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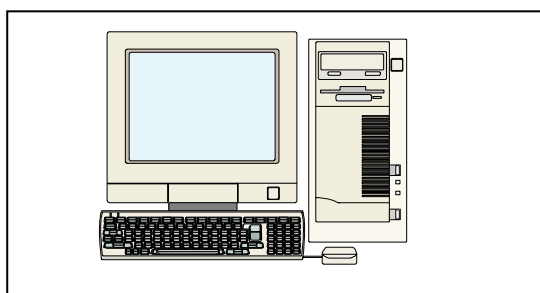
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Prof. dr.ing. VALENTIN I.POPA

- **42 de ani de activitate în slujba învățământului superior și a cercetării în domeniul celulozei și hârtiei -**



Domnul profesor univ.dr.ing. Valentin I. Popa s-a născut la data de 15 decembrie 1946 în orașul Panciu. Absolvent al liceului “Ion Slavici” din Panciu, a urmat cursurile facultății de Chimie Industrială a Institutului Politehnic din Iași, obținând în 1969 diploma de inginer chimist în specialitatea Celuloză, hârtie și fibre artificiale.

În anul 1976 susține teza de doctorat “Cercetări în domeniul chimiei algelor marine”, devenind doctor inginer. În același an primește Premiul “Gheorghe Spacu” al Academiei Române pentru studiile efectuate în domeniul chimiei algelor marine. Începând cu anul 1969 desfășoară activitate didactică și științifică în cadrul Institutului Politehnic Iași (în prezent Universitatea Tehnică “Gheorghe Asachi” din Iași) unde parcurge toate treptele carierei didactice: asistent (1969-1977), șef de lucrări

(1977-1990), conferențiar (1990-1992) și profesor (1992). În anul 1992 i se atribuie calitatea de conducător de doctorat.

Pentru prestigioasa activitate didactică a domniei sale este distins în 1986 cu Premiul Ministerului Invățământului. A predat cursuri de Chimie macromoleculara, Tehnologie organică, Mecanica filării polimerilor, iar în prezent este titularul disciplinelor de Chimia lemnului, Știința lemnului, Procese biotehnologice în industria de celuloză și hârtie și Strategia cercetării. A condus peste 150 de proiecte de diploma, 20 de lucrări de dizertație, iar în calitate de conducător de doctorat a finalizat 30 teze până în 2011.

Contribuțiile științifice ale domnului profesor Valentin Popa sunt numeroase și însumează peste 600 de lucrări publicate și comunicate, care se referă la izolarea,

caracterizarea și modificarea chimică și biochimică a componenților chimici ai biomasei vegetale, proprietățile biologice ale compușilor polifenolici și ligninici, procesele de bioremediere și protecția mediului. Este autor sau coautor la 37 de cărți publicate în țara și în străinătate. A participat și a condus peste 60 de programe de cercetare cu finanțare internă și externă: *Growth, Eurolignin, Ecobinders, Polysaccharides, Creativity in Higher Education, COST*. A colaborat la organizarea a numeroase manifestări științifice interne și internaționale, dintre care 13 simpozioane internaționale în România și 15 în țările europene în domeniul celulozei și hârtiei, ingineriei mediului și polizaharidelor.

Domnul profesor Valentin Popa este membru al unor prestigioase asociații profesionale din țară și străinătate: *Asociația Tehnică pentru Industria de Celuloză și Hârtie din România, Societatea Română de Bioinginerie și Biotehnologie, Societatea de Inginerie Chimică, Societatea de Chimie din România, International Association of Scientific Papermakers, International Academy of Wood Science, International Lignin Institute – membru în consiliul de conducere, American Chemical Society*.

Domnul profesor Valentin Popa este membru al comitetelor de redacție ale revistelor *Celuloză și Hârtie, Buletinul Institutului Politehnic Iasi, Environmental Engineering and Mangement Journal* și referent la publicațiile: *European Polymer Journal, Journal of Applied Polymer Science, Holzforschung, Cellulose, Industrial Crops and Products și Biomacromolecules*. De asemenea, este editor șef al revistei *Cellulose Chemistry and Technology*, publicație a Editurii Academiei Române.

În perioada 2001-2005 a fost membru al Consiliului Național de Evaluare și Acreditare Academică și evaluator ARACIS. Domnul profesor Valentin Popa a fost secretarul științific al Consiliului Profesorat al Facultății de Chimie Industrială (1996-2000), Decan al acestei facultăți (2000-2004), iar în perioada 2004-2008 a fost prorector al Universității Tehnice “Gheorghe Asachi” din Iași. În anul 2003 a primit titlul de “Cetățean de Onoare” al orașului Panciu, iar în anul 2004 a fost distins cu Ordinul “Meritul pentru învățământ” în grad de Mare Ofițer. Este membru corespondent al Academiei de Științe Tehnice din România, secția Inginerie Chimică.

Se poate afirma că activitatea profesorului Valentin Popa, deosebit de prolifică pe multiple planuri, îmbină în mod fericit didacticul și științificul cu managerialul, ceea ce îi conferă o puternică amprentă europeană. Devotat școlii superioare, exigent în tot ceea ce întreprinde, domnia sa continuă cu devotament, inspirație și pasiune tradiția bogată a școlii ieșene de inginerie chimică.

Cu ocazia zilei de naștere, consiliul de conducere și colectivul redacțional ale revistei *Celuloză și Hârtie* îi urează profesorului Valentin Popa mulți ani cu sănătate și putere de muncă pentru a contribui, cu valoarea și prestigiul domniei sale, la progresul școlii superioare de celuloză și hârtie din țara noastră.

Consiliul de conducere și Colectivul redacțional al Revistei *Celuloză și Hârtie*

ALKALINE PULPING AND OXYGEN DELIGNIFICATION OF RAPESEED FIBERS TO A LOW KAPPA NUMBER

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Abstract

The aim of this study was to investigate the use of rapeseed (*Brassica napus*) stalks as a source of cellulosic fibers with low lignin content by means of alkaline pulping followed by oxygen delignification. Chemical pulping was carried out by sulphate and soda-anthraquinone method under varying conditions. Time to achieve maximum temperature (60 minutes), maximum temperature (170°C), reaction time at maximum temperature (60 minutes), solid-to-liquid ratio (1:5) were kept constant in all experiments. The influence of active alkali (18, 20 and 22% sodium hydroxide on oven-dried stalks) on pulp yield, screening reject, lignin residual content and intrinsic viscosity was studied. Results indicated that alkali charge was an important parameter on yield and kappa number of the pulps. Addition of 0.1% anthraquinone (on oven-dried stalks) to the alkaline liquor as an additive in soda pulping determines a significant reduction of kappa number. The total pulp yields and kappa number was decreased with increasing the alkali charge ratio. It was found that kappa number values in soda-anthraquinone pulp samples were lower than sulphate pulps at similar pulping condition. The residual lignin left in the pulp was subsequently removed in a bleaching stage, with oxygen treatment in a pressurized vessel at elevated temperature and in an alkaline environment. Results showed that rapeseed pulps were delignified to a low Kappa number without significant loss in viscosity. It is concluded that the rapeseed stalk have the potential for being used for obtaining cellulosic pulp.

Keywords: cellulose fibres, nonwood, rapeseed stalks, pulp.

Rezumat

Scopul acestui studiu a fost de a investiga utilizarea tulpinelor de rapiță pentru obținerea fibrelor celulozice cu conținut redus de lignină prin fierbere alcalină urmată de delignificare cu oxygen. Procesul de fierbere s-a desfășurat după procedeul sulfat și natron-antrachinonă în diferite condiții, astfel: durata de atingere a temperaturii de fierbere (60 minute), temperatura de fierbere (170°C), timpul de reacție la temperatura maximă (60 minute), iar raportul solid – lichid (1:5) a fost menținut constant în toate experimentele. S-a studiat influența adaosului de alcalii active (18, 20 și 22%) asupra randamentului de fierbere, cantității de refuz la sortare, conținutului de lignină reziduală și viscozității intrinseci. Rezultatele au evidențiat faptul că, cantitatea de alcalii este un parametru important care influențează randamentul și cifra Kappa. Adaosul de 0,1% antrachinonă la leșia de fierbere ca aditivi în procesul de fierbere natron determină o reducere semnificativă a cifrei Kappa. Randamentul total și cifra Kappa au scăzut cu creșterea cantității de alcalii active. De asemenea, în aceleași condiții ale procesului, în fierberee natron/antrachinonă, valorile cifrei kappa ale celulozelor obținute au fost mai reduse decât procesul de fierbere sulfat. Conținutul de lignină reziduală a fost îndepărtat în secvențele de albire, prin tratare cu oxygen în mediu alcalin și în condiții de temperatură și presiune ridicate. Rezultatele au arătat că celuloza din tulpine de rapiță a fost delignificată la o valoare redusă a cifrei Kappa fără reducerea semnificativă a viscozității. În concluzie, tulpinele de rapiță pot constitui o sursă potențială de fibre celulozice.

Cuvinte cheie: fibre celulozice, plante anuale, tulpini de rapiță, celuloză

I. INTRODUCTION

Nonwood fibers have an extended history as raw materials used in production of paper, long before the wood began being utilized in papermaking (Sixta, 2006a). Today, the production of nonwood in worldwide pulp production is around 20 million tonnes (figure 1), but analyzing forecasts and trends in recent years, it is expected to grow at least until it reaches maximum production capacity reached in the 90's of 25 million tones. Analyzing the share of nonwood in world pulp production (figure 1) it can be stated that the utilization increases continuously in the last ten years. Overall, the

ratio changed from 6% in the 60's to 11% in the last decade (Faostat, 2011).

Rapeseed (figure 2), known scientifically as *Brassica napus* L., a bright yellow flowering member of the Brassicaceae family, is a very important and widely cultivated arable crop throughout the world for the production of animal feed, vegetable oil for human consumption and production of biodiesel for powering motor vehicles (Tofanica and Gavrilescu, 2010). Rapeseed, also known as canola, has achieved worldwide commodity status, being cultivated extensively in Europe, Asia and North America due to the policies to encourage the production and use of bio-fuels (European Commission, 2010).

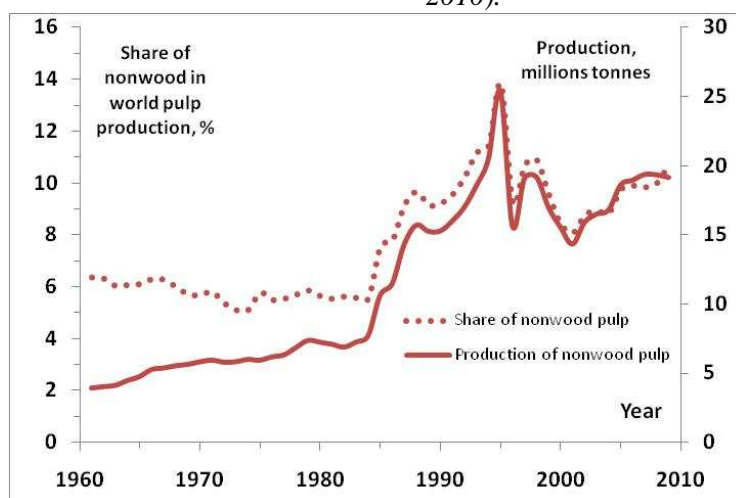


Fig. 1 Share and production of nonwood pulp in total world production (FaoStat, 2011)

Biomass productivity of winter oilseed rape is the product of the growth rate and the duration of the vegetative period (Diepenbrock, 2000). Winter rapeseed total biological yield ranges from 10 to 20 metric tons of dry forage/ha. The harvest index of rapeseed, the proportion of seed dry matter to total biomass (seeds and stalks), varies between approximately 0.28 and 0.50. Thus, seeds represent 28–50% of total biomass and the remaining crop residues, especially stalks represent 20-72% of total biomass (Rathke et al., 2006). In European Union, an economic seed yield of winter oilseed rape is situated in the range of 3 and 4 tons per hectare and corresponds to 3 to 10 tons of stalks.

The seed is the valuable, harvested component of the crop (figure 3), while the stalks remain on the field and serve in the crop rotation to increase the humus content in the soil, but also for incorporation, immobilization and bio-transformation of available nitrogen and sulphur to stable organic forms in nutrient-poor soils (Bhupinderpal-Singha et al., 2006). The stalks status as a solid waste in many instances means that they could be a cheap raw material. It can be processed to obtain fibers, chemicals and energy via various chemical conversion processes, into a lignocellulosic feedstock biorefinery (Tofanica and Gavrilescu, 2010)



Fig. 2 *Brassica napus*



Fig. 3 Rapeseed stalks remain on the field after seed harvesting

The results of morphological study showed that rape stalks contained short fibers with similar morphological properties to the common nonwood and hardwood fibers (Tofanica et al., 2011a). The mean fiber length, 1.2 mm, is similar with those for other nonwood fibers such as esparto grass and common reed, and hardwood species such as eucalyptus and common beech. A maximum dimension fiber length was found 1.99 mm and minimum fiber length was found 0.71 mm. Rapeseed fibers width ranges between 9.10 μm and 19.60 μm , with an average value of 13.1 μm . Cell wall thickness ranges from 1.77 to 3.08 μm , with 2.25 μm average. Maximum lumen diameter was found as 13.44 μm and minimum was found as 4.34 μm .

Fiber length and width, cell wall thickness and lumen diameter of fibers from rapeseed stalks, a fiber little-known in the pulp and paper industry, are very similar with those from hardwoods and can replace wood fibers in a variety of composites, paper and paperboard products.

Chemical composition analysis' results showed the lignin content was comparable to other nonwood and hardwood papermaking fiber resources (Tofanica et al., 2011a). Rapeseed's holocellulose content ranges between 70-75% (cellulose 38-42%), lignin content between 17-21% and ash content of 2-5%. The chemical composition of rapeseed is comparable with chemical composition of cereal straws. The amount of cellulose influences the properties of fibers, economics of fiber production and the utility of the fibers for various applications.

The main chemical pulping methods applied to nonwood raw materials, adapted from processes for the delignification of wood raw materials, are as follows (Leponiemi, 2008):

- Sulphate (Kraft) process - uses a mixture of sodium hydroxide and sodium sulphide as main active chemical agents to dissolve the lignin;

- Soda-anthraquinone (Soda-AQ) process - uses sodium hydroxide as cooking chemical and anthraquinone as a catalyst for delignification. Addition of anthraquinone in pulping accelerates the delignification reactions, blocks peeling reactions by oxidizing polysaccharide end groups and increases the screened yield of pulp.

In chemical alkaline pulping, an oxygen delignification stage after pulping enhances the effectiveness of the pulping stage. The oxygen delignification process reduces the amount of alkaline charge in the first pulping stage and reduces the need for bleaching chemicals in further bleaching sequences, without affecting pulp yield as negatively as other methods of extended delignification (Bajpai, 2005; Sues, 2010).

The oxygen stage decreases formation of adsorbable organic halogens (expressed as AOX) in pulp and paper mill effluents when chlorine-based chemicals are used in subsequent bleaching of the pulp. In addition, regarding emission levels associated with the use of other bleaching chemicals used, oxygen delignification decreases biological oxygen demand ($\text{BOD}_{5 \text{ or } 7}$), chemical oxygen demand (COD) and colour of the wastewaters.

However, oxygen has lower selectivity at lignin removal than chlorine or other chemical pulp bleaching agents. Therefore, oxygen delignification is used to decrease kappa number of the pulp to low values only by 40-50%, because an attempt at greater reduction in kappa values is expected to lead to degradation of carbohydrates in the pulp and loss of pulp quality.

This investigation offered valuable information for using rapeseed stalks in pulping and bleaching processes by the use of kraft and sulphur-free pulping and environmentally friendly bleaching. In addition, the obtained data will contribute on reducing the high amounts of reagents used in pulping and bleaching stages, and to increase the quality and properties of the final paper products.

The research focuses on the characterization and evaluation of these agricultural residue products as raw materials for pulping and papermaking industry. The cellulosic fibers obtained from these raw materials by kraft and soda/anthraquinone pulping (soda-AQ), followed by a bleaching stage, with oxygen treatment, were characterized by pulp yield, kappa number and viscosity.

This knowledge will lead to a better utilization of these lingocellulosic raw materials and to the developing of interest for these nonwood fibers. Rapeseed stalks as agricultural residues, may have potential in the future as raw materials for fiber production for different paper products.

II. EXPERIMENTAL

Materials

The rapeseed stalks, free of leaves and roots, were collected after seed harvest from Vaslui County, Romania. The stalks were air dried and stored in a dry location. For pulping, the stems were manually cut into pieces of about 3-5 cm in length. All results were reported on oven-dry weight basis.

Methods

Pulping. Kraft and Soda- anthraquinone pulping was performed in a laboratory rotating batch reactor with a total volume of 10 L, equipped with electric heating and automatic temperature control. 300 g of rapeseed stalks (on dry basis) and corresponding pulping liquor (parameters as seen in table 1) were used, so that pulping was performed with the desired active alkali charge.

The following experimental conditions were applied in soda-AQ pulping:

- Alkali charge was 18, 20 and 22% as NaOH, based on oven-dry weight of stalks;
- Ratio of rapeseed stalk to cooking liquor was 1:5 (water was added);
- After 100°C, heating rate was realized to reach the cooking temperature in 60 minutes;

- Cooking temperature was 170°C;
- Cooking time was 60 minutes at maximum temperature;
- Anthraquinone in 0.1% charge (on o.d. stalks) was used in all soda-AQ processes.

The cooking parameters were selected in order that pulp lignin content being below the fiber liberation point. The corresponding H-factor (Sixta, 2006b) for current cooking profile at 170°C and 60 minutes was 1038.

Table 1 Composition of pulping liquors used for delignification

Kraft pulping		Soda-AQ pulping	
Compounds	Concentration (g NaOH /L)	Compounds	Concentration (g NaOH /L)
NaOH	107.2	NaOH	100
Na ₂ S	30.4	Na ₂ S	-
Na ₂ CO ₃	20	Na ₂ CO ₃	-
Total alkali	157.6	Total alkali	100
Active alkali	137.6	Active alkali	100
Effective alkali	114.7	Effective alkali	100
Sulfidity 22.1%		Sulfidity 0%	

After digestion, the brown stock was washed thoroughly with water until no color in the resulting water was observed and the alkali residue removed. Then, pulp was screened on a vibratory screen with 0.25 mm slots.

The total yield was determined as percentage of dry matter obtained after pulping based on oven-dried raw materials. The fiber yield was the screened fraction, while the unscreened portion was the rejected yield.

