

Chemicals come to an alliance with the sector eco-efficiency

Essential to guarantee the pulp and paper sector productivity, chemicals nowadays must also obligatorily present environmentally friendly characteristics. In this respect, biotechnology appears as a rather attractive alternative

By Marina Faleiros

The pulp and paper area has already revolutionised the way it works in the forest area, which perform at present a production per hectare which is three times as much as that obtained 20 years ago. But the transformation in search for higher productivity and a good relationship with the environment extends beyond this, also reaching an area which is not so much aimed at, but is all the same rather polemical and essential for industry: the chemical part.

It is a fact that the sector is greatly dependent on chemicals in its process. From wood cooking and pulp bleaching up to the coating performed, e.g., on the sheet where this story is printed on, everything in the pulp and paper sector passes through the molecules of the chemical additives. Though they are often pointed at as great environment villains, several researches and investments showed that no action is spared by the sector in order to search for the best relationship with nature and at the same time to produce better at lower costs.

The first great step in this path was already taken some time ago. At present, all great national pulp manufacturers adopt the ECF (Elemental Chlorine Free) process, which means an extremely significant environmental gain, as the use of elemental chlorine was eliminated from the bleaching process. "Considerably less polluting agents, such as ozone and hydrogen peroxide, appeared in the last decade. But



International Paper is one of the companies that use enzymes intending to reduce consumption of traditional chemicals

the standard technology has taken shape with the use of chlorine dioxide, which is environmentally rather acceptable", says Jorge Luiz Colodette, a doctor of Federal University of Viçosa and a specialist in pulp production. He points out that bleaching is just the second highest pulp production cost, only losing in the ranking to wood.

Now, small – but not less important – transformations are being achieved step by step, at each mill and by each chemical and equipment supplier striving for eco-efficiency by means of improvements on machines and new chemical element options, for instance. For Colodette and other specialists heard by the reporting

staff of O Papel, there is not only one alternative to follow, since the possibilities of research are enormous. "A promising way is that of enzymes and at present the initiative is being taken to identify which is the best strain for each phase of the various industrial processes, since even at very similar mills the enzymes may present different behaviours. Therefore, everything in the future tends to be very personalised", anticipates Sérgio Borges de Almeida, Paper Process Technology coordinator of Votorantim Celulose e Papel (VCP).

Enzymes are biological catalysts accelerating chemical reactions and having



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high specificity, which allows them to be designed for each type of action intended. "In 2004 we presented seminars speaking about this technology and of how enzymes might be used, for instance, at prebleaching and for deposits control at paper production". After some years, this has already become reality in the sector", says Luiz Wanderley Pace, Senior Researcher of Buckman. According to him, the search of the sector is not only limited to lower toxicity products, also including those coming from renewable sources, which is the case of enzymes.

"GREEN" AGENTS FOR THE PULP

The enzyme producers are engaged in developing ever new, genetically engineered enzymes. According to Colodette, among the enzymes presenting good potential are the xylanases and ligninases. "Both of them succeed in minimising the consumption of traditional reagents, as, e.g., chlorine dioxide". In the case of xylanases, a scission is made of the lignin complexes with carbohydrates. By bleaching it is intended to eliminate lignin bound to the element cellulose itself and the catalyst does the binding break, facilitating bleaching by an indirect way. "This is a great field of study for people working with genetic engineering, an area where evolution is progressing very rapidly", states the professor.

For Pace it is also a fact that the application of enzymes makes a difference in terms

of chlorine dioxide saving. "The enzymes do not replace the dioxide or peroxide, but they reduce consumption of these products to a considerable extent and therefore make the process less aggressive". In some cases, the application may also make the fibre refining process easier, which contributes to reduce energy consumption and is within the concepts of eco-efficiency.

International Paper (IP) uses at present enzymes in its delignification stage, intending to reduