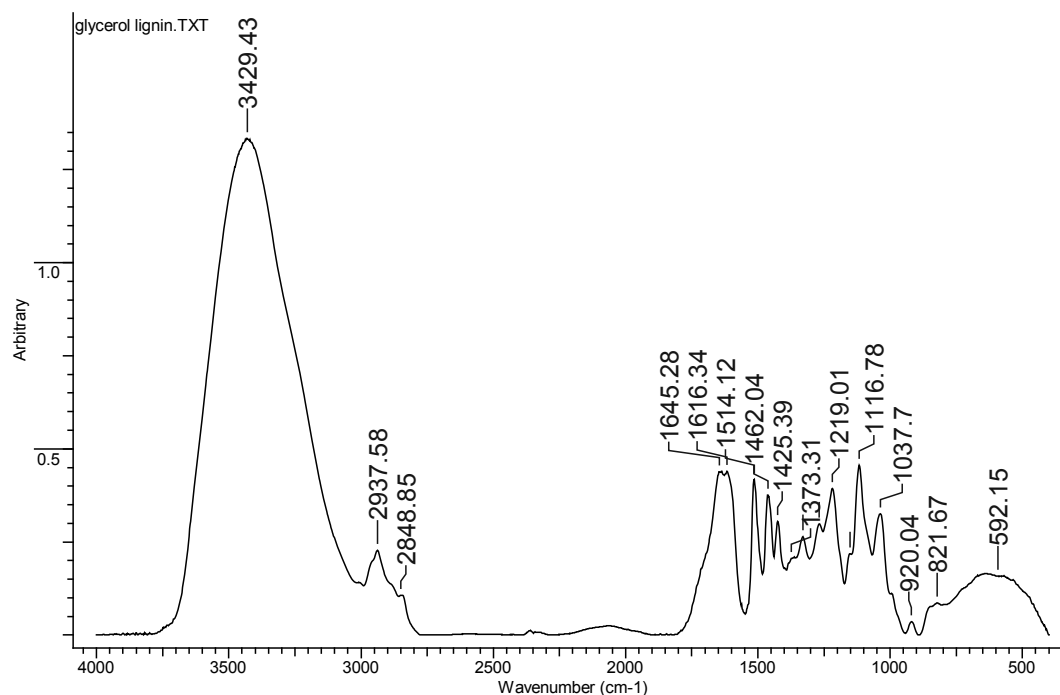


Fig. 4 Hemp woody core glycerol lignin FTIR spectra

Kraft hemp woody core lignin and glycerol lignin FT-IR spectra show multiple peaks: at  $3405\text{ cm}^{-1}$  hydroxyl group stretch,  $1714\text{ cm}^{-1}$  C=O stretch in unconjugated ketones, carbonyls and in ester groups (frequently of carbohydrate origin); conjugated aldehydes and carboxylic acids absorb around and below  $1700\text{ cm}^{-1}$ ;  $1635\text{ cm}^{-1}$  C=O stretch in conjugated p-subst, aryl ketones;  $1517\text{ cm}^{-1}$  aromatic skeletal vibration in lignin;  $1458\text{ cm}^{-1}$  C-H deformations;  $1425\text{ cm}^{-1}$  aromatic skeletal vibrations;  $1373\text{ cm}^{-1}$  aliphatic C-H stretch in  $\text{CH}_3$ ;  $1267\text{ cm}^{-1}$  G ring along with C=O stretch;  $1116\text{ cm}^{-1}$  aromatic C-H in plane deformation.

## CONCLUSIONS

The current work shows the possibility of obtaining papermaking pulp by using both conventional pulping process and glycerol alkaline. Increasing alkali charge in glycerol pulping process leads to pulps with lower kappa number but also lowers the yield. The obtained pulps have good mechanical characteristics and are easy to refine. Refining to suitable degree takes place in short time, by thus using less energy.

The obtained lignin was subjected to preliminary analysis by UV-VIS and FTIR spectroscopy. Spent liquor recovered lignin is a further subject for study toward suitable valorization

by hydroxymethylation and other modification methods.

## REFERENCES

1. D. Dutta, J.S. Upadhyaya, C.H. Tyagi, A. Kumar, M. Lala, *Studies on Ipomea carnea and Cannabis sativa as an alternative pulp blend for softwood, An optimization of kraft delignification process*, 2008, *Industrial Crops and Products*, 28, 128–136;
2. V. Dang, K. L. Nguyen, *Characterisation of the heterogeneous alkaline pulping kinetics of hemp woody core*, 2006, *Bioresource Technology*, 97, 1353–1359.
3. U. Buranov, G. Mazza, *Lignin in straw of herbaceous crops*, *Industrial crops and products*, 2008, 28, 237–259.
4. K. Wang, Feng Xu and R. Sun, *Molecular characteristics of kraft-AQ pulping lignin fractionated by sequential organic solvent extraction*, 2010, *Int. J. Mol. Sci.*, 11, 2988–3001.
5. S. Y. Lyn, *Characterisation in solution: spectroscopic methods ultraviolet spectrophotometry*, 1992, *Methods in Lignin*

- Chemistry, Springer-Verlag, Berlin. 75-80.
- 6.E. Saberikhah, J. Mohammadi Rovshandeh\* and P. Rezayati-Charani, *Organosolv pulping of wheat straw by glycerol*, 2011, Cellulose Chemistry and Technology, 45 (1), 67-75,.
- 7.M. Muurinen, *Organosolv pulping – A review and distillation study related to peroxyacid pulping*, 2000, Publishing house Oulu Yliopisto, Oulu, 70-71.
- 8.A. Gilca, A. M.Capraru, S. G. and V. I. Popa, *Agents for wood bioprotection based on natural aromatic compounds and their complexes with copper and zinc*, 2011, Cellulose Chemistry and Technology, 45 (3-4), 227-231.
- 9.D.E. Stoica, B.M. Tofanica, D. Gavrilescu, *Consideration of refining of nonwoods pulps*, 2010, Celuloză și Hârtie, 51, 6-7.

## NEW PERSPECTIVES ON THE HYDROLYTIC CONVERSION OF VEGETAL MATERIALS

Adina Elena Pânzariu, Th. Măluțan<sup>1</sup>

„Gheorghe Asachi” Technical University of Iași,

*Author correspondence:* <sup>1</sup>Faculty of Chemical Engineering and Environmental Protection, Str. Prof.dr. docent Dimitrie Mangeron, no. 73, 700050 Iasi, Romania  
*email:* [thmalu@ch.tuiasi.ro](mailto:thmalu@ch.tuiasi.ro)

### Abstract

This paper presents the results obtained from the hydrolysis of the vegetal materials with hot water under pressure. The effects of the hydrolysis of biomass were analysed in the laboratory, within the temperature range of 150-230°C and high pressure (400 atm). The efficiency of the hydrolytic treatment was estimated through the yields in sugars and the severity of the hydrolysis. Thus, hydrolysates were analyzed regarding the sugars content through the High Performance Liquid Chromatography technique (HPLC) using a Supelcogel C 611 column and demineralized water as mobile phase, as well as through UV-VIS Spectroscopy and fluorescence. The advantage of the pre-treatment with hot water under pressure is that it does not use any mineral catalyst which makes the process more attractive from the economical and ecological point of view.