Kappa number, determined according to TAPPI Test Method T236 - Kappa Number of Pulp, analyzed the screened pulp for degree of delignification. The limiting (intrinsic) viscosity of selected pulps was measured according to ISO standard 5351:2010 Pulps – Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution.

Oxygen delignification. Pulps were further delignified, in the same reactor, using a oxygen delignification stage at elevated temperature in an alkaline environment. 100 g of pulp samples were mixed with 1% magnesium sulphate (on o.d. pulp), 3% sodium hydroxide (on o.d. pulp) and then adjusted to 3% consistency using distilled water. In all bleaching experiments, reactor was pressurized with oxygen at 0.5 MPa and heated at 100°C for 60 min. At the end of reaction, the

reactor was cooled and the oxygen pressure was released.

After oxygen delignification, the liquor was separated from the pulp and was thoroughly washed with water until completely removing alkali residue remained in the pulp. The kappa number and viscosity of the oxygen-delignified pulps were determined according to the same standard test methods as used for the cooked pulps.

All experiments were replicated to obtain reproducible data.

III. RESULTS AND DISCUSSION

The pulping and bleaching potential of rapeseed stalks were investigated in this study. Pulping conditions and pulp yields obtained in kraft and soda-AQ pulping are given in table 2.

Depending on pulping conditions, both cooking experiments lead to similar yields (38-39%) with very low amount of screened rejects. As previously reported in alkaline pulping (Tofanica and Gavrilescu, 2011), results have shown that in all processes the delignification rate increase by increasing the alkali charge, delignification being extended as proven from the low kappa number of the cellulose fibers obtained (illustrated in figure 3 and 4). This finding could be explained by the advance of delignification, which reduces the total yield, because of the dissolution of lignin in pulping liquor, and on the degradation and solubilization of other components from plant tissue - especially the hemicelluloses. The total pulping yields for kraft and soda-AQ pulps were similar to those obtained earlier from this nonwood raw material under the similar conditions (Tofanica et al., 2010; Tofanica et al., 2011b).

Table 2 Pulping conditions and pulp characteristics in Kraft and Soda-AQ experiments

Pulp sample		Alkali charge, %	Temperature, °C	Fibers yield, %	Rejected, %	Total yield, %
Kraft	A-6	18	170	39.0	0.7	39.7
	A-9	20	170	38.9	0.0	38.9
	A-12	22	170	38.2	0.0	38.2
Soda-AQ	B-6	18	170	38.4	0.5	38.9
	B-9	20	170	38.6	0.0	38.6
	B-12	22	170	38.5	0.0	38.5

Delignification conditions showed clear differences in kappa number and viscosity values (table 3) of rapeseed pulps. These values decrease with the increasing alkali charge from 18-22% with every additional alkali charge. In general, a lower alkali charge lead to a higher kappa number

and pulp viscosity. It was observed that an increase in alkali charge at a constant 2% alkali charge rate, results in a clear reduction in kappa number, while in intrinsic viscosity differences were minor.

Table 3 Oxygen delignification of Kraft and Soda-AQ pulps from rapeseed stalks

Pulp sample		Yield		Kappa number			Intrinsic viscosity, mL/g		
		Bleaching, %	Overall, %	Before	After	Drop, %	Before	After	Drop, %
Kraft	A-6-O	94.8	37.6	72	48	33	830	822	1
	A-9-O	96.0	37.3	46	26	43	802	770	4
	A-12-O	98.6	37.7	39	22	44	786	764	3
Soda-AQ	B-6-O	93.9	36.5	58	35	40	812	804	1
	B-9-O	97.0	37.4	35	20	43	768	737	4
	B-12-O	98.1	37.8	28	14	50	753	732	3

The pulp bleachability was assessed in a simple oxygen delignification stage, chosen in all sequences due to its simplicity in use, efficiency and selectivity as a chlorine-free agent, but also to

its successful use in bleaching of nonwood pulps. Bleaching and overall yields, kappa numbers and intrinsic viscosities of pulps after oxygen stage are summarized in table 3.

Bleachability was found to be influenced by the alkali charge of the initial pulp, with the lower lignin content pulp being more responsive to oxygen delignification conditions. These results demonstrate that reactivity of the lignin in the pulp towards bleaching increases as the extent of delignification is increased.

Figures 4 and 5 show the effect of alkali charge on yield and kappa number of the kraft and soda-AQ pulps after pulping and after oxygen stage. In addition, for both the kraft and soda-AQ pulps, viscosity values seemed to correlate well with alkali charge addition.

Viscosity values were low and did not show too much difference between the samples. However, viscosity decreased steadily with an increased delignification rate as alkaline charges were employed. As indicated, kraft pulps suffered a 1-4% decrease in viscosity units, whereas soda-

AQ pulps showed a similar decrease. As shown in figure 5, the conditions that favored greater kappa reduction also caused additional damage to carbohydrates, accompanied with a reduction in the pulp viscosity.

Depending on initial pulp, bleaching yields varies between 93-98%, what represents about 36-38% compared to the initial mass of rapeseed stalks. The rate of delignification, expressed as kappa number of the pulps, shows differences between kraft and soda-AQ pulps. The pulps from kraft process presents a drop of 33-43% in terms of kappa number, while the soda-AQ pulps show an enhanced reducing of kappa number at levels of 40-50%. On the other hand, the pulps had no differences in terms of intrinsic viscosity regardless of type of delignification, decreases observed being 1-4%.

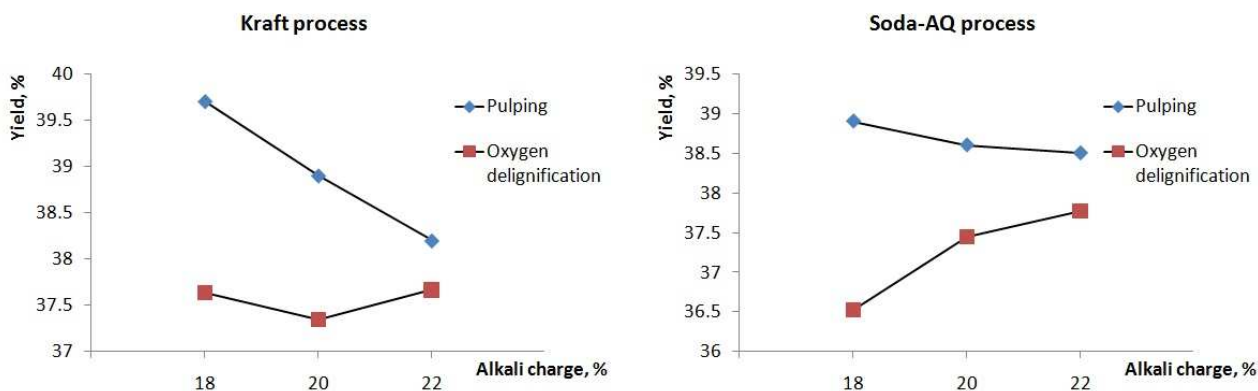


Fig. 4 Effect of alkali charge on total yield of kraft and soda-AQ pulps after pulping and oxygen delignification.

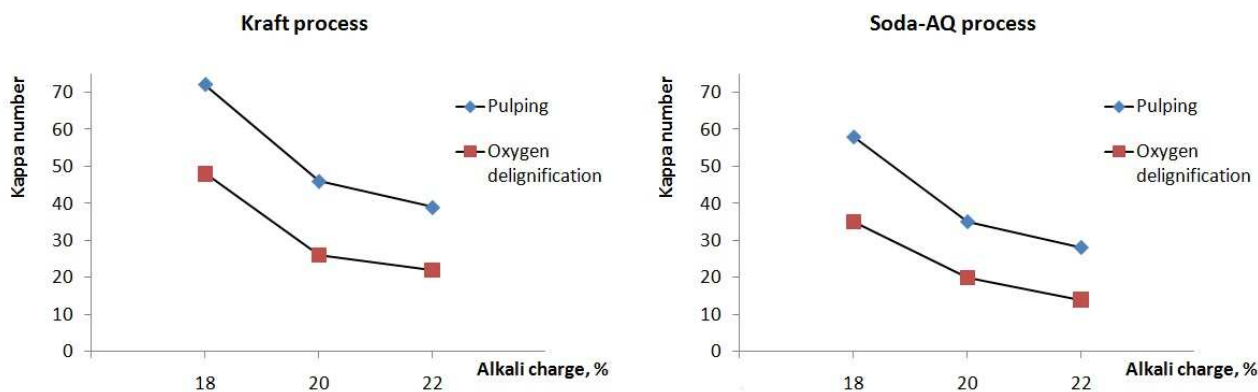


Fig. 5 Effect of alkali charge on kappa number of kraft and soda-AQ pulps after pulping and oxygen delignification

The oxygen delignification stage caused the kappa number of the pulp to drop 14-24 units over the conditions used in these experiments (figure 6). The kappa number diminish was greater at kraft pulps, but cause percentage drop in kappa number similar to soda-AQ pulps.

Considering the overall yield, the pulping done with Soda-AQ resulted in better yield after cooking, but after oxygen delignification the overall yield were similar when calculated gravimetric. On the other hand, as overall selectivity is considered, the pulps with higher alkali charge and with subsequent oxygen delignification was more selective towards lignin removal by taking into account dissolution of lignin.

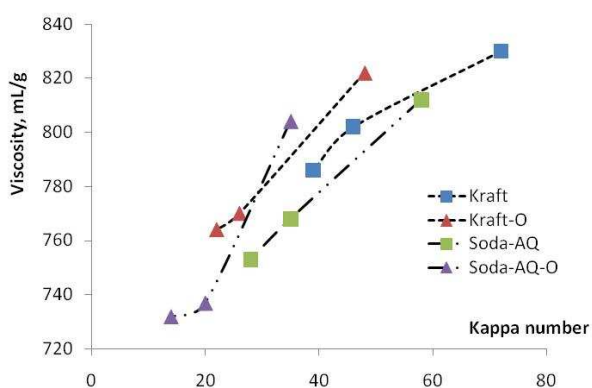


Fig. 6 Effect of alkali charge on kappa number of kraft and soda-AQ pulps after pulping and oxygen delignification

Besides delignification, oxygen bleaching was aimed to increase pulp brightness. Although the highest brightness could be obtained by applying the most severe delignification conditions, mild to moderate conditions are preferable in order to prevent the viscosity of the corresponding pulp decreases to an unacceptable level.

IV. CONCLUSIONS

The kraft and soda-AQ pulps from rapeseed stalks can be bleached to kappa number values bellow 30, by a short oxygen bleaching sequence, maintaining satisfactory yield levels and without affecting pulp viscosity. The soda-AQ pulps showed the highest bleachability in terms of kappa number values, while the kraft pulps had a better bleachability in terms of intrinsic viscosity values.

Both alkaline processes led to satisfactory pulped and bleached yields. Compared to kraft pulps, soda-AQ delignification is more effective

resulting in pulps with considerably lower kappa number.

Regarding bleaching it was demonstrated that rapeseed alkaline pulps could be bleached easily in a short oxygen delignification sequence. Despite the high kappa number after pulping, an oxygen stage is very efficient in reducing the degree of delignification.

Reactions in alkaline medium during oxygen bleaching of rapeseed pulps led to partial removal of lignin - resulting in pulps with considerably lower kappa number, and to moderate carbohydrate degradation - providing good yields and low intrinsic viscosity losses of bleached pulps.

Oxygen delignification as the first stage bleaching sequence has shown its ability to reduce the lignin content of high kappa number rapeseed pulps with minor reduction in yield and viscosity. An oxygen delignification stage appear to be beneficial for further bleaching sequences. For a better utilization of rapeseed stalks as a fiber source, the application of alkaline pulping and one oxygen delignification stage provide an alternative for obtaining a small kappa number pulp with good intrinsic viscosity values.

Figure 6. Oxygen delignification effect on kappa number of kraft and soda-AQ pulps (decrease in units of kappa number).

V. ACKNOWLEDGEMENTS

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ENERGY SAVINGS IN PAPER MACHINE VACUUM SYSTEM HOW TO UTILIZE MODERN PROCESS AND VARIABLE SPEED DRIVE TECHNOLOGY

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Abstract

Energy price is soaring beyond all expectations. On the other hand, new technologies are emerging to tackle this challenge. But how much energy can be saved without putting paper production in risk? In paper industry, we are used – for a good reason – to be rather conservative in applying new inventions. Savings in one cost factors tend to be marginal in relation to overall cost and income. Any disturbance in production, however, will cost a lot in lost profits. The rising price of energy is putting a pressure on paper production. Besides the pulp production, paper machine lines consume significant amount of energy, when the production volumes are high and the unit processes are heavy users of energy. Out of these pumping cost and paper machine drives are the heavy users. New technologies in process design, pumping principle and variable speed electric drives can cut the pumping energy bill dramatically. Vacuum pump choice and mode of operation has a significant impact on energy consumption. High power is used to produce the vacuums needed in drainage and web handling, i.e. for suction boxes and suction rolls. Further on, these vacuum elements often represent big portion of the friction increasing machine drive loads. Dimensioning the system can be a tricky task, because so many variables are involved, and many of them (such as raw material, water, water temperatures) are often beyond the control – at least beyond economical control – of the machine personnel. By utilizing energy efficient pumping principle and controllable technology, this obstacle can be overcome.

Key words: *energy, paper, paper machine, vacuum elements, unit processes*

Rezumat

Prețul energiei este în continuă creștere, depășind toate așteptările. Pe de o parte, noi tehnologii sunt în curs de dezvoltare pentru a aborda această provocare. Dar cât de multă energie poate fi salvată pentru a pune producția de hârtie în afara riscului. Ne-am obișnuit ca industria de hârtie să fie mai conservatoare în ceea ce privește noile invenții. Economii la unul din factorii de cost tind să fie marginale în raport cu costurile globale și veniturile. Prin urmare, orice perturbare a producției, va avea efect pronunțat asupra pierderii profitului. Creșterea prețului energiei va pune presiuni asupra producției de hârtie. Alături de producția de celuloză, liniile mașinilor de hârtie consumă cantități semnificative de energie, atunci când volumul producției este ridicat, iar unitățile de proces sunt mari consumatori de energie. Dintre acestea, sistemele de pompare și sistemul de acționare a mașinii de hârtie sunt mari consumatori de energie. Noile tehnologii în procesul de proiectare, principiul de pompare și variatoarele electrice de viteză pot reduce semnificativ valoarea facturii la energie. Alegerea pompei de vacuum și a modului de operare au un impact semnificativ asupra consumului de energie. Pentru producerea vacuumului necesar în deshidratarea și conducerea benzii de hârtie sunt necesare cutii și valțuri sugare de putere mare. Dimensionarea sistemului este o sarcină dificilă, datorită foarte multor variabile care sunt implicate, multe dintre ele (cum ar fi materiile prime, apa, temperatura apei) sunt adesea greu de controlat. Prin utilizarea principiului eficient de furnizare a energiei și a unei tehnologii controlabile, aceste obstacole pot fi depășite.

Cuvinte cheie: *energie, hârtie, mașină de hârtie, elemente de vacuum, unități de proces*

Moreover, the behavior is varying significantly by the age of the felt, and by the type of the felt. Measurements bring facts and knowledge to the art of paper making. Utilizing them efficiently, one can:

- find the optimal vacuum levels
- select the best performing felts and fabrics
- schedule the fabric changes and cleaning shutdowns optimally

- locate the causes for process disturbances quickly
- find the bottlenecks in doctoring and water handling

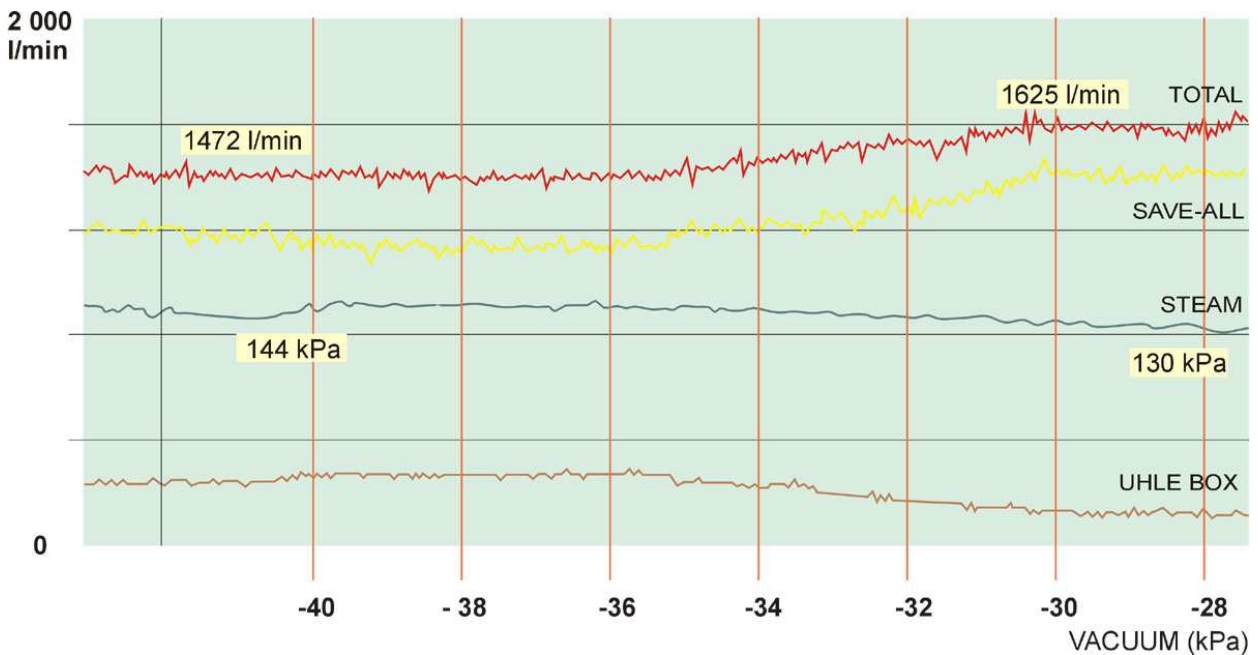


Fig. 2 Felt dewatering values in relation to uhle box vacuum level

System controllability

The first big steps in this adjusting the vacuums down can be done by reconnecting the piping and shutting down obsolete pumps.

After that, the system controllability comes into the picture. The good old technology meets its shortages here. Water ring pumps often have rather limited control range, between the collapse of the water ring and the overload due to frictions in rotating the water. Old type multistage blowers cannot be operated with variable speed, due to mechanical resonances and/or only one or two large aggregates serving the whole PM. Fixed speed large aggregate means that vacuum control must be done with valves or guide vanes that significantly reduce the energy efficiency.

Combining the good things of the two old systems – power efficiency of turbo blowers and versatility of water ring pump systems – together with variable speed electric drive technology brings the energy efficiency to new level. All this

comes without giving up the system reliability of multi-pump system. With traditional water ring pumps there is typically piping arrangement that allows backup connection system is functional even when one of the water ring pumps is out of service. Or there is even a spare pump available to maximize the system availability. The same kind of arrangement is possible with a multiple turbo system such as Ecopump.

The above mentioned as background, a system consisting of 3-6 variable speed turbo blowers is radically more energy efficient than the traditional alternatives. The power consumption can be brought down by 30..60% depending whether the old system is based on turbo or water ring technology.

The equipment to enable such a turbo consists of:

- High speed AC motor capable to operate from zero to 500kW/10000rpm range
- Frequency converter configured to this rpm range

- One or two turbo impellers directly mounted on the high speed motor shaft
- High performance water and drop separation system

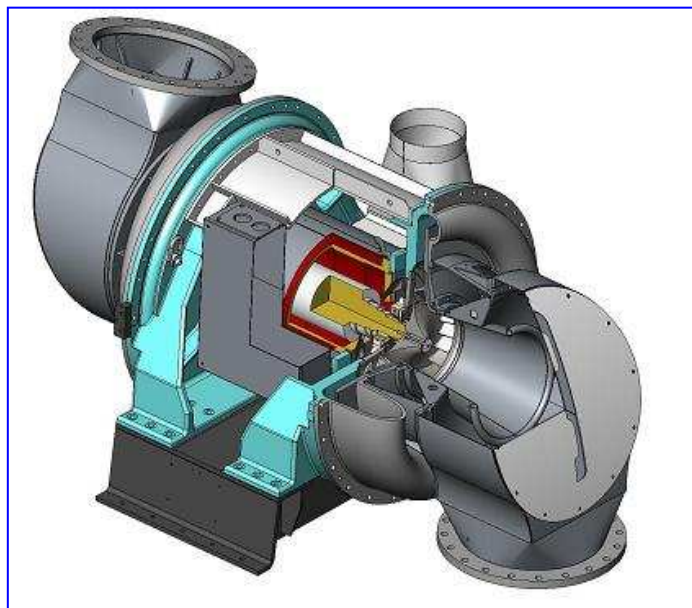


Fig. 3 Ecopump Turbo unit

The system consists typically of 3-6 turbo blowers, which is configured like typical water ring pump system, which offers good system control and backup possibilities which makes this kind reliable and easy to operate. Turbo principle gives initially highest possible efficiency. On top of this, the speed control makes the savings from capacity control available.

From investment point of view, the controllable high speed offers good savings, too. Because of the high speed, the size of equipment is limited – which is reduces the floor space needed. Further on, the mass is low – and does not require heavy fundamentals. Good balanced equipment does not vibrate much. But any vibrations are on high frequency, which makes the dampening with simple measures more efficient. Vacuum control is mostly done with the variable speed. This reduces the number of large (and often automatic) valves. Only the individual suction positions of, for example, wire suction boxes require control valves. When moving large amounts of air, making noise is unavoidable. But since the noise is of high frequency (around 2000Hz), it is rather easy to dampen, which reduces the cost of silencing and makes the system environmentally friendly. All these together: the total investment cost is lower than with traditional techniques.

Variable speed drives are nowadays standard technology in the mills. Utilizing them in vacuum system is a natural step in improving energy efficiency. With this solution specially developed to economical pumping performance, this great potential can be utilized.

Vacuum surveys and system optimization

A good way to proceed in this energy and water saving investment planning is a procedure consisting of three steps:

- 1) Light survey
- 2) Full process survey and project plan
- 3) System rebuild

Light survey

The work goes as follows. A system expert visits the mill for one day. During this day he collects the basic data on the system: production tonnage, grade etc on one hand, power consumption on the other hand. With this data, the benchmark numbers can be calculated. This step can easily be done by the mill personnel, but sometimes the data is not readily available or it is not reliable. If this first round suggests that there is good potential for improvement, the further steps are to be taken.

Full survey

To verify the findings in the light survey, a full study is then made. This means measuring each and every variable in vacuum system function onsite, with calibrated equipment. Quite often, the gauges and sensors that are installed at the machine, are not giving exactly right values. They may be good enough for daily operation, but not good enough to reveal leaks and throttling, for example. Based on this measurement data, the real efficiency of the system is then calculated.

The ratio thermodynamic power or the air removed from the suction position is compared to the electric power consumed at pumps. It is quite common for the water ring pump systems that some vacuum positions work with only 10% energy efficiency. Any efficiency level over 30% can be considered good result for this kind of pumps. For a turbo system, over 50% efficiency should be reached to be considered normal or good. However, a lot of power is often wasted in

Rebuild

The survey report comes with a project plan. It provides:

- Schematic description on the modification suggested
- Layout plan
- Calculations on the energy savings
- Materials list (BOM)
- Cost estimate

The rebuild itself is backed with engineering support, installation supervision and commissioning. Further on, the new system will be optimized after new running patterns are established.

In the following cases, there are some examples from real life.

Reference Cases

Tens of systems are already in use. The longest operating experience is already over 7 years at Laminating Papers Kotka PM1 – and the mill

throttling, because a multistage turbo aggregate can't be adjusted to the capacity actually needed.

By eliminating excessive leaks and throttling, and reconnecting the piping more optimally, significant savings can often be reached. The saving can be realized by simply shutting down excess pumps after reconnecting – or by changing the rotation speed, which requires investing in new gear set. For multistage turbo system, this optimization is often complicated, because shutting down one of the two (or alike) turbo aggregates represent such a big portion of total capacity.

Changing some or all of the pumps to speed controlled turbo provides good savings. This applies especially to low vacuum (<40kPa) positions, because here moving the air takes relatively little power vs. the power needed to rotate the water ring. Another good potential for saving are the variable vacuum (felt uhle boxes) positions. Sometimes the suction roll positions give good payback, too, even though here the water ring pumps are at its best.

people are quite happy with the system. It produces the vacuum needed, is easy to adapt to process changes and does not cause any trouble – but the power cons is 40% less than with the earlier water ring pump system.

Stora Enso Oulu PM6

Here the existing pumps were reconnected by utilizing dewatering measurements to determine the actual need for vacuum capacity. Out of 11 large water ring pumps, 3 were shut down. The power saving was about 1000kW – practically without investment. Some minor piping modifications were required, though. (Figure 4)

The equipment and required (the Ecoflow System was there already) was:

- Some piping modifications and valves only

The results:

- Power consumption was cut by 1 200 kW
- Seal Water consumption was cut by 480 000m³/a

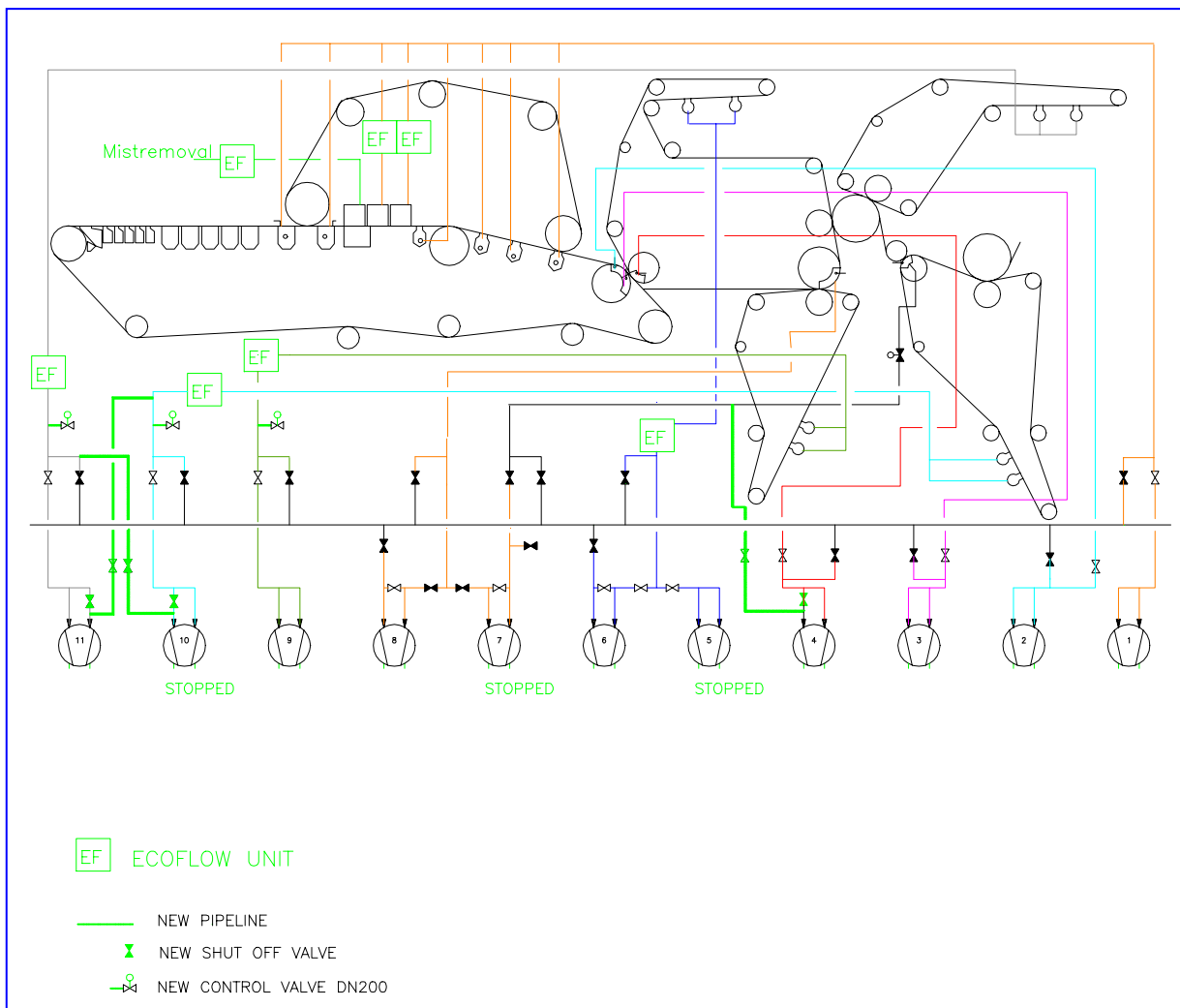


Fig. 4 Ecoflow Unit

Stora Enso Kaukopää PM8

Here, a system consisting of two multistage blowers was rebuilt to run one multistage turbo and one variable speed turbo. The saving realized was 900kW and at the same time the system reliability was significantly improved, when the multistage turbo unit shut down was left as spare unit. (This backup was considered necessary, due to severe problems with the old multistage blowers.) (figure 5) .The equipment and required was:

- EP 500 Turbo with electric drive

- Modification of the existing water separator 1 ea
- 7 valves (5 automatic, 2 manual)
- Drain pump
- Some piping modifications

The results:

- Power consumption was cut by 900kW
- Water separation was improved, now does not cause problems anymore
- Backup capacity available

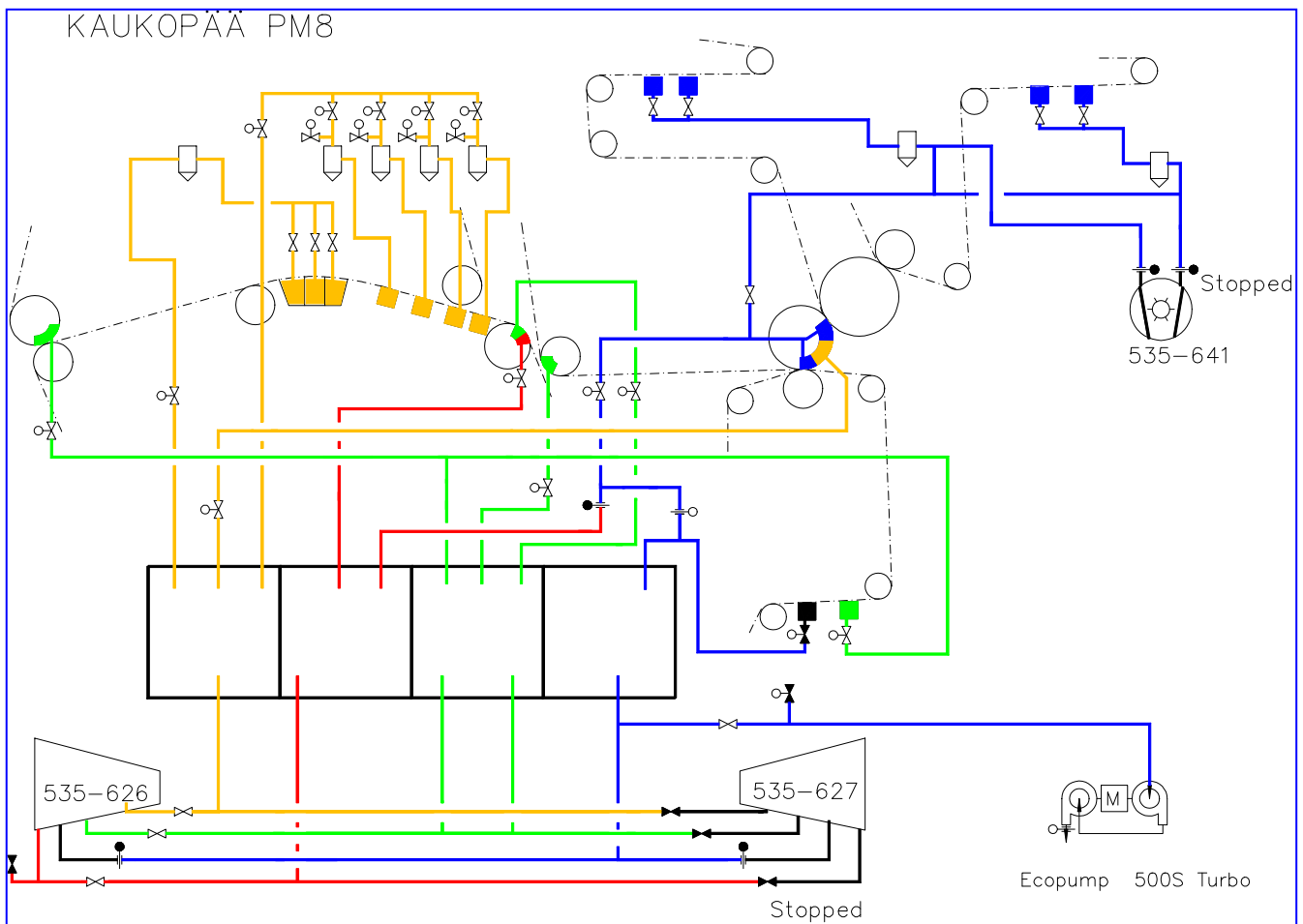


Fig. 5 Stora Enso Kaukopää PM8

M-Real Tako

Here, a rather old system consisting of 5 water ring pumps, consuming 700kW electric power, was rebuilt by replacing 4 of them with one Ecopump Turbo. The old pump serving couch roll was kept, because the vacuum level of this position was significantly different from those other positions. (figure 6) The equipment and required was:

- EP 315 Turbo with electric drive
- Water separators 2ea
- 7 valves (5 automatic, 2 manual)
- Drain pump
- Some piping modifications

The results:

- Power consumption was cut by 50% the reduction being 350kW
- Seal Water consumption was cut by 80%, the reduction being 280000 m³/a

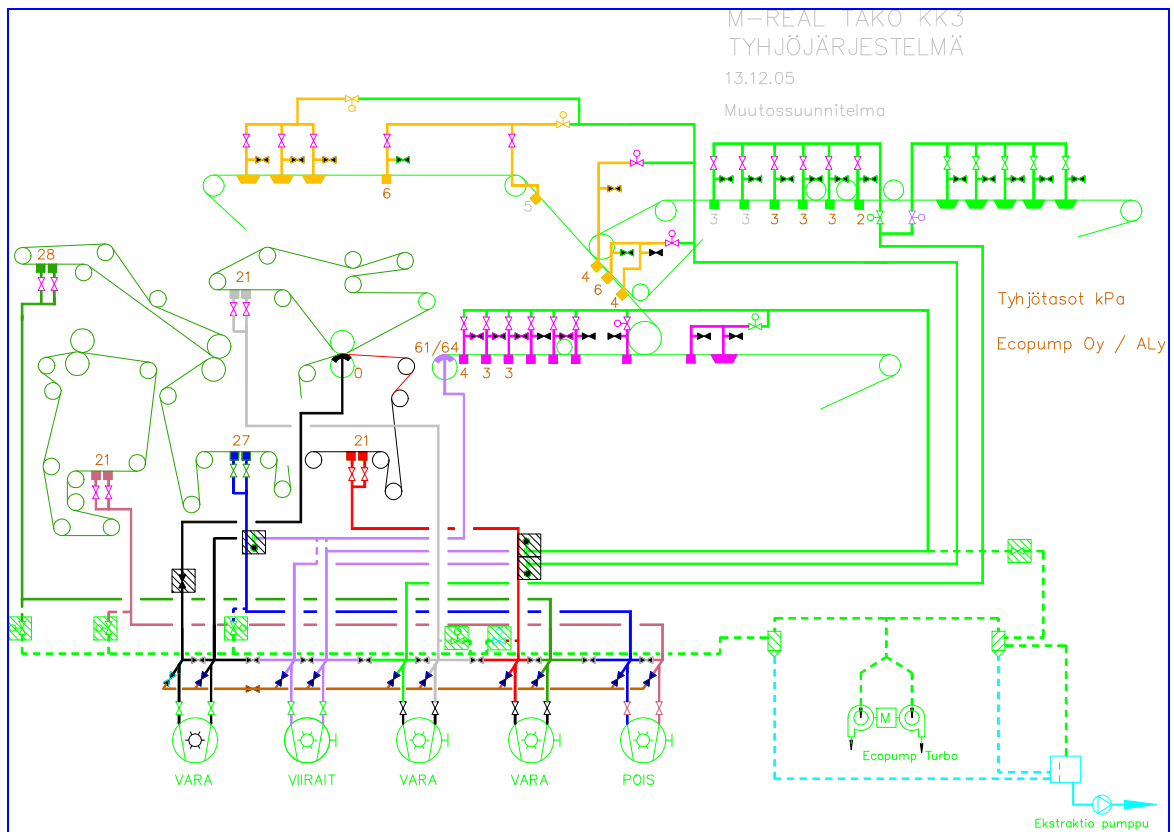


Fig.6 M-Real Tako

RESEARCH REGARDING THE MANUFACTURING OF THE FOOD-PACKAGING PAPER WITH BARRIER PROPERTIES

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Abstract

The new packaging materials from cellulosic fibers for oily and grease foodstuffs represent an important segment of the packaging materials market and it must to integrate into the system of food quality assurance, from food packaging up to the consumer. The paper presents some information regarding: a) main characteristics that induce the food-packaging quality of paper; b) laboratory paper fabrication flow; c) elaboration of working recipes for the base paper and mass/surface treatment recipes for impermeabilization and setting of process parameters – preliminary tests; d) analysis and characterization of papers obtained and evaluation of their conformity with food security requirements.