**Key words:** *Hydrolysis, Vegetal materials, Sugars, Biomass*

### Rezumat

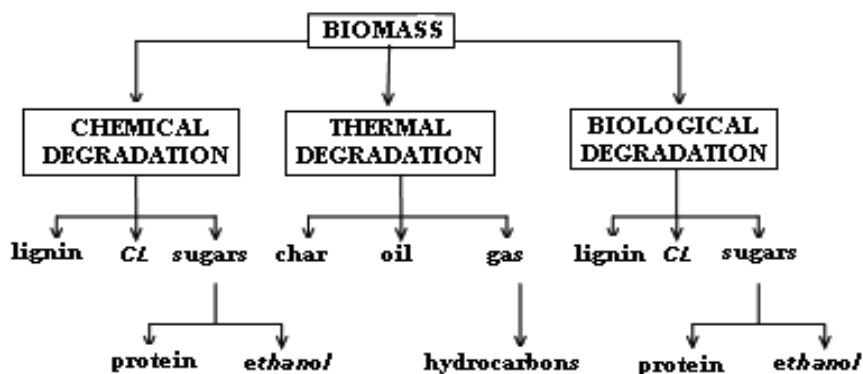
Industria forestiera poate asigura materii prime regenerabile fiind probabil singurul sistem industrial la scara mare capabil de a asigura o dezvoltare durabila. Biomasa include reziduuri agricole si forestiere, portiuni mari de deseuri municipale solide, plante erbacee si lemnoase si constituie o materie prima cu mare disponibilitate in raport cu valorificarea hidrolitica si are un cost scazut. In aceasta lucrare se prezinta rezultatele obtinute la hidroliza materialelor vegetale cu apa fierbinte sub presiune. Efectele hidrolizei biomasei lignocelulozice au fost investigate in laborator, in intervalul de temperaturi 150 - 190° C si presiuni ridicate (400 atm). Performanta tratamentului hidrolitic a fost evaluata prin determinarea randamentului in zaharuri si estimarea profunzimii hidrolizei. Astfel, hidrolizatului colectat a fost analizat in vederea dozarii substantelor reducatoare prin tehnica cromatografiei de lichide de inalta performanta (HPLC) folosind o coloana Supelcogel C 611 si apa deionizata ca faza mobila, precum si prin spectroscopia UV-VIS si fluorescenta. Avantajul pretratamentului cu apa fierbinte sub presiune este ca nu foloseste nici un catalizator mineral ceea ce face procesul mai atractiv din punct de vedere economic si ecologic.

**Cuvinte cheie:** *Hidroliză, Materiale vegetale, Zaharuri, Biomasa*

## INTRODUCTION

Due to the complexity of the chemical structure of biomass, the yields in the reducing substances depend on the origin of the raw vegetal material and on the applied hydrolysis technologies. From the complex valorisation of the biomass point of view, the following directions stand out:

- Thermolysis (combustion, pyrolysis, gasification, liquefaction);
- Chemical decomposition (hydrolytic treatments);
- Biochemical degradation (fermentation treatments).



CL - cellulignin

Fig. 1 The complex valorization of biomass

### The hydrolytic treatments of the biomass

The distinct treatments of the hydrolysis of pentosans and hexosans are achieved in complete immersion conditions of the chips in liquid where it is associated both the hydrolysis process of the polysaccharides and the sugar extraction process from the material [1]. In the conversion processes of the polysaccharides into sugars during the hydrolysis reaction, due to the acid pH and high temperature, several dehydration reactions of the monoses obtained occurs to the furfural (F) and hydroxymethylfurfural (OMF), in progress

simultaneously with their decomposition. These conversions take place as a result of the successive reactions of fragmentation, dissolution and hydrolysis of the polysaccharides from the vegetal tissue. Due to the existence within the wood of the two fractions of fast (PUH) and slow (PGH) polysaccharides hydrolyzed, both the pentosans and the hexosans will be dissolved, with positive effects on the concentration in reducing substances but with negative effects on the yield concerning the furfural and the hydroxymethylfurfural [2]. Figure 2 shows a possible of integral hydrolysis of the biomass.

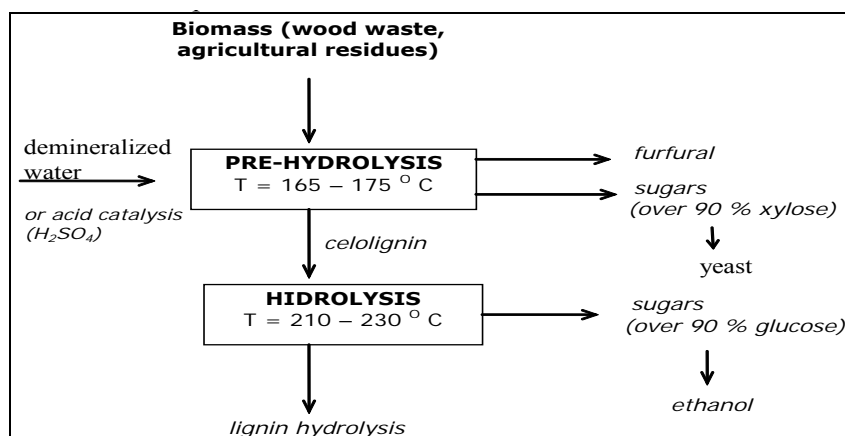


Fig. 2 The main products which can be obtained from the integral hydrolysis of plant materials