Key words: *packaging, cellulose fibres, foodstuffs, food security, waterproofing treatments*

Rezumat

Noile materiale din fibre celulozice pentru ambalarea alimentelor cu conținut de uleiuri și grăsimi reprezintă un segment important din piața materialelor de ambalare și trebuie să se integreze în sistem, prin asigurarea calității alimentului, pe lanțul ambalaj alimentar – consumator. Lucrarea prezintă câteva informații legate de : a) principalele caracteristici induse de calitatea hârtiei ca ambalaj pentru produse alimentare; b) obținerea hârtiei de ambalaj în laborator; c) elaborarea unor rețete pentru hârtia suport și tratamentele în masă și la suprafața acesteia în scopul conferirii proprietăților de barieră; d) analiza și caracterizarea hârtiilor obținute și evaluarea conformității cu cerințele privind siguranța alimentară

Cuvinte cheie: *ambalaje, fibre celulozice, alimente, siguranță alimentară, tratamente de impermeabilizare*

I. INTRODUCTION

Packaging materials for foodstuffs must have good barrier properties to protect the contents from exterior influences such as oxygen, light, water and water vapour, oil, grease, etc, and do not contain potentially toxic compounds that can migrate into food. [1]

Activities carried had the following objectives:

1. Study of phenomena taking place in the fibrous material chemical and mechanical processing and

evaluation of the mass and surface impermeabilization treatments

2. Setting the correlation between absorbability, specific surface of recovered fibrous material and the operating principle as regards the impermeabilization additive

3. Elaboration of working recipes for the base paper and mass/surface treatment recipes for impermeabilization and setting of process parameters – preliminary tests

4. Analysis and characterization of papers obtained and evaluation of their conformity with food security requirements [2,4]

II. EXPERIMENTAL PROGRAM AND ACHIEVED RESULTS

1. Fibre swelling

- At a simple water immersion, without any mechanical treatment, the volumetric swelling degree of hardwood pulp was 38% and for softwood pulp, 32%.
- Regardless the pulp grade, the swelling degree rises slowly when the pH increases and registers a maximum pH of 9.3.
- Presence of electrolytes in water changes the swelling capacity of cellulosic fibres in the following order: $Ca^{2+} < Mg^{2+} < Na^{+}$.

2. Pulp refining

- pulp refining has been carried out in holender: 1.5 – 2% consistency; lever arm load - approx. 54 N; cylinder rotation frequency - approx. $8.3 s^{-1}$
- freenesses : 30°SR, 40°SR, 50°SR

- main refining effects on fibers are : a) dimensional modifications, b) external fibrillation and increase of external specific area respectively, c) internal fibrillation, that results in the modification of elasticity and plasticity of cellulosic fibres and compactibility, respectively.

3. Elaboration of the base paper recipes and mass/surface treatment recipes for impermeabilization and setting of process parameters – preliminary tests

In order to produce a barrier paper 2 directions have been approached and aimed to:

- a. Identify and set some recipes for producing some barrier papers by implementing some mass impermeabilization treatments.
- b. Identify and set some recipes for producing some base papers and applying surface treatments to provide barrier properties to the paper.

Table 1 Recipes for producing some barrier papers by applying some mass impermeabilization treatments

No	Recipe		
	S5-2%	S5-3%	S5-4%
1	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% Fluorochemical agent -2%	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% Fluorochemical agent – 3%	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% Fluorochemical agent – 4%
2	S6-2%	S6-3%	S6-4%
	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% CaCO3 – 20% Fluorochemical agent – 2%	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% CaCO3 – 20% Fluorochemical agent– 3%	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% CaCO3 – 20% Fluorochemical agent – 4%
3	S7-2%	S7-3%	S7-4%
	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% Zeolite – 20% Fluorochemical agent – 2%	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% Zeolite – 20% Fluorochemical agent – 3%	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2% Zeolite – 20% Fluorochemical agent – 4%

For the preliminary tests a cationic fluorochemical aid has been used, soluble in hard water and that does not require a retention aid.

Analysing the results obtained the following conclusions can be drawn:

- Mechanical and capillary-hygroscopic strength properties are influenced by a series of factors such as: type of fibre, freeness, content of filler and nature of filler, sizing system etc. (Figure 1)

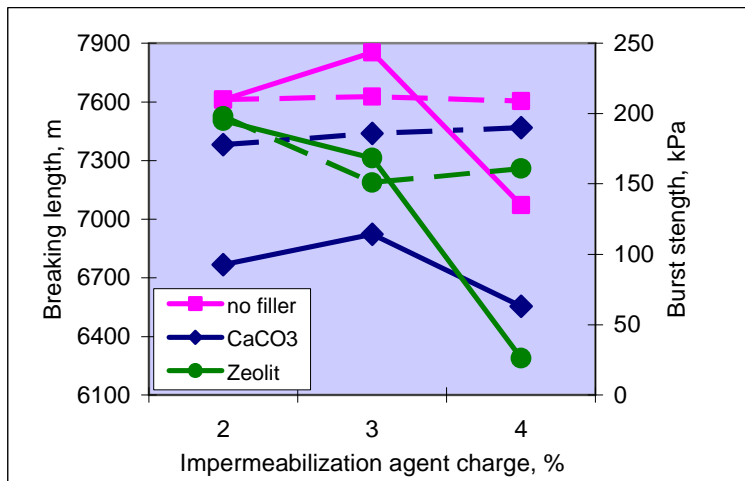


Fig.1 Influence of mass impermeabilization treatment on mechanical strength properties
 — breaking length
 - - - burst strength

- The impermeabilization aid also plays the role of a sizing aid, fact proved by reduction of water absorption at the same time with increasing the charge of this component. This reduction is more marked in case of the paper produced filler free and the paper produced using zeolite as a filler. Most likely, interfibre

penetration reduces its intensity, as a result of blocking the interfibre capillary flow by zeolite and reducing the fibres swelling potential by absorbing a higher quantity of impermeabilization aid on their surface (combined with reducing the high dimension pores and the high swelling potential of fibres refined more intensely). (Figure 2).

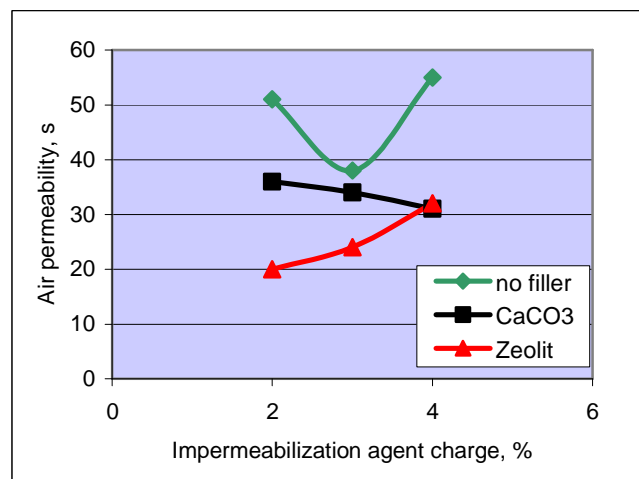
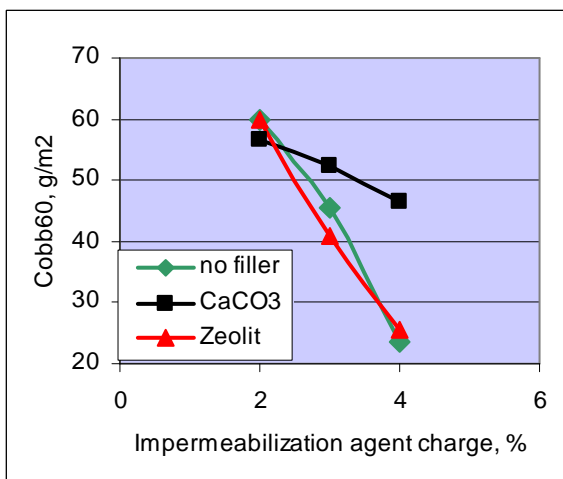


Fig.2 Influence of filler on water absorbability and air transit strength

- The impermeability degree (Figure 3) is influenced by the quantity of polymer adsorbed for a uniform fibre coating. The presence of filler results in an increase of specific paper area influencing the consumption of cationic aid for the same performance level. In order to get values of the KIT test higher than 6, the impermeabilization aid consumption increases

as follows: no filler < Zeolite < CaCO₃. It should be mentioned that in order to produce a paper with KIT 6 – 7, suitable for pastry packaging, 20% zeolite can be used as a filler (for a 3 – 4% charge of mass impermeabilization aid), that means a cellulosic fibrous material saving.

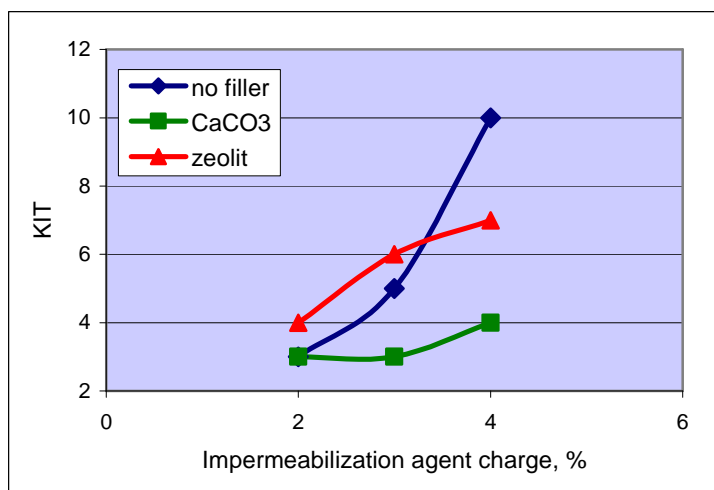


Fig.3 Influence of impermeabilization aid on oil and grease paper strength

- Between the surface of the biggest pores – that determines the grease strength – and the general distribution of pore size – that determines air permeability – there is a close

relation. It is noticed the rise of air transit strength at the same time with increasing the impermeabilization aid charge in case of using zeolite as a filler. [4]

Table 2 Recipes for producing some base papers and application of surface treatments to provide barrier properties to the paper

No.	Recipe		
	S1b	S1c	S3b
1	50 % hardwood pulp 40°SR 50 % softwood pulp 40°SR Kymene - 2%	50 % hardwood pulp 50°SR 50 % softwood pulp 50°SR Kymene - 2%	30 % hardwood pulp 40°SR 70 % softwood pulp 40°SR Kymene - 2%
2	S3c	S8	S9
	30 % hardwood pulp 50°SR 70 % softwood pulp 50°SR Kymene - 2%	30 % hardwood pulp 40°SR 70 % softwood pulp, 40°SR Kymene - 2%; Zeolite – 20% Aquapel 210 – 2,5%	30 % hardwood pulp, 40°SR 70 % softwood pulp, 40°SR Kymene - 2%; CaCO3 – 20% Aquapel 210 – 2,5%

Samples S1b, S1c, S3b and S3c have been treated at surface with a solution containing: potato oxidized starch (5%) and zeolite - 2, 4, 6%
Samples S8 and S9 have been treated at surface with a solution containing: potato oxidized starch (3.5%); fluorochemical agent (L)– 0.4% / Chitosan (CH) – 0.8% / activated carbon – 0.1; 0.3% (C); EDTA (c = 80g/l) – 0.8 %; Na₂CO₃ (c=10%) – 0.1%

Analyzing the results the following is noticed:

- Barrier properties of papers improve by increasing the softwood pulp charge and raising the cellulosic fibrous material freeness.
- The lowest value of water absorption Cobb₆₀, namely 34.9g/m² is registered for the paper produced of 50% softwood pulp and 50% hardwood pulp, both refined at a freeness of 50°SR, surface treated with a starch solution containing 2% zeolite (Figure 4)

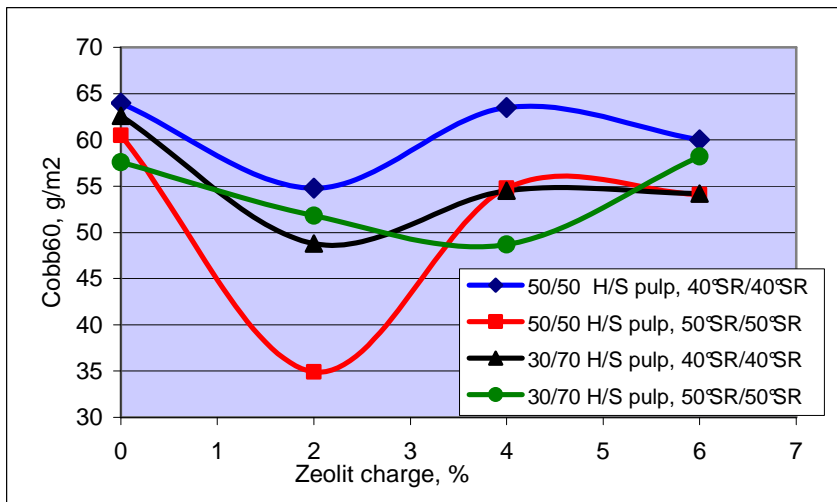
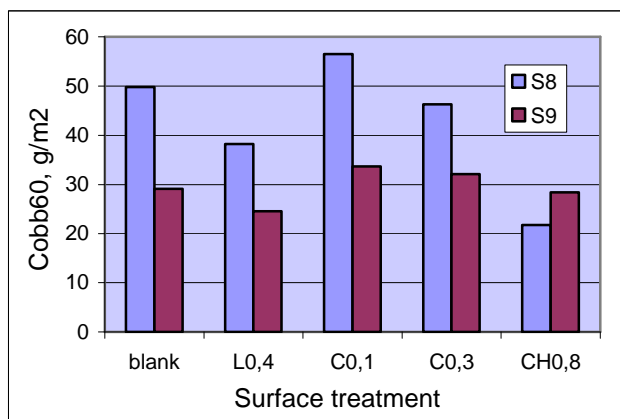


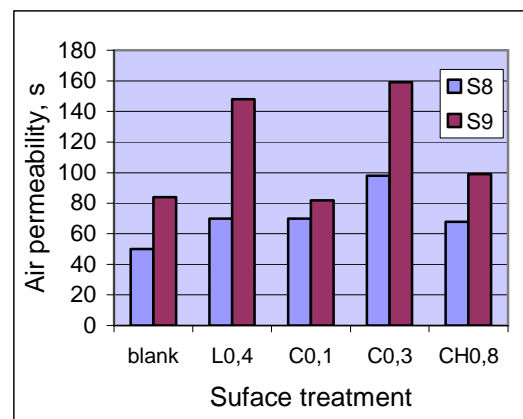
Fig.4 Influence of zeolite treatment on paper strength to water penetration

- Paper barrier properties improve by applying surface treatments. The lowest values of water absorption is registered in case of recipes with zeolite and surface treatment with Chitosan 0.8%, in case of recipes with calcium

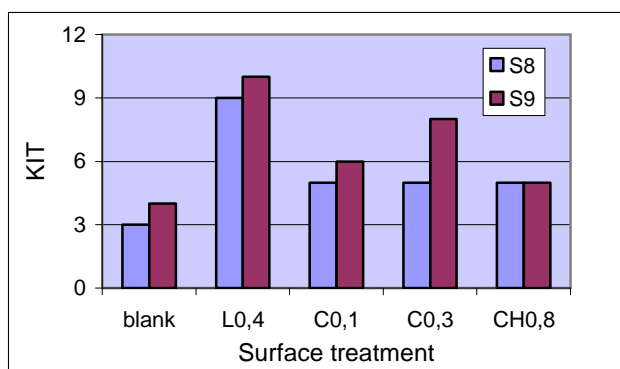
carbonate and fluorochemical agent surface treatment, respectively.
 - Impermeability degree, measured by the KIT value, as regards the zeolite treated papers has values higher than 9.



a)



b)



c)

Fig.5 Influence of surface treatments on capillary-hygroscopic characteristics
 a) Cobb water absorption;
 b) Gurley air permeability, s ;
 c) Impermeabilization degree KIT

- In case of non-sized papers, filler free, by applying surface treatments with solutions containing various zeolite charges (4%, 6%) reduces the paper air permeability significantly, obtaining values higher than 4000 s. Permeability also diminishes in case of sized papers and with a content of filler, by applying surface treatments with fluorochemical agent, Chitosan and active carbon. The highest values are registered for papers containing CaCO₃ and surface treated with a solution containing 0.3% active carbon, 0.4% fluorochemical agent, respectively.
- If the base paper is sized, enough impermeabilization aid is not absorbed in the fibre mass and as a result the impermeability degree expressed by the KIT value is much lower than in case of unsized paper. A KIT of 6 has been obtained in case of a base unsized paper, a KIT of 3 respectively in case of papers produced with a sizing aid charge of 2.5%.
- Base characteristics - a paper very refined or sized, diminishes the treatment performance as it prevents the impermeabilization aid penetration in paper mass. In line with the impermeabilization degree required to be obtained, the Cobb absorption of base paper is adjusted. This paper is to be surface treated.
- Paper surface treatment with impermeabilization polymers has the advantage to be more economic than paper mass treatment, as it is carried out with much

lower impermeabilization aid consumptions. (Figure 5).

4. Permeability to water vapour

Barrier properties in terms of water vapour permeability were determined by specific analyses, in conformity with SR EN ISO 15106-1: 2005 – Determination of water vapour transmission rate. Part 1: The method with humidity detector. The range of humidity in measure chamber: 5%– 50% RH. The range of temperature: 5 – 70°C. The device measures the time necessary for increasing of humidity into the top chamber since a predefined minimum value up to predefined maximum value.

The measured time is compared with the time registered in the calibration process of the standard film with known permeability and the result is expressed as water vapour transmission rate in g/m²/24h. Test cycle is repeated until results variation achieved a defined repeatability level, indicating that the sample attained equilibrium. The results of water vapour permeability test at 38°C, are presented in the table 3.

Table 3 Results of water vapour permeability test at 38°C

No	Sample	P (38 °C) (g/m ² ·day·atm)	PC* (38 °C) (g·mm/m ² ·day·atm)	Thickness (µm)
1.	S _{1a}	210,62	23,17	110
2.	S _{1b}	220,62	13,24	60
3.	S _{1c}	220,90	15,46	70
4.	S _{2a}	210,62	21,06	100
5.	S _{2b}	238,34	19,07	80
6.	S _{2c}	251,58	17,61	70
7.	S _{3a}	232,28	20,91	90
8.	S _{3b}	251,58	17,61	70
9.	S _{3c}	238,34	14,30	60
10.	S _{4a}	226,42	24,91	110
11.	S _{4b}	232,28	13,94	60
12.	S _{4c}	238,34	19,07	80
13.	S _{1bZ₂}	220,90	17,67	80
14.	S _{1cZ₂}	251,58	25,16	100
15.	S _{3bZ₂}	251,58	27,67	110
16.	S _{3cZ₂}	251,58	22,64	90

*Permeability index (PC) is reported at the tested film thickness in mm

In the series of samples S1 – S4 not recorded important differences between water vapour permeability values at 38°C; the lowest value was obtained for “a” samples. In the series S1bZ2 and

S3bZ2 is not also observed the significant differences between water vapour permeability values at 38°C; the lowest value was obtained for S1bZ2 sample.

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CHITOSAN DERIVATIVES FOR SURFACE PAPER COATING

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Abstract

As a result of increasing environmental concerns, there is an extensive research effort on using renewable resources to create sustainable, biodegradable coating systems. The application of chitosan as a coating on paper sheets could be an alternative to commercial systems that often use synthetic polymers as coatings. Chitosan is a linear polysaccharide derived from chitin, a major component of crustacean and insect shells. The advantages of chitosan are its biodegradability, antimicrobial activity, recyclability, and its compatibility with paper matrices. Generally, bio based coatings films containing natural polymers, like chitosan, is typically hydrophilic and has limited liquid water and water vapor barrier properties. In order to change the hydrophilic character of chitosan films and also to increase chitosan solubility in water over a wide pH range, which is important for its application as antimicrobial agent, one strategy is to synthesize and apply, as coating agents, water chitosan derivatives, such as alkyl-, carboxymethyl-, hydroxyalkyl-, quaternary- or cianoethyl-chitosan derivatives. Chemical modification of chitosan is of prime interest because the modification would keep the original physicochemical and biochemical properties of chitosan and, in addition, would bring new properties depending on the nature of the group introduced.

Key words: *surface sizing, paper coating, biopolymer, chitosan, barrier properties*

Rezumat

Ca rezultat al intensificării cerințelor privind protecția mediului, există un interes deosebit de cercetare asupra utilizării resurselor regenerabile, pentru a obține sisteme de acoperire durabile și biodegradabile. Aplicarea chitosanului ca aditivi pentru acoperirea hârtiei poate fi o alternativă la sistemele comerciale de acoperire, care adesea utilizează polimeri sintetici. Chitosanul este o polizaharidă cu catenă liniară derivat din chitină, o componentă majoră a crustaceelor și cochiliilor de insecte. Avantajele chitosanului sunt: biodegradabilitatea, activitatea antimicrobiană, reciclabilitatea și compatibilitatea cu componenții hârtiei. În general, straturile de acoperire pe bază de filme *bio*, conțin polimeri naturali, cum ar fi chitosan, sunt hidrofile și au capacitate limitată de barieră la apă și la vaporii de apă. În scopul modificării caracterului hidrofili al filmelor de chitosan și pentru a crește solubilitatea acestuia în apă într-un domeniu larg de pH, important pentru aplicarea ca agent antimicrobian, o strategie constă în a sintetiza și utiliza ca agent de acoperire, derivații de chitosan, cum ar fi: alchil-, carboximetil-, hidroalchil-, quaternar- sau cianoetil- chitosan. Modificarea chimică a chitosanului este de interes major deoarece trebuie să păstreze proprietățile fizicochimice și biochimice inițiale ale acestuia și în plus, trebuie să aducă noi proprietăți în funcție de natura grupelor introduse.

Cuvinte cheie: *încleiere la suprafață, cretarea hârtiei, biopolimer, chitosan, proprietăți de barieră*

I. INTRODUCTION

The paper, which consists of a porous cellulose network, is often surface treated for various decorative or functional reasons, such as improving printability, brightness and opacity, but also to improve its barrier properties to liquids, water vapors, oxygen, oil or aromas. The treatment of the paper surface in order to control its surface properties has been thoroughly explored. Two general approaches for the treatment of the paper surface are usually considered: *surface sizing*, the most frequently used processes for applying an aqueous coating to a paper substrate, and *coating process* which uses a different type of chemical formulation, including a pigment, a binder, a co-binder and a dispersant.

Surface sizing usually is performed by the application of an aqueous suspension of a polymer (e.g., cationic starch) alone or combined with a synthetic polymer, such as poly (styrene-co-acrylate) or poly (styrene-co-maleic anhydride). In surface sizing, the solid content of the coating is limited and is typically lower than 10% to 15%¹, the main advantage over internal sizing being the excellent retention of the polymer solution, providing 'instant' hydrophobation of paper surface.

The main role of surface sizing is to promote surface properties, e.g. strengthen the surface and bind particles, such as fibres and fillers, to the surface, but also to control some relevant paper surface properties such as porosity, roughness, and surface energy, in order to promote an adequate interaction with inks and to improve the final printing quality.^{2, 3} For surface sizing mostly polymeric sizing agents are used.⁴ The surface sizes or hydrophobing agents can be divided conveniently into the following categories: alkyl ketene dimmer, rosin-based products, and synthetic polymeric materials. Of these the synthetic polymeric materials are the most important in modern surface sizing. They have been developed specifically for application at the surface and are able to produce novel properties in the sheet.

Coating process, unlike surface sizing, use a different type of chemical formulation, including a pigment (with kaolin, calcium carbonate, titanium dioxide, aluminium oxide, and silica being the most common ones used), a binder (mostly polyvinyl alcohol or latexes such as styrene butadiene), a co-binder (e.g., carboxymethylcellulose), a thickener (e.g., carboxymethyl cellulose) and a dispersant (a

cationic polymer additive). The selection of the pigment and adhesive combinations is responsible to a very great extent for the resulting characteristics of the finished paper.⁵ Typically between 5g/m² and 30g/m² of coating are applied, the upper limit only being used in board coating. Coating paper or board increases the homogeneity of the surface and considerably improves its optical characteristics such as gloss, smoothness, brightness and opacity. Compared with the open, porous structure of a natural paper, coated papers show a much more homogeneous and closed surface, leading to more uniform ink receptivity and better ink holdout than uncoated papers.⁶

II. PAPER BARRIER PROPERTIES

The barrier properties are important because during processing and use, paper and cardboard comes in contact with different fluids which can penetrate the surface through various mechanisms and at different speeds. In some cases it is desirable for fluids to penetrate the structure of the paper with some controlled speed, which is a complex function of fluid and paper properties, and contact time. For some areas, the use of paper and paperboard, such as the packaging, required a wide range of barrier properties, depending on the nature of packaging material, storage conditions and transport. Packaging papers must provide barrier properties to water, gas, fats or flavors, depending on the composition and properties of products that comes into contact.⁷

Water barrier properties are required for packaging papers that came into contact, temporarily or permanently, with aqueous liquids. Depending on the contact time, the barrier properties is achieved by different methods: temporary barrier properties can be achieved by mass application of waterproof resins (synthetic polymers) or surface-treatment with polymer dispersions, emulsions or waxes with hydrophobization capacity (paraffin); permanent barrier properties are obtained by surface paper coating with one or more layers of different materials, applied by extrusion and/or lamination: polyvinylidene chloride (PVdc), polyethylene (PE), metalized polyethylene terephthalate (PET), polypropylene (PP), PET coated with silicone oxide.

Fat barrier properties are required when the packaging product contains oil or fat to be held within the container, because any loss of ingredients will be reflected in a lower quality product. To obtain the barrier properties,

greaseproof paper for packaging can be covered with aluminium foil, polyvinylidene chloride (PVdc). Polyethylene (PE), polypropylene (PP) and ionomer resins (Surlyn®) provide excellent barrier properties of fat.

Gas barrier properties are important to protect sensitive products from contamination, from atmospheric oxygen that trigger oxidative degradation processes or to protect products that are affected by the loss of flavor. To obtain gas barrier properties one can be used aluminum foil, ethylene vinyl alcohol (EVOH), polyvinylidene chloride (PVdc), PET aluminum metalized, PET coated with silicone oxide or wax coatings.⁸

III. CHITOSAN AND CHITOSAN DERIVATIVES FOR SURFACE COATINGS

Currently, many synthetic chemical additives are used in paper manufacture to improve or enhance the strength and printability of paper or to develop barrier properties to water, gases, fats or aromas. This is done by treating surface with different coating formulations that is mainly based on synthetic polymers: acrylic polymers, vinyl acrylic or styrene acrylic copolymers, vinyl acetate homopolymers, dispersants, rheology modifiers.⁹ The main disadvantages of these treatments are loss of recycling potential, reducing the capacity of composting and biodegradation, limitation of packaging use in contact with foods, non-renewable raw materials consumption. Many of these problems may be overcome by replacing synthetic materials with biopolymers from renewable resources,¹⁰ that are biodegradable, non-toxic and environmentally more benign than their synthetic counterparts, so there is a trend in papermaking to use these materials where possible.

In the last few decades, science and technology has started to move in the direction of renewable raw materials that are environmentally friendly and sustainable. Biopolymers, such as cellulose, chitin, chitosan and starch have been assessed, not only as sustainable resources, but also as attractive materials with interesting properties and functionalities.¹¹ Also, in papermaking, naturally renewable biopolymers have been the focus of much research in recent years, because of their potential as biodegradable films and coatings for food packaging. Biopolymer-based packaging materials originated from naturally renewable resources offer favorable environmental advantages of

recyclability and reutilization compared to conventional petroleum-based synthetic polymers. Biopolymer films and coatings may also serve as gas and solute barriers and complement other types of packaging by minimizing food quality deterioration and extending the shelf life of foods.¹²

Chitosan can be considered an alternative for replacing of some synthetic polymers, being a biopolymer obtained from renewable resources (shells of certain crustaceans) and meeting a number of important characteristics that make this polymer advantageous for numerous applications: it has a defined chemical structure; it can be chemically and enzymatically modified; it is physically and biologically functional; it is biodegradable and biocompatible with many organs, tissues, and cells; it can be processed into several products including flakes, fine powders, beads, membranes, sponges, cottons, fibers, and gels. Consequently, chitosan has found considerable application in various industrial areas. In paper industry, chitosan can be considered an alternative to commercial systems, that often use synthetic polymers as coatings, for the development of barrier properties, because have a number of important properties appropriate for applications in this field: is a cationic biopolymer, has the ability to form films, has antimicrobial properties, it is biodegradable and non toxic.

The combination of chitosan with paper is not new. The incorporation of chitosan in paper and paperboard, as a papermaking additive or as a surface coating, has been previously investigated and showed the aptitude of chitosan to form strong thin films that could be successfully applied onto paper surfaces, thus improving the performance of the coated paper, in terms of final properties. It has been used as an additive in papermaking and for surface treatments to improve the properties of paper. Chitosan coatings (0–30 g/m²) adhere well to paper surface and reduce the oxygen permeability. Also, incorporation of chitosan in the stock solution of the papermaking process results in a better paper consistency and provides good mechanical and gas barrier properties.¹³

Cellulosic fibers and chitosan are a very compatible fiber-binder system. Due to their chemical similarity, they readily form hydrogen bond to one another. The hydroxyl groups of chitosan have the potential to form hydrogen bonds with weakly polar areas of fiber surfaces, therefore contributing to paper strength development, if the fibers come sufficiently close in order to meet the required geometry conditions.

Therefore, the film-forming potential of chitosan not only facilitates the formation of van der Waals forces between the fibers, but also provides suitable conditions for hydrogen bonds to occur.¹⁴

Chitosan derivatives for paper coating

However, chitosan poor solubility in aqueous water, at pH above 6.5, and in most of common-used organic solvents, and also hydrophilic character of its films limits its utilizations in coating formula. Despite some improvement of paper properties, association of paper and chitosan was not yet suitable to food application because of water sensitivity, inherent to a majority of polysaccharides. Many works attempted to decrease water and moisture sensitivity of polysaccharides and one solution can be chemical modification of polysaccharides themselves.

Chemical modifications of chitosan are increasingly studied, having the potential of providing derivatives with new applications. These derivatives differ depending on specific reactions which involve the $-NH_2$ groups at the C-2 position or nonspecific reactions of $-OH$ groups at the C-3 and C-6 positions (especially esterification and etherification).¹⁵ The chemical modification refers to: *O-hydroxyalkylation*, carried out to obtain readily water-soluble chitosan; *reductive N-alkylation*, allowed the enhancement of chitosan chelating properties with metal ions; *O- and N-carboxyalkylations*, allowed the synthesis of anionic chitosan; *tosylation and N-phthaloylation* used as protective methods to carry out further modifications of chitosan; *acetylation and acylations*, occurred primarily on amino groups and carried out to modify hydrophilic/hydrophilic balance of chitosan, to make it soluble in organic solvents, to enhance its affinity with nonpolar compounds in separation technologies, or to engineer drug delivery systems.¹⁶ Another chemical route to improve the water solubility of chitosan, without changing its cationic character, is the introduction of an enough number of permanent positive charges in its chains. This can be done by preparing quaternary chitosan salts, via the covalent addition of a substituent containing a quaternary ammonium group or by the quaternization of the amino groups already present in chitosan. The latter route has been studied by a number of authors mainly by carrying out the methylation of the amino sites of chitosan.¹⁷

In papermaking, water-soluble chitosan derivatives have been used as retention and drainage aid agents in wet-end systems because of

their strong interaction with cellulosic substrates or mineral fillers. Nevertheless, their use as coating agents is still poorly explored.^{11, 18} Some studies¹⁸ evaluated the barrier properties against moisture and the liquid water sensitivity of chitosan coated papers. They showed that the chitosan coating led to a significant decrease of the paper moisture transfer, but the surface hydrophilicity remained high. Other studies have shown that a biodegradable laminate consisting of chitosan-cellulose and poly-caprolactone can be used in modified atmosphere packaging of fresh products. However, many problems still have to be solved before chitosan can be of commercial interest, replacing e.g. poly (ethylene-co-vinyl alcohol). Processing of chitosan is a relatively unexplored field, compared to the more conventional materials and the majority of the applications are still in a developing stage.¹⁹

Some researchers²⁰ explored the ability of bilayer chitosan-coated paper as fat barrier. The chitosan layer could act as a lipid trap coating to decrease fat transfer if the pH of the chitosan film-forming solution was adjusted to 5.5 to 6 prior to coating. In an attempt to decrease both treatment cost and fat transfer, chitosan was associated with various polymers. Incorporation of sodium alginate considerably increased the fat barrier of coated papers. Another work²¹ reported that chitosan-coated greaseproof papers exhibited excellent grease resistance within the coat weight range of 2.4 to 5.2 g/m². Due to the large amount of hydrogen bonds, biopolymer films of chitosan are hydrophilic, which makes them excellent barriers to non-polar substances, such as oxygen and some aroma compounds. Also, in some studies,^{21,22} paper was coated with chitosan or chitosan/carnauba wax to obtain a packaging material with good barrier properties towards oxygen, nitrogen, carbon dioxide and air.²³

Regarding the same barrier properties of paper, it was also made a comparative study on the effects of chitosan and three alkyl-chitosan derivatives with different alkyl chain lengths, obtained by alkylation reaction with different aldehydes with 8, 10 and 12 carbon atoms. The coating formulations were made using both polymer solutions as single material for paper coating, and polymer solutions combined with calcium carbonate particles. The results show that alkyl-chitosan has the ability to form films, to reduce the water absorption capacity and air permeability of paper surface, mainly due to the closure of surface pores, and partly to the presence of hydrophobic alkyl chains. The hydrophobic effect is more evident in the case of alkyl-derivative with the highest substitution

degree and longest alkyl chains. The presence of the calcium carbonate particles in coating formulas increases the paper surface hydrophobicity by various degrees, according to the composition of polymer/CaCO₃ formulas.²⁴

Quaternary-chitosan derivatives are known as having a special antimicrobial activity, which is recommended as a material used to treat the paper surface. Solubility in water is also real advantages over unmodified chitosan. The utilization of quaternary-chitosan derivatives in papermaking has show a huge increase in dry strength index of paper, especially breaking length and burst resistance. These effects can be attributed to coagulation ability of quaternary-chitosan, leading to synergistic interactions that may lead to optimizing the papermaking process.^{25, 26}

IV. CONCLUSIONS

Chitosan has emerged as a novel type of bio-functional material due to its versatile biological activity, excellent biocompatibility and complete biodegradability in combination with low toxicity. Chitosan has good adhesion onto cellulose fibres and could be used as an environmentally friendly coating material.

Chemical modification of chitosan to generate new functional materials is of prime interest because the modification would not change the fundamental skeleton of chitosan, would keep its original physicochemical and biochemical properties and finally would bring new properties depending on the nature of the group introduced. Chitosan and its derivatives have great potential in a wide range of applications, thanks to a unique combination of specific properties: biocompatibility to living tissues, non toxicity, antifungal and antimicrobial activity, coagulation capacity, high capacity of reaction, selectivity.

The results obtained so far recommend chitosan and its derivatives as excellent additives for paper coating, which can substitute other synthetic additives currently applied in the surface treatment of paper. The use of chitosan derivatives (e.g. carboxymethyl chitosan, alkyl chitosan or quaternized chitosan) in the papermaking is a new direction that could lead to a new class of chemical additives – multifunctional bio-additives.

V. ACKNOWLEDGEMENTS

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SURFACE SIZING AND COATING OF LINER AND CARDBOARD

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Abstract

UMV was founded in 1876 and became sister company with former BTG Coating Systems in 2002. The two companies were combined and got the name UMV Coating Systems in 2007. UMV Coating Systems is a supplier of coating machines since 1973 and the initial product was the Billblade coater, one of the most sold coaters in the world.

Keywords: coating, surface sizing, sizer, gravure, liner, flutting, starch

Rezumat

UMV s-a înființat în anul 1876 și în anul 2002 devine companie "sora" BTG Coating Systems. Cele două companii s-au unit sub numele de UMV Coating Systems în anul 2007. UMV Coating Systems este un furnizor de instalații de cretare încă din anul 1973, recunoscut prin produsul Billblade coater, unul dintre cele mai vândute echipamente de cretare din lume.