By treating the vegetal materials with hot water under pressure, slightly improved yields can be achieved in pentoses and reduced amounts of by-product. The thermal regime is achieved at range of temperatures 150-230°C from several seconds up to one hour depending on the work's temperature [3]. It seems that through this treatment there was no significant impact on the cellulose and the lignin with advantages in the subsequent valorisation of the cellulignin. Due to the weak acid pH the issues connected with corrosion are reduced which triggers a diminished operating cost. The advantage of these methods lies in the use of the water as a hydrolysis agent, lessened substance in the by-products of the sugars thus lowering the costs of hydrolysis reagent recovery, more ecological techniques [4].

## EXPERIMENTAL PART

The raw material used was beech sawdust with the following chemical composition: ethanol-benzene extractives = 2,43 %; cellulose = 45,94 %; lignin = 26,56 %; PUH = 36,28 %; PGH = 36,06 %. The cellulose, lignin, PUH and PGH contents were determined according to the classic methods of analysis (the cellulose through the nitro-alcoholic method, the lignin through the Klason-Komarov method) [5].

All the experiments were carried out in an apparatus which consists of a column reactor type with dimensions 4.6 x 150 mm, design in the our laboratory. For each pre-treatment process were used 5-6 grammes of sawdust and hot demineralized water. The reactor was heated at temperatures of 140°C, 150°C or 190°C from the room temperature for 10-90 minutes. By means of a HPLC pump, demineralized water was added achieving a constant flow of 0.2 mL/min, after having risen the temperature to 140°C, 150°C respectively.

The hydrolysis of pentosans was carried out within 100 minutes, timed after having reached the running temperature (140-150°C). Then, the reactor was cooled at room temperature through a cooling coil for about 30 min. The hydrolysates was analyzed in order to establish the content of the reducing substances and the separated fractions (UV-VIS spectroscopy, fluorescence, HPLC). After that, the temperature was risen up to 180°C, 190°C respectively and the flow at 2 mL/min. The hydrolysis of hexosans was achieved under these conditions for 10 minutes. The flowthrough hydrolysis was achieved after the temperature had

been risen to 140°C, the hydrolysates being collected at 140°C, 160°C and 180°C. The hydrolysates obtained from the experiments were subjected to a second hydrolysis with H<sub>2</sub>SO<sub>4</sub> 4% for 60 min at 121°C. The samples were then neutralized with CaCO<sub>3</sub> in order to remove the inhibitor chemical compounds which resulted after the pre-treatment (furfural, hydroxymethylfurfural, acid residue), then centrifugation, filtered and analyzed [4,6,7]. The hydrolysates were analyzed using the same methods mentioned above.

### The concentration of the reducing substances (RS)

The total reducing substances were analyzed using the method with dinitrosalicylic acid (DNS), measuring the absorbance at 540 nm with the UV-VIS JascoV 550 Spectrophotometer.

### The pH measurements

The pH of each sample was measured with a pH-meter (8000 model, VWR Sci), immediately after cooling at room temperature, the samples were neutralized with CaCO<sub>3</sub> at a pH ranging between 5-6 [8].

### UV-VIS spectroscopy

The UV-VIS spectra were recorded on a JASCO 550 spectrophotometer, using quartz cells for liquids with a volume of 1 mL, absorption region 200÷800 nm, scan speed 200 nm/min and 1 nm resolution. Spectra processing was carried out on a special Spectra Manager Program series.

### Fluorescence spectroscopy

The fluorescence emissions of the hydrolysates were registered on a luminiscence spectrometer Perking Elmer LS 50B, using cuvettes with a liquid volume of 1 mL, at wavelngts excitation of 350 nm, the absorbtions being evaluated in the 400÷600 nm region. Spectra processing was performed with a specialized FLWinLab series program.

### High performance liquid chromatography (HPLC) of hydrolysates

The analysis of the hydrolysates was achieved on a HPLC column Supelcogel C611, (300 x 7.8 mm) and it was used demineralized water as a mobile phase. The HPLC system consists of a Varian 9010 pump, Waters 717 autosampler, HPLC column oven, programmable UV-VIS Waters 486 detector connected with a RI (refractive index) Shimadzu RID-10A detector and a personal computer for the data aquisition. The chromatograms obtained were

processed in OriginLab 7,5 for Windows. Working conditions: demineralized water, solvent flow 0,5mL/min,  $\lambda=190$  nm, 60°C column temperature, 35 minutes elution time.

## RESULTS AND DISCUSSION

### UV-Vis Spectroscopy and fluorescence

In table 1 are presents optical data of the hydrolysates from batch and flowthrough experiments.

*Table 1 Optical characteristics of the hydrolysates obtained under continuous and discontinuous hydrolytic processes*

Experiment code	Treatment	$\lambda_{\text{emission}}$ (the fluorescence)	Abs., UV-VIS
140_HPP	140° C - hydrolysis of pentosans in batch mode under pressure (400 atm)	431	278
180_HHP	180° C - hydrolysis of hexosans in batch mode under pressure (400 atm)	455	284
150_HPFP	150° C - hydrolysis of pentosans in discontinuous mode	430	280
190_HHFP	190° C - hydrolysis of hexosans in discontinuous mode	430	280
150_HPP	150° C - hydrolysis of pentosans in batch mode under pressure (400 atm)	459	278
190_HHP	190° C - hydrolysis of hexosans, in batch mode under pressure (400 atm)	485	279
140_HC	140° C - hydrolysis in flowthrough mode	425	284
160_HC	160° C - hydrolysis in flowthrough mode	426	277
180_HC	180° C - hydrolysis in flowthrough mode	419	279

The analysis of the UV-VIS spectra recorded for the hydrolysates obtained from hydrolysis of pentosans emphasizes distinctive bands at 278 nm and 280 nm, highlighting the low-molecular lignin fractions dissolved in the solution, alongside with sugars degradation compounds (furfural). In the hydrolysis of hexosans, it prevails the absorption bands of approximately 284 nm, 279 nm respectively. Based on the UV-VIS spectra, the fluorescence analysis was performed using excitation wavelenghts of 350 nm, characteristic of lignin. The recorded spectra indicates fluorescence emissions in the range 370-550 nm. The analysis of the fluorescence spectra shows a movements of the emission maximum from 431 nm (140\_HPP) to 485 nm (190\_HHP) when the hydrolysis was performed in a flowthrough mode. These bathochromic effects are caused by, most likely, the structural transformations of the lignin

fragments released in solution. The bands recorded are differs both as position and intensity depending on the treatment used.

### HPLC analysis

The analysis of the hydrolysates by HPLC points out the complexity of the reaction mixture. Thus, we find out that the hydrolyates presents sugars of hexoses and pentoses as well as low-molecular lignin fragments alongside with degradation products of sugars (furfural, hydroxymethylfurfural, methylfurfural, acetic și formic acids). For this reason, the analysis of the hydrolysates requires the use of two HPLC columns specific for each chemical compound groups. Figures 3 and 4 shown the chromatograms obtained from the sugars analysis on a Supelcogel C 611 column.