Cuvinte cheie: cretare, înclieiere la suprafață, presă de înclieiere, gravură, hârtie capac, hârtie strat ondule, amidon

TWIN™ Sizer, HSM

UMV Coating Systems started the development of roll coating technology in the middle 1980ies, in order to make it possible to coat and surface size weak base sheets with high recycled fiber content and or low basis weights and the first TWIN™ Sizer, HSM was installed in 1991 at Papateries Bourray France to coat and surface size, low basisweights recycled printing paper.

TWIN™Sizer, HSM technology has in the meantime been sold to 75 references for different applications, surface sizing, pigmenting, and coating on various base sheets from Bible paper to board. Installed ON- and OFF line.

The basic technology behind the TWIN™Sizer, HSM is the premetering principle. It is based on the wire winding of the metering roll thus creating a volumetric metering with long service life due to the big diameter and mass of material. The cost level for the refurbishment of the wire wound roll is the cost of the wire itself which is about 1/5 compared to the corresponding costs for the conventional rod premetering principle. The large HSM premetering roll is

found to be forgiving to small particles in the base paper or in the media. This has resulted in that most TWIN™Sizer, HSM units are installed for treatment of base sheets with up to 100 % recycled fibers. The most important application being surface sizing of Liner & Fluting based on recycled fibers, where the volumetric premetering allows for uniform application of wet amounts up to 20 gsm per side, which is of interest when penetration is wanted.

The strength improvements that are achieved by starch surface sizing with TWIN Sizer, HSM can be demonstrated by an example for 180 gsm testliner.

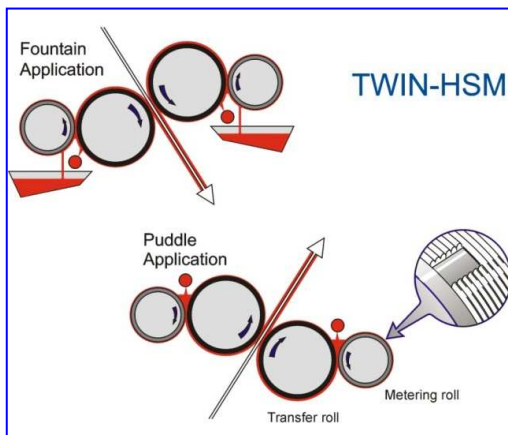
A base sheet RCT value of 1,3 kN, would be improved by 25 % by 6 gsm total application and 35 % by 8 gsm total application. A base sheet Burst Index value of 1,5 kPa/gsm, would be improved by 25 % by 6 gsm total application and 30 % by 8 gsm total application.

The TWIN™ Sizer, HSM is based on the volumetric premetering technique, which has a working range from 8 - 20 gsm wet application, depending on choice of wire diameter. The dry pickup is controlled by the solids of the media for a chosen wire diameter.

TWIN™Sizer, Gravure

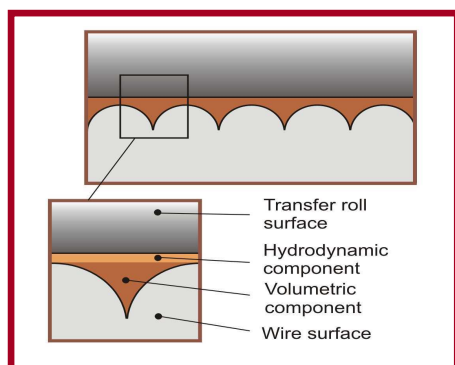
In order to get a working range that also takes care of low wet amounts, 4-8 gsm, like the Gate Roll principle as well as 8-20 gsm, then UMV Coating Systems developed the TWIN™ Sizer, Gravure, where a gravure roll is the base for the premetering.

This technology gives a two dimensional coatweight control where the dry coatweight/pickup is controlled by a combination of the gravure roll speed and chosen solids level. The TWIN Sizer, Gravure can due to the possibility to apply low wet amounts run at high speed +1500 m/min minimizing fogging that otherwise is a problem by roll coating. The gravure pattern gives a uniform application due to the fine distribution of the engravings in the gravure roll. There are 80 cells/cm.



Application

The web run has impact on the application of starch/media. If the web run is upwards then the application is done into a pond that is formed between the transfer roll itself and the HSM metering roll. If the web run is downwards, then the application is done via a spray application.



An interesting example is at Korsnäs Frövi mill where they apply reverse side treatment with the actual TWIN Sizer, Gravure applying 3 gsm coating at high solids with excellent distribution.

Pilot trials show that printing paper can be treated with 5 gsm wet amount (0,5 gsm dry at 10 % solids, 0,75 gsm dry at 15 % solids mening 4,5 gsm water to be evaporated) of starch solutions with completely stripe free distribution.

TWIN™ Sizer, HSM technology

The TWIN™SIZER, HSM as such is a premetered size press and can be supplied in either upwards or downwards web run. The functionality of the TWIN™SIZER, HSM can be divided into three different functions: application, premetering and transfer.

Fig.1 TWIN™SIZER, HSM with upwards or downwards webrun

Premetering

The premetering is done with a wire wound roll, the HSM roll, and it is in principle volumetric, dependent on the wire diameter, but it is also partly hydrodynamic, because of the big diameter of the HSM roll (see Figure 1 and Figure 2). The level of hydrodynamic impact depends on the viscosity of the media and the speed of the web.

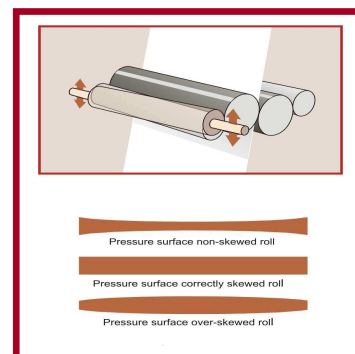


Fig.2 HSM premetering and skewing principle

The hydrodynamic component of the premetering lubricates the metering zone and reduces wear of the rubber transfer roll surface.

The volumetric part of the premetering is most dominating for low viscous solutions utilized by surface sizing. The pickup and distribution is very stable in this case.

To ensure the good distribution CD/MD except for the volumetric premetering there is a skewing mechanism, see Figure 2 , installed on the premetering roll. It's function is to give the same linear pressure all across the machine between the metering roll and the transfer. The reason for having this variable crowning is to make it possible to run with different linear pressures between the HSM and transfer roll. The linear pressure is normally run between 5-10 kN/m, dependent on application, surface sizing, pigmenting or coating.

Transfer

The transfer roll hardness by TWINTMSIZER, HSM technology, can be chosen in a wide range from 20-90 P&J by the HSM premetering technique. The choice is dependent on the need for penetration of media and the need for a good film forming. Soft transfer rolls give good covering characteristics and hard transfer rolls give penetration. Surface sizing of Liner & Fluting with TWINTM SIZER, HSM

About fifteen years ago the paper industry started to utilize metered size presses (MSP) for surface sizing of fluting and liner. The MSP:s gives approx. 25% higher production capacity and approx. 35% less drying cost compared to the

pond size press for a given number of drying cylinders. It gives also same strength development for the important parameters such as Burst, RCT, and CCT.

Based on 12 years experience from excellent performance by surface treatment of base sheets containing recycled fibers it was quite natural to enter the Liner & Fluting market with the TWINTMSIZER, HSM technology. The metering element, the HSM roll, has a big diameter compared to the metering rod of other conventional MSP:s and therefore more forgiving for recycled fibers. This result in minimal risk for streaks caused by fibers stuck in the nip between the metering element and the transfer roll.

The first TWINTMSIZER, HSM for surface sizing of Liner & Fluting was installed in Asia and has now been running since 2001. Due to the excellent performance fourteen more TWINTMSIZER, HSM units have been sold for this application. The widths of the units are 4,5-7 m and they are running at speeds 600-1200 m/min.

Specific issues by corrugated Liner & Fluting

The quality/strength improvement of corrugated medium is dependent on the amount of starch that is applied. The higher amounts of starch the higher the strength improvements. The solids of the starch solution and TWINTMSIZER, HSM conditions determine the starch amount applied. The below table shows the wide range that can be controlled by the conditions/settings for the premetering.

Table 1 Starch pickup versus solids

<i>Solids %</i>	Dry pickup gsm Total both sides	Wet Pickup Total both sides.
12%	2,5 - 7 gsm	20 - 55 gsm
16%	3 - 8gsm	18 - 50 gsm
20%	4 - 9 gsm total	20 - 45gsm

The surface sizing of Liner & Fluting requires a relatively big wet amount in order to apply a high starch amount for strength improvement and penetration. A high solids increases the viscosity and this result in low penetration. In order to improve the penetration it is essential to increase the temperature in order to get lower viscosity for better penetration.

In many installations customers want to be able to run with premetered mode for low basis weights and with pond size press mode for high basis weights. The upper border line for premetering is in the range of 180 gsm. The wet pickup by premetering is determined by the choice of wire diameter and linear load between the HSM premetering roll and the transfer roll.

The pickup level from 20 gsm total to 40 gsm total, both sides, can be applied through premetering. To go from 40 gsm total to 53 gsm total both sides needs mini-pond or pond mode.

A TWIN™ Sizer, HSM in downwards webrun can be run in all three modes; premetered -, minipond- and pondmode.

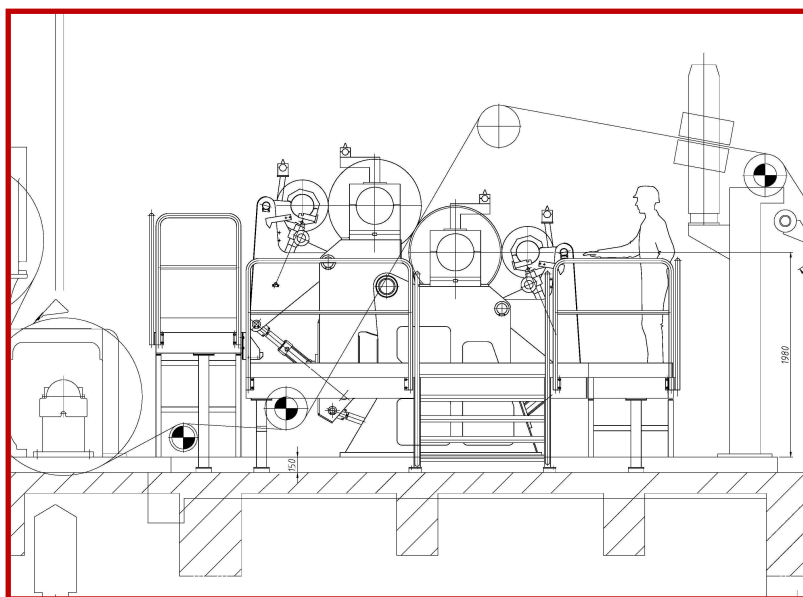


Fig. 3 Surface sizing of Liner and Fluting with TWIN™ SIZER, HSM

Above figure show a typical lay-out for the TWIN™Sizer, HSM for surface sizing of Liner & Fluting.

comparably deeper penetration. The linear pressure used, is up to 40 kN/m and the rubber hardness is, as a rule, 30 P&J by surface sizing of Liner & Fluting.

Particles from Base Sheet and Starch Quality passes the Premetering area

Starch Conversion – Impact on Starch Stability

The big diameter of the premetering roll gives a low specific linear pressure between the HSM metering surface and the transfer roll. This in its turn means that loose particles that often occur in base sheets of recycled fibers, can pass the metering surface without causing streaks. It is appealing from cost perspective to utilize the lowest grade of native starch, for instance Tapioca starch. The lowest grade is not cleaned to the same extent as more expensive grades and it has particles that to a high degree originate from the shell of the Tapioca. These particles can swell and cause problems in the circulation systems. Low-grade starch needs better screening in the circulation system.

The starch quality and the relation between solids, temperature and viscosity are important for the development of the strength improvement and the operation of the sizing unit. As seen in the **table 1**, it is possible to get the same pickup at different solids. The choice is based on quality and energy considerations. In other words lower solids, means lower viscosity and deeper penetration but the drying energy demand will increase.

Transfer - Impact on Penetration

Pre-converted starches (normally oxidized) have a stable relation between temperature, solids and viscosity. The drawback is the higher costs. The other solution is to convert native starch at the mill, which means lower costs and is therefore the rule for corrugated Liner & Fluting.

By surface sizing of Liner & Fluting there is basically a need for penetration to achieve optimum product characteristics. Low viscosity, high linear pressure and hard rubber surface gives

The converting of the native starch is basically done with two different prevailing techniques; APS and enzyme conversion. The APS is less stable, meaning that the viscosity increases rapidly by loss of temperature in the starch. The

enzyme conversion gives comparatively a more stable relation between viscosity and temperature.

RCT, Ring Crush Test, improvement by surface sizing

Expected strength improvements by surface sizing of Liner & Fluting

The quality/strength improvements expected by surface sizing of Liner & Fluting was studied in pilot scale. See below graphs. The surface sizing starch utilized at the trials was a pre-converted oxidized maize starch.

The RCT, Ring Crush Test value increases with starch amount. as can be seen in figure 4.

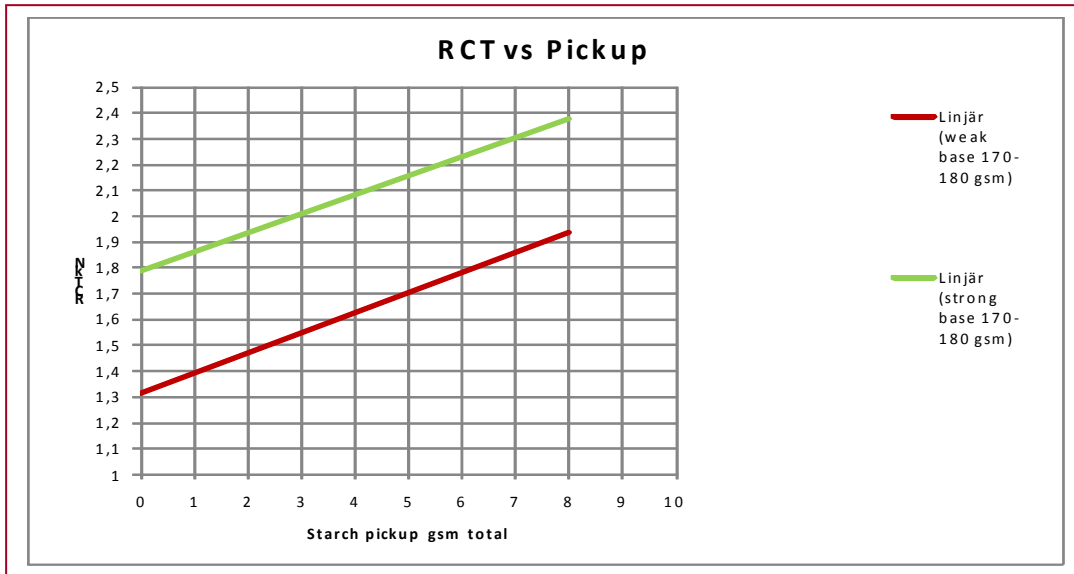


Fig. 4 RCT Ring Crush Test

Burst Index, improvement by surface sizing

The Burst index increases by increased starch amount as can be seen in figure 5.

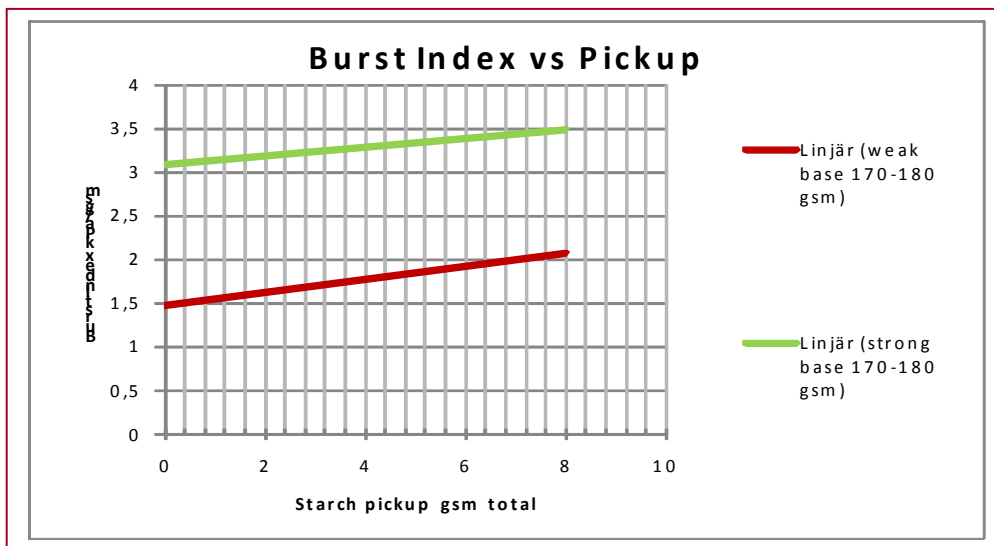


Fig. 5 Burst Index

TWIN Sizer, Gravure, Technology

The TWIN Sizer, Gravure as such is a premetered size press and is supplied for either upwards or down wards web run. The TWIN™Sizer, Gravure is introduced because it has a wider range of application compared to conventional premetered size presses. It can except for the normal premetered

application range also apply low wet amounts like the Gate Roll but with better coatweight/pickup control, profiles and microscale distribution.

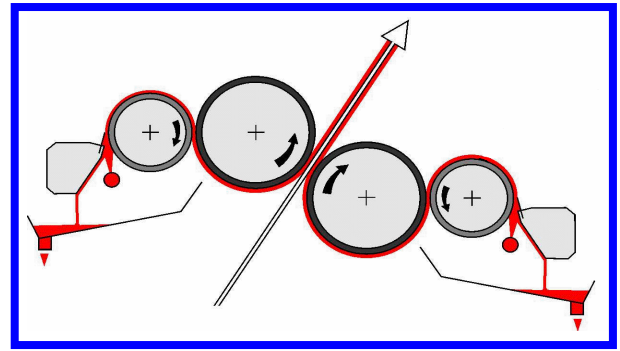
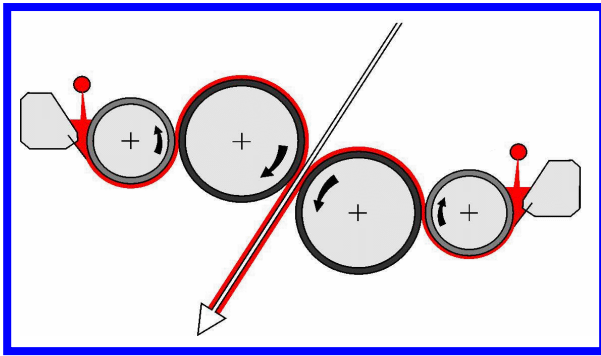


Fig. 6 TWIN™Sizer, Gravure with downwards resp.upwards

The functionality of the TWIN Sizer, Gravure can be divided into three different functions: application, premetering and transfer.

run is downwards, then the application is done via INVO® Jet pplication. See figure 6 above.

Application

The web run has impact on the application of starch/media. If the web run is downwards the application is done into a pond that is formed between the gravure roll itself and the metering blade beam. If the web

Premetering

The premetering is done by metering the media into the gravure roll cells with the help of a steel blade with a soft polymeric tip. The gravure roll is presented in the below figure 6,

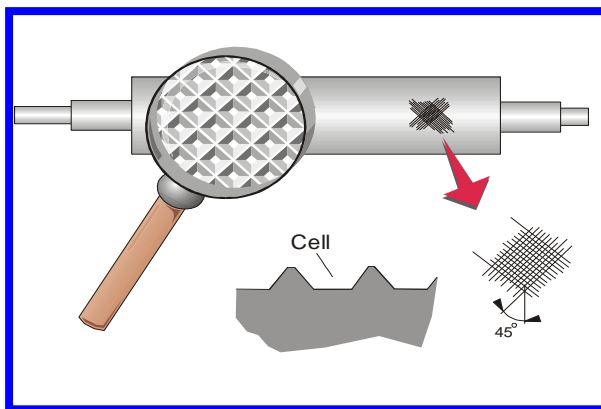


Fig. 7 Gravure premetering roll

The Gravure premetering is a based on the volumetric principle. The premetered volume is controlled by choice of cell size and the speed of the gravure roll in relation to the transfer roll/machine speed. (In special cases it can be of

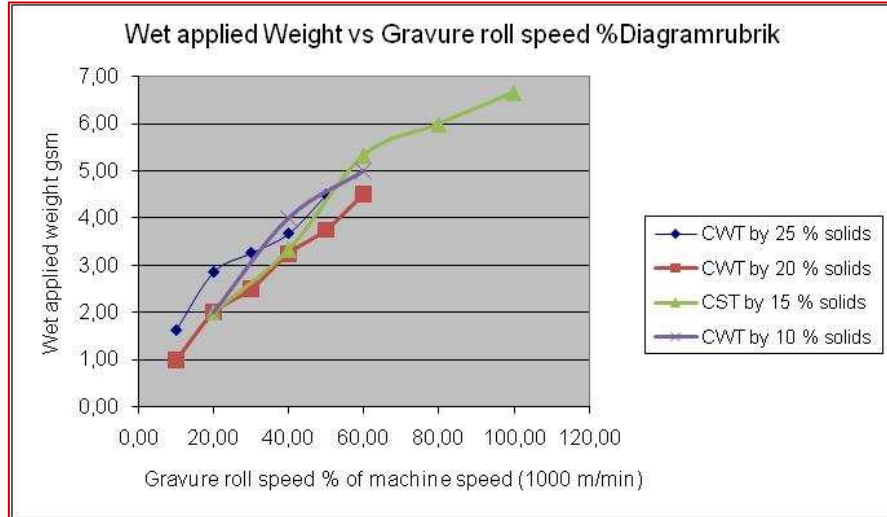
interest to utilize a hydrodynamic component, like for instance by coating with clay color at high solids in order to avoid bleeding.)

The below graphs show, the coatweight control by surface sizing. In this case the cell volume is 20 cm³/m².

I can be concluded that it is easy to control the amount of starch by control of the gravure roll ratio to transfer roll speed. The Graphs are based on the choice of cell volume 20

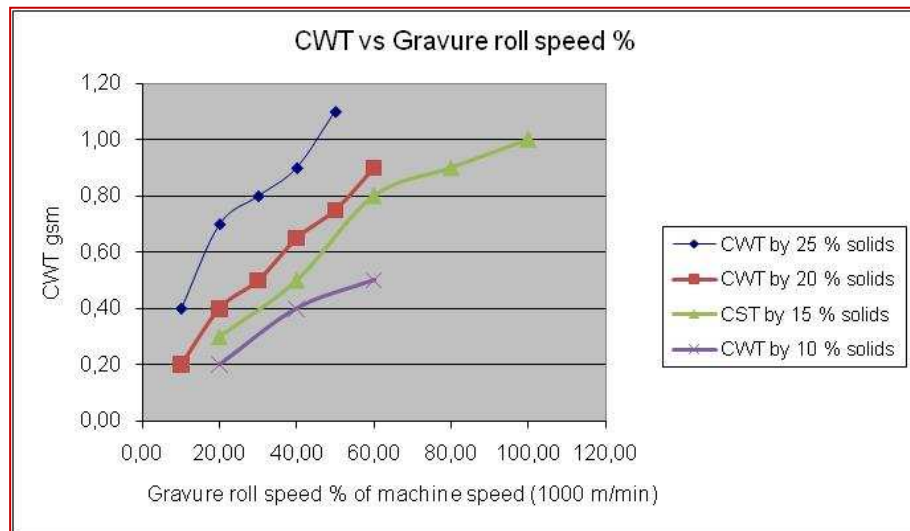
cm³/m². Bigger cellvolume give a higher range of CWT/pickup.

The Wet applied weight in the graph below shows that we have similar behavior applied wet amount versus Gravure roll speed for all solids levels; 10, 15, 20 and 25 %.



The below graph shows the relation between dry CWT/pickup of starch versus the gravure roll speed.

(The deviation from a straight line can be explained by difficulties to measure low pickup levels.)



Transfer by TWIN Sizer, Gravure

The transfer roll hardness by TWIN Sizer, Gravure technology, can be chosen in a wide range from 20-90 P&J by the Gravure premetering technique. The choice is dependent on the need for penetration of media and the need for a good film forming. Soft transfer rolls give

good covering characteristics and hard transfer rolls give penetration.

The indirect premeting done in the TWIN™ Sizer, Gravure, see explanation in adjacent figure 8, is beneficial, since it protects the rubber surface from wearing. The good properties of the surface is kept longer than by direct premeting like Rod or HSM. In our mill experiences we have seen 7

times prolonged time between regrinding of the rubber transfer roll surface.

The good condition of the surface also ensures a good distribution/patternfree treatment. This is of high importance especially by low wet

amounts, in the range 5-9 gsm. (If the rubber surface has markings, then this will immediately be seen in the treated paper or board.)

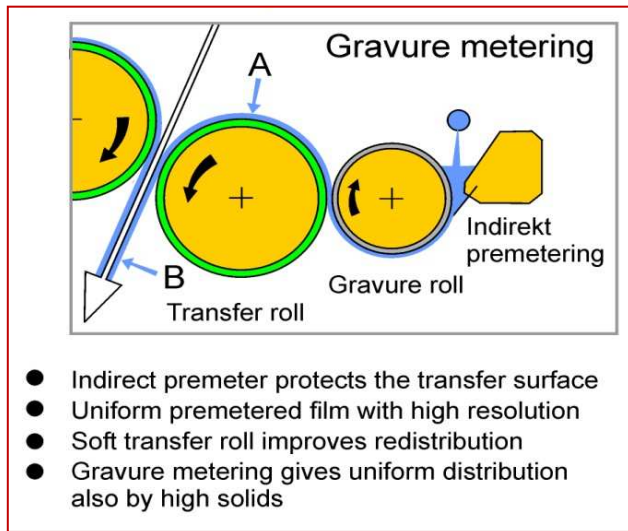


Fig. 8 Indirect gravure premetering and transfer principle

Quality by Gravure pre-metering

Since the film consists of the small pixels (app. 80 cell/cm) developed by the gravure roll we get a uniform distribution by the premetering. This means that the redistribution in the transfer point is less critical. Therefore it is possible to reduce the wet amount and still get a good

distribution. In the below graphs, we can see two interesting examples. It concerns surface sizing of wood containing paper with 0,5 gsm at 10 % and 0,8 gsm at 15 % solids. In both cases this means a water amount of 4,5 gsm. We can see a uniform coverage by this small amount of starch. The energy demand is also low.

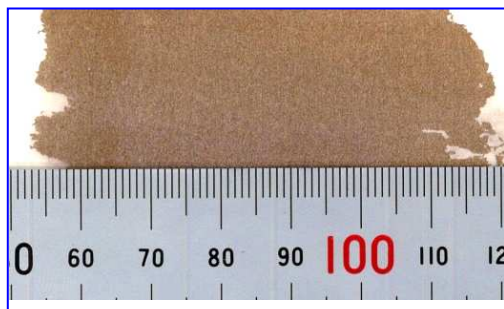


Fig. 9 Surface sizing of woodcontaining sheet with 0,5 gsm at 10 % solids Iodine



Fig. 10 Surface sizing of woodcontaining sheet with 0,8 gsm at 15 % Solids Iodine

TWIN™ Sizer, Gravure for reverse side treatment of cardboard.

The coverage characteristics by roll coating can be applied single sided by the TWIN™ Sizer,

Gravure coater. Below is one example at Korsnäs Frövi Board Mill.

TWIN™ Sizer, Gravure, Korsnäs, Frövi mill

A TWIN™ Sizer, Gravure (MONO) coater was installed, October 2006, on the board machine in the Korsnäs, Frövi mill with the target to improve the surface sizing of the reverse side on coated liquid packaging board and general packaging board produced with unbleached back. Furthermore the new coater made it possible to produce a new developed general packaging board grade with a low grammage film coating on a bleached bottom side.

The reverse side coater was chosen in competition with conventional MSP's. The decision factors were the high controllability and flexibility, necessary to meet the multipurpose

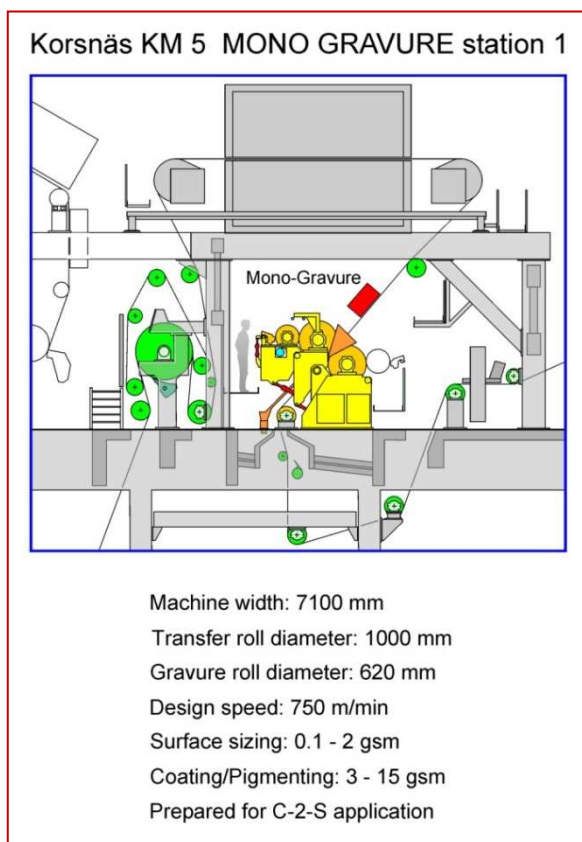
needs by the project.

The experience shows that the reverse side treatment in Korsnäs Frövi mill is characterized by good coverage and uniform distribution.

Good printability results are achieved also at low coat weights. The targets set up for the new developed product and existing products are achieved.

The coater meets high operational demands with good controllability and availability.

The uniform distribution and coverage makes it possible to apply small amount getting excellent printing results.



*Fig. 11
 TWIN™ Sizer, Gravure coater (MONO) installed
 at Korsnäs Frövi Board mill*

Machine design in Korsnäs Frövi

Below pictures show a foto of the TWIN™ Sizer, Gravure installed in Korsnäs Frövi and corresponding Process explanation.



Fig. 12 Foto TWIN™Sizer, Gravure coater(MONO) installed at Korsnäs Frövi Board mill

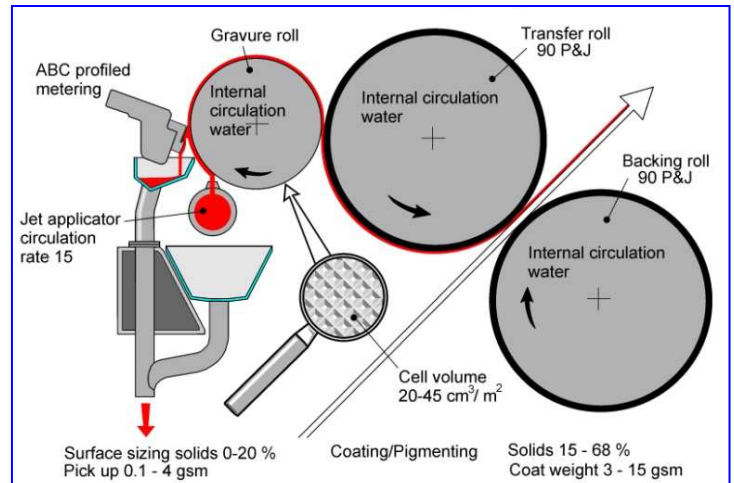
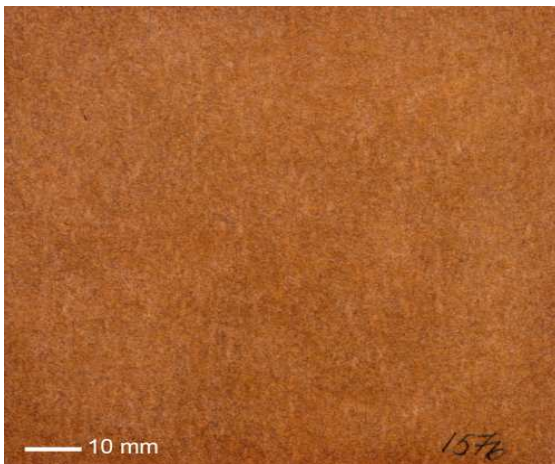


Fig. 13 Process explanation TWIN™Sizer, Gravure coater(MONO) installed at Korsnäs Frövi Board mill

Quality by surface sizing and pigmenting at Korsnäs Frövi mill

The below picture shows the starch distribution on the reverse side of the board.



The applied pickup is 0,35 gsm of starch applied at 4 % solids.

Fig. 14 Starch distribution (Iodine) by 0,35 gsm applied at 4 % solids with TWIN™Sizer, Gravure at Korsnäs Frövi Board mill.

Pigmenting on the reverse side of the board

The TWIN™Sizer, Gravure is also utilized for pigmenting on the reverse side of the board.

As can be seen a very small amount 3 gsm dry improves the Printability, Print Mottle. The naked eye can clearly see an improved WTL (White Top Mottle) on the unprinted sheet.



Fig. 15 Printing on Uncoated reverse side



Fig. 16 Printing on 3gsm pigmeting applied with TWIN Sizer, Gravure (MONO on reverse side)

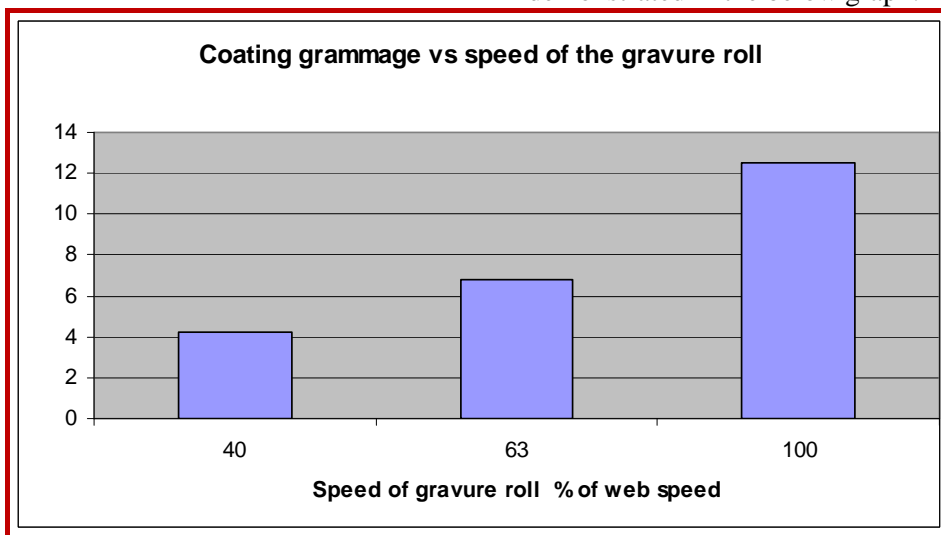
The Improved Print mottle can be seen in the above printing images. The improvement is also explained in the below graph comparing different methods and pickup levels.

By Carton Board it is essential to keep the basis weight low to geet bulk and stiffness.

3 gsm application with TWIN™Sizer, Gravure offered a good solution under these conditions.

Coat weight control in Korsnäs Frövi mill

The controllability of the coatweight is demonstrated in the below graph.



CONCLUSION

The premetered size press is a good option for surface sizing of Liner and Fluting in modern production lines. It has less drying needs compared to the conventional pond size press and can be run at substantial higher production speeds.

The penetration of starch depends on the viscosity of the starch and the transfer roll hardness. The viscosity of the starch is dependent on the temperature and it is therefore important to have good control of the starch temperature, from cooking to the point of application.

The Liner & Fluting mills often combine the possibility to run pond and premetered size press, in which case high basis weights are run in

pond mode and low basis weights are run in premetered mode.

The Gravure premetering technique has a big application range, from coating to small amounts like the Gate Roll but with better coat weight control, profiles and distribution/pattern. Gravure premetering technique is successfully operated in board mill environment. It meets the demands on; flexible applications, good printing characteristics (also at low pickups), uniform distribution and excellent control the wet and dry coatweight.

**TEZE DE DOCTORAT
- 2011 -****Domeniul Inginerie Chimică – Universitatea Tehnică Gheorghe Asachi Iași –
Facultatea de Inginerie Chimică și Protecția Mediului****1. Teza de doctorat: CERCETĂRI PRIVIND OBȚINEREA ȘI CARACTERIZAREA
CELULOZELOR DE MARE RANDAMENT****Autor: Gheorghe Duțuc – SC SOMEȘ SA Dej****Conducător științific: Prof.dr.ing. Dan Gavrilescu**

Alinierea la legislația Uniunii Europene cu privire la protecția mediului și a folosirii materialelor din resurse regenerabile, impune identificarea unor soluții tehnice și tehnologice pentru încadrarea indicatorilor de poluare în limitele impuse de cadrul legal și reducerea impactului ecologic al activităților economice desfășurate în sectoare prioritare ale economiei. Aceste soluții vizează eforturi pe planuri multiple care includ cercetarea științifică și dezvoltarea în direcția îmbunătățirii tehnologiilor și echipamentelor.