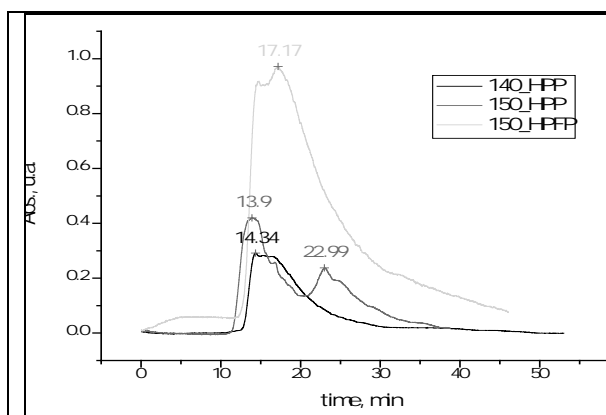


Fig.3 Chromatograms obtained from the analysis of the liquid from biomass hydrolysis in batch mode

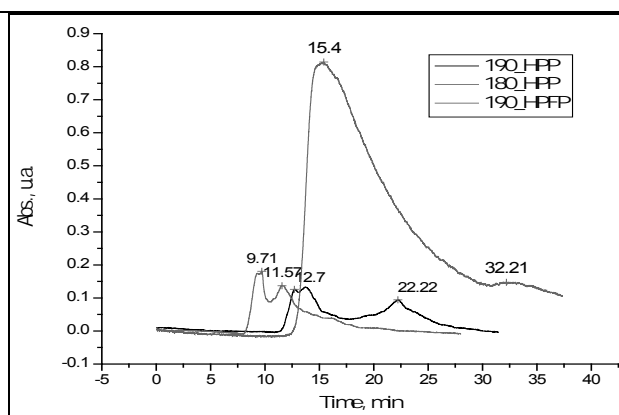


Fig.4 Chromatograms obtained from the analysis of the hydrolysates from flowthrough mode

The analysis of the chromatograms points out the fact that, depending on the hydrolysis mode (secvential, batch, flowthrough, with hot water under pressure), the type of the sugars differs from one case to another. Thus, under pressure conditions it observed the presence of a significant amount of glucose. In the case of the hydrolysis in an flowthrough mode, during the first stages was obtained the pentoses (arabinose, xylose) and afterwards mostly glucose.

**The pH values**

It became obvious that once the temperature increased, the pH's value decreases both in an discontinuous mode and in an continuous mode one, which can be explained with the increase in the acidity of the reaction medium.

Exp.c od	140-HPP	180_H HP	150_HPF P	190_HHP P	150_HP P	190_HHP	180_H P	140_H C	160_H C	180_H C
<b>PH</b>	4.95	3.60	4.48	3.66	4.65	3.60	3.51	3.99	3.14	3.2

**Reducing substances content**

When rising the temperature from 140°C, 150°C in an batch mode under pressure (400 atm) the yields increase approximately 5 times and when it is not

used hot water under pressure, the increase in the yields is only 4 times. In the hydrolysis of hexosans case the most convenient hydrolytic regime seems to be the one in one step (180\_HP) in flowthrough mode when the best yields are reached.

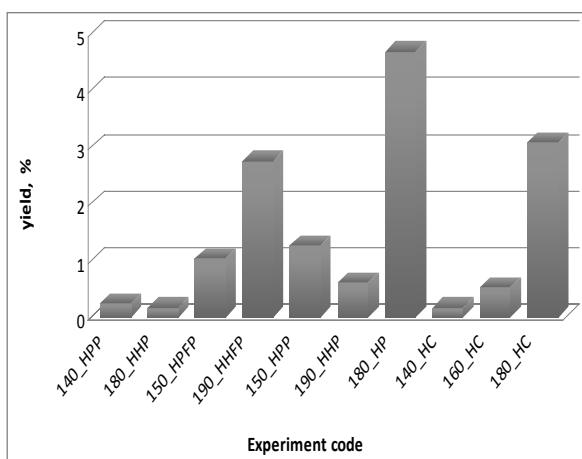
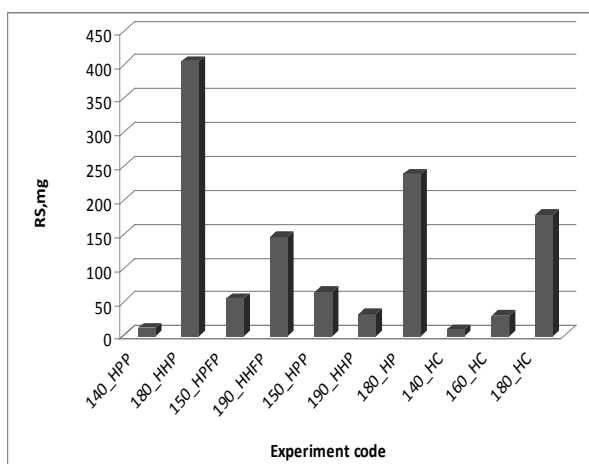


Fig. 5 The reducing substances amounts and yields from batch and flowthrough modes, comparatively

### The chemical composition of the cellolignins

Regarding to the chemical composition of the cellolignins it stands out an alteration more or less significant of the fast and slow hydrolyzed polysaccharides depending on the hydrolysis mode

applied and a constant composition in lignin which indicates a chemical fastness of the lignin polymer as opposed to the hydrolytic processes applied. The cellulose content from the residue is approximately constant when using a moderate conditions of hydrolysis (H150\_190\_PP).

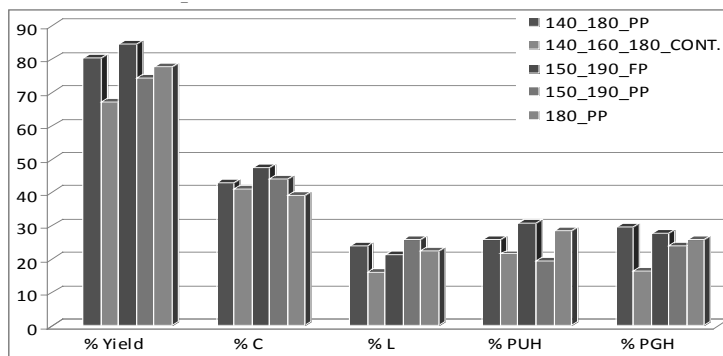


Fig. 6 Comparison of the chemical composition of cellolignins obtained in flowthrough and batch mode

### CONCLUSIONS

- It was studied the treatment of the hydrolysis using as catalyst the demineralized water under various time, temperature and pressure conditions.
- Although the increases of the yields in the reducing substances are not spectacular in presence of demineralized water, however the subsequent valorisation of the cellolignins presents indubitable advantages due to the polysaccharides protection during the first stage of pre-hydrolysis.
- For the integral valorisation of biomass, it is recommended the use of the hydrolysis in two steps: pre-hydrolysis with hot demineralized water under pressure followed by the hydrolysis of cellolignin.

### ACKNOWLEDGEMENTS

This paper was realised with the support of POSDRU CANTUMDOC “DOCTORAL STUDIES FOR EUROPEAN PERFORMANCES IN RESEARCH AND INOVATION” ID79407 project funded by the European Social Found and Romanian Government.

### REFERENCES

- [1] Rozmarin Gh., Popa V.I., Tehnologia proceselor hidrolitice și fermentative, Ed. Univ. Teh.“Gh. Asachi” Iași, (1994).
- [2] Malutan Th., Valorificarea complexă a biomasei, Ed. Performantica, Iasi, (2008).
- [3] Balat M., Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review, Energy Conversion and Management, 52, 858-875, (2011).
- [4] Díaz M. J., Cara C., Ruiz E., Romero I., Moya M., Castro E., Hydrothermal pre-treatment of rapeseed straw, Bioresource Technology, 101, 2428-2435, (2010).
- [5] Rozmarin Gh., Popa V.I., Grovu-Ivănoiu M., Doniga E., Chimia compușilor macromoleculari și chimia lemnului. Metode de analiză, Tipografia I. P. Iași, (1984).
- [6] Ingrama T., Rogalinski T., Bockemühlb V., Antranikianb G., Brunnera G., Semi-continuous liquid hot water pretreatment of rye straw, J. of Supercritical Fluids, 48, 238-246, (2009).
- [7] Carvalho F., Duarte L. C., Gírio F. M, Hemicellulose biorefineries: a review on biomass pretreatments, Journal of Scientific & Industrial Research, 67, 849-864, (2008).
- [8] Liu C., Wyman C. E., The Effect of Flow Rate of Compressed Hot Water on Xylan, Lignin, and Total Mass Removal from Corn Stover, Ind. Eng. Chem. Res., 42, 5409-5416, (2003).