Lucrarea de doctorat contribuie la aceste deziderate, abordând din punct de vedere practic și teoretic probleme legate de tehnologia de fabricare a celulozei prin procedeul sulfat, respectiv a celulozei de mare randament prin studierea a două etape: impregnarea lemnului cu soluția de reactivi și etapa de delignificare propriu-zisă.

Obiectivul general lucrării de doctorat a constat în investigarea procesului de fierbere a celulozei cu scopul creșterii randamentului și selectivității acestuia precum și a compatibilității cu mediul. Se

utilizează aditivi, precum polioxometalații în faza de impregnare iar surfactanții și antrachinona, în procesul de fierbere efectivă

Obiectivele derivate din obiectivul general al lucrării se referă la:

- Analiza, optimizarea și caracterizarea procesului de impregnare și fierbere, atât în faza de laborator cât și de micropilot.
- Studiul factorilor de influență a proceselor de impregnare și fierbere, atât în cazul procedurii clasice cât și în cazul procedurilor aditivate
- Identificarea unor soluții de creștere a randamentului selectivității proceselor de fierbere în condițiile utilizării aditivilor și a reducerii consumului energetic.
- Elucidarea unor aspecte privind mecanismul procesului de impregnare și respectiv fierbere a tocăturii din lemn cu reactivi din clasa polioxometalaților, surfactanților și a antrachinonei.
- Caracterizarea celulozelor obținute, din punct de vedere papetar.

- Aplicații industriale de fierbere la randamente ridicate.

Lucrarea este structurată în 4 capitole pe o extindere de 216 pagini, iar tematica abordată este de mare actualitate în țară, unde problema valorificării superioare a materiei prime vegetale

este stringentă datorită scăderii rezervelor de lemn. Creșterea randamentului de obținere a celulozelor tehnice este o necesitate și din punct de vedere economic, deoarece determină scăderea cheltuielilor cu materia primă.

2 Teza de doctorat: **EVALUAREA IMPACTULUI DE MEDIU AL TEHNOLOGIILOR DE RECICLARE A HÂRTIEI ȘI CARTONULUI**

Autor: Alina Iosip

Conducător științific: Prof.dr.ing. Elena Bobu

Problema reciclării hârtiei și cartonului devine din ce în ce mai stringentă în ultima vreme, având în vedere că maculatura (hârtia și cartonul recuperate pentru reciclare) reprezintă peste 50% din materia primă de bază pentru industria hârtiei. Prin procesul de reciclare a hârtiei și cartonului se reduce impactul asupra mediului al produselor din hârtie prin scăderea consumului de lemn, apă și energie, precum și prin reducerea suprafețelor de teren pentru depozitarea deșeurilor și implicit a emisiilor în aer. Pe baza acestor argumente, în prezent, industria hârtiei și cartonului este una dintre industriile cu cea mai mare tradiție în reciclare, fiind o parte importantă în sustenabilitatea sectorului industrial prin contribuții directe la conservarea resurselor și îmbunătățirea sănătății sociale.

În managementul deșeurilor, majoritatea studiilor de evaluare a impactului de mediu analizează procesul de reciclare a hârtiei și cartonului ca pe o opțiune pentru „sfârșitul vieții”, neluând în calcul influența pe care calitatea

maculaturii utilizată la fabricarea hârtiei din fibre reciclate o are asupra mediului.

În acest context teza de doctorat *“Evaluarea impactului de mediu al tehnologiilor de reciclare a hârtiei și cartonului”* are ca obiectiv evaluarea efectelor calității maculaturii asupra impactului de mediu al unui sistem de fabricare a hârtiei din 100% fibre reciclate. Pentru analiză și evaluare se utilizează principiile evaluării ciclului de viață al produselor și serviciilor (LCA), metodă relativ nouă dezvoltată după anul 1960, și care a cunoscut o dezvoltare considerabilă după anul 2000 și în industria papetară.

Obiectivul general al lucrării a fost de a evalua efectele pe care calitatea maculaturii le are asupra impacturilor de mediu ale unui sistem de fabricare a hârtiei din fibre reciclate, prin aplicarea principiilor evaluării ciclului de viață (LCA) al produselor sau a serviciilor.

Obiectivul derivat constă în elaborarea unui model și a unei baze de date pentru studii LCIA, care să poată fi utilizate la analiza comparativă a

impacturilor de mediu a tehnologiilor de sortare a maculaturii și respectiv, să furnizeze informații pentru luarea deciziilor cu privire la tehnologia care are cel mai mic impact de mediu.

Fundamentarea științifică și tehnică a studiului se bazează pe simularea impacturilor de mediu care pot fi influențate de calitatea maculaturii, considerând trei faze importante ale ciclului de viață al fibrelor reciclate: sortarea maculaturii ca proces tehnologic care determină calitatea finală a maculaturii înainte de a fi livrată către fabrica de hârtie; prelucrarea maculaturii pentru obținerea pastei din fibre reciclate (instalație complexă din cadrul fabricii de hârtie); utilizarea pastei din fibre reciclate la fabricarea hârtiei (mașina de fabricat hârtie).

Teza de doctorat are **158** pagini, este împărțită în **7** capitole ce conțin **27** tabele, **75** figuri și **196** referințe bibliografice. În *primul capitol* “**Introducere**” este analizat stadiul actual al reciclării hârtiei și cartonului și a metodelor utilizate pentru evaluarea impactului de mediu al reciclării ca opțiune de management. *Capitolul 2* – “**Calitatea maculaturii: definiții, factori de**

influență și metode de monitorizare” sintetizează principalele elemente care definesc calitatea maculaturii și soluțiile pentru îmbunătățirea acestora, punând accentul pe procesele de colectare și sortare. *Capitolul 3* include o documentare privind “**Evaluarea impactului de mediu prin studii LCA**” care constituie suportul pentru abordarea principalului subiect al tezei de doctorat – evaluarea impactului de mediu la reciclarea hârtiei. *Capitolul 4* prezintă “**Influența calității maculaturii asupra eficienței reciclării hârtiei și cartonului**” de unde au fost obținute informații care au constituit o bază importantă pentru studiul detaliat în *Capitolul 5* – “**Influența calității maculaturii asupra impactului de mediu la fabricarea hârtiei capac pentru carton ondulat**”. *Capitolul 6* completează studiul anterior și include “**Evaluarea impactului de mediu la fabricarea cartonului ondulat din diferite materiale papetare**”. Teza de doctorat se finalizează cu *Capitolul 7*, care conține “**Concluziile generale**” desprinse din cercetările efectuate și studiile de literatură parcurse.

3. Teza de doctorat: **DERIVAȚI AI UNOR POLIMERI NATURALI CU FUNCȚIE DE CONSOLIDARE A CĂRȚILOR ȘI DOCUMENTELOR PE SUPORT GRAFIC**

Autor: PUIU PETREA

Conducător științific: Prof.dr.ing. Sorin Ciovică

Conservarea și restaurarea documentelor pe suport papetar constituie un domeniu intens de cercetare orientat în direcția identificării unor noi soluții tehnice și tehnologice eficiente pentru salvarea de la deteriorare și chiar dispariție a patrimoniului documentar din biblioteci, muzee și arhive.

Investigațiile în domeniu se concentrează pe aplicarea unor tehnologii eficiente de eliminare a acidității suportului papetar, de protecție față de biodegradare și de restabilire a proprietăților fizico-mecanice.

În acest context, lucrarea de doctorat „**DERIVAȚI AI UNOR POLIMERI NATURALI CU FUNCȚIE DE**

CONSOLIDARE A CĂRȚILOR ȘI DOCUMENTELOR PE SUPORT GRAFIC

este orientată către identificarea unor sisteme de aditivi compatibili cu hârtia și cu materialele de scriere (ornamentare) care contribuie decisiv la creșterea durabilității cărților și documentelor grafice din patrimoniul cultural.

Pentru atingerea acestui obiectiv, studiile întreprinse la scară de laborator au vizat următoarele aspecte:

- Evaluarea potențialului de utilizare a gumelor vegetale exudate din specia Prunus ca adezivi pentru consolidarea cărților și documentelor grafice, comparativ cu eterii celulozici aplicați în acest scop.
- Modificarea chimică a carboximetilcelulozei și metilcelulozei prin introducerea de grupe

funcționale care să mărească rezistența polimerului la atac fungic.

- Investigarea comportării suportului papetar și a hârtiei consolidate cu eteri celulozici și gume exudate la îmbătrânire termică, higrotermică, radiolitică și evaluarea rezistenței la biodegradare.
- Optimizarea procesului de consolidare a hârtiei.
- Evaluarea reversibilității adezivilor utilizați pentru consolidarea cărților și documentelor grafice.

Teza de doctorat este structurată în 8 capitole, însumează 164 pagini și conține 159 figuri, 71 tabele și 214 referințe bibliografice.

4. Teza de doctorat: "CERCETĂRI PRIVIND OBTINEREA ȘI CARACTERIZAREA FIBRELOR CELULOZICE DIN PLANTE ANUALE"**Autor: Bogdan Marian Tofănică****Conducător științific: Prof.dr.ing. Dan Gavrilescu**

La ora actuală, tendința mondială de fabricare a celulozei este orientată către utilizarea pe scară tot mai largă a plantelor anuale ca materie primă, atât din motive economice, cât și în scopul conservării resurselor naturale din lemn.

În acest context, lucrarea de doctorat "**Cercetări privind obținerea și caracterizarea fibrelor celulozice din plante anuale**" are ca obiectiv principal obținerea celulozei din rapiță, prin procedeul de fierbere sulfat și natron cu antrachinonă, caracterizarea fibrelor obținute și evaluarea potențialului papetar al acestora. Teza de doctorat aduce contribuții și la protejarea mediului înconjurător prin valorificarea

deșeurilor din agricultură, în speță tulpinile de rapiță din culturile autohtone din regiunea de Nord Est a României.

Teza de doctorat este structurată în 6 capitole în care au fost abordate și studiate următoarele aspecte:

- studiul culturii rapiței din punctul de vedere al determinării cantităților de tulpini disponibile după recoltarea semințelor, în unele areale din partea de nord-est a României (județele Iași și Vaslui);
- investigarea tulpinilor de rapiță privind particularitățile anatomo-morfologice; în acest sens s-au determinat cantitativ și s-au

studiat calitativ părțile plantei utilizabile la obținerea fibrelor celulozice;

- studiul datelor biometrice al fibrelor celulozice de rapiță, prin determinarea dimensiunilor fibrelor și indicilor morfologici prin care se apreciază calitatea fibrelor ca sursă de materie primă pentru obținerea celulozelor;
- caracterizarea din punctul de vedere a compoziției chimice a tulpinilor și a fibrelor celulozice din rapiță; compararea cu alte materii prime folosite la fabricarea celulozei;
- studiul delignificării tulpinilor de rapiță prin procedee alcaline (sulfat și natronantrachinonă),
- în vederea obținerii de celuloze cu conținuturi de lignină diferite;
- cercetări privind înălbirea unor celuloze din tulpini de rapiță prin procedee fără clor elemental și procedee total lipsite de clor; aprecierea influenței delignificării cu oxigen, ca etapă preliminară înălbirii;
- caracterizarea celulozelor obținute din punct de vedere al proprietăților papetare.

Domeniul: Ingineria și protecția mediului
Universitatea Dunărea de Jos Galați – Facultatea de Inginerie Brăila

1. Teza de doctorat: **“MODELAREA MATEMATICĂ A INDICATORILOR DE CALITATE A CORPURILOR DE APĂ DE SUPRAFAȚĂ ȘI A APELOR UZATE”**

Autor: Mat. Valerian N. Antohe

Conducător științific: Prof.dr.ing. Constantin Stanciu

**Conducător științific în cotutelă: Prof. univ. dr. hab. mat-fiz. Vasile
MARINA**

În prezent, apele de suprafață constituie principala sursă pentru consumul de apă, dar în același timp și principalii receptori ai efluenților rezultați din diverse activități. În aceste condiții, corpurile de apă nu trebuie să conțină poluanți care să contribuie la perturbarea sănătății populației. În vederea implementării directivelor Consiliului CE pentru promovarea utilizării durabile a apei și a protecției pe termen lung a resurselor disponibile, se fac eforturi susținute în sectoarele relevante de activitate pentru găsirea celor mai bune soluții tehnologice de prevenire și protecție a cursurilor naturale de apă.

În acest context, teza de doctorat : **“Modelarea matematică a indicatorilor de calitate a corpurilor de apă de suprafață și a apelor uzate”** are ca obiectiv proiecția unei scheme algoritmice de analiză numerică a seriilor temporale specifice parametrilor de calitate a corpurilor de apă de suprafață și ape uzate. În teză sunt aduse contribuții la analiza, modelarea și predicția evoluției în spațiul temporal al unor indicatori de calitate ai apei Dunării (grupa oxigenului dizolvat) și analizează utilizarea unor ecosisteme naturale pentru decantarea suspensiilor totale.

Aria de investigare este încadrată istoric într-un segment important din zona Dunării de

Jos, reliefând o stare de fapt a evoluției parametrilor de calitate a mediului, a evoluției acestui proces și a urmărit realizarea unor proceduri de îmbunătățire a demersurilor necesare optimizării sistemului de observație și acțiune în timp util împotriva degradării corpurilor de apă.

Principalele aspecte studiate în cadrul tezei de doctorat pe parcursul a 5 capitole (209 pagini) sunt:

- Analiza indicatorilor de calitate a apelor Fluviul Dunărea, pe parcursul anilor 1992-2006 pentru principalul corp de apă de suprafață în zona Brăila pe distanța în km pe Dunăre 132-375, proiectarea unui model matematic de analiză a datelor specific analizei numerice a seriilor temporale folosind programe informatice și algoritmi proprii de analiză realizate sub diferite medii de programare.
- Realizarea unui model matematic propriu corpurilor de apă prezente în arealul studiat și elaborarea unor forme funcționale matematice specifice seriilor temporale care să redea cât mai fidel, sintetic și corelațional evoluția și interacțiunea dintre o serie de indicatori de calitate ai modelului studiat.
- Construirea unui complex de algoritmi de uniformizare, prelucrare și analiză a datelor (AUPAD), care să permită completarea datelor

lipsă în istoricul bazelor de date, prelucrarea prin metode proprii analizei numerice a seriilor temporale ale bazelor de date, identificarea unor funcții analitice ce pot modela evoluția parametrilor de stare ai corpurilor de apă și identificarea unor predicții ale acestor evoluții.

- Analiza și realizarea modelului matematic care să reflecte impactul zonelor urbane principale din arealul studiat (orașele Brăila și Galați) asupra apelor Dunării și influența zonelor umede asupra

nivelului de calitate a corpurilor de apă. Elaborarea unor soluții în sensul considerării zonelor umede și bazine de decantare primară și de autoepurare.

- Elaborarea de soluții în cazul deversării apelor uzate urbane prin regândirea unor aspecte legate de urbanizare, reconsiderarea sistemului de canalizare, micșorarea impactului negativ asupra apelor Dunării și corpurilor de apă în arealul studiat.

2. Teza de doctorat: **“CONTRIBUȚII PRIVIND EVALUAREA IMPACTULUI EVACUĂRIILOR INDUSTRIALE ȘI AGRICOLE DIN JUDEȚUL BRĂILA ASUPRA APELOR DUNĂRII”**

Autor: Chim. Nicoleta Rotariu Roadevin

Conducător științific: Prof.dr.ing. Constantin Stanciu

În contextul actual al progresului tehnico-științific, al re tehnologizării și creșterii continue a producției industriale, protecția mediului a devenit una din principalele probleme ale contemporaneității. Cu atât mai mult, protecția surselor de apă și utilizarea sustenabilă a resurselor naturale constituie preocupări de importanță vitală având în vedere importanța acestora și legislația specifică în continuă schimbare.

În acest context, lucrarea de doctorat elaborată de dna Chim. Nicoleta Rotariu Roadevin, are ca obiectiv principal evaluarea impactului activităților agricole și industriale din județul Brăila asupra fluviului Dunărea.

Problematica abordată este de mare importanță, iar caracterul multidisciplinar al aplicării aduce contribuții principiilor dezvoltării durabile, având în vedere că evaluarea impactului de mediu este o componentă a acesteia. Importanța și necesitatea problematicii studiate

este dată pe de o parte de schimbarea structurii economiei din zona analizată prin creșterea ponderii activităților agricole față de cele industriale, iar pe de altă parte de faptul că fluviul Dunărea este colectorul către Marea Neagră, al tuturor evacuărilor din județele riverane din amonte, din punct de vedere al impactului acestora asupra calității apelor și în special în Delta Dunării și în zona costieră a Mării Negre.

Teza este structurată în două părți: Partea I conține studiu documentar, iar Partea a II-a cuprinde rezultatele experimentale. Teza este structurată pe cinci capitole. *Capitolul 1* abordează principalele aspecte legislative privind calitatea apelor. Sunt prezentate problematicile actuale de mediu, aspectele legislative, cadrul actual strategic și juridic pentru promovarea programelor de măsuri de reducere a poluării apelor. Tot în acest capitol este abordată și viziunea Strategiei Dunării precum și pilonii ce stau la baza gospodăririi durabile a resurselor de

apă. *Capitolul 2* prezintă indicatorii de poluare ai apelor, potențialele surse de poluare precum și indicatorii fizico-chimici care caracterizează starea de calitate a apelor de suprafață. *Capitolul 3* pornește de la aspectele generale și ajunge în final la cazul nostru particular și anume starea de calitate a apelor fluviului Dunărea. În acest capitol se prezintă caracterizarea apelor din România și starea de calitate a râurilor interioare. O atenție deosebită se acordă caracterizării indicatorilor fizico-chimici ai apelor fluviului Dunărea, ce traversează județul Brăila. În *Capitolul 4* sunt prezentate contribuțiile privind evaluarea impactului și riscului asupra apelor Dunării. Sunt redate o serie de elemente teoretice a structurii procesului de evaluare a impactului asupra mediului precum și metodele și tehnice disponibile în prezent. Sunt abordate apoi tehnicile de analiză și gestionare a riscului, domeniu mai puțin dezvoltat în literatura de specialitate.

Capitolul 5 face referire la apele menajere care sunt colectate pe raza județului și Brăila și apoi sunt deversate în fluvial Dunărea. Plecând de la aceste deversări, se prezintă partea tehnică a noi stații de epurare a apelor uzate Brăila, care este prima stație de epurare amplasată într-un județ riveran Dunării. *Capitolul 6* prezintă concluziile finale desprinse de-a lungul cercetărilor și sunt specificate direcțiile viitoare de cercetare, în perspective continuării tezei. Teza cuprinde 85 de tabele, 137 de grafice și se încheie cu 300 de referințe bibliografice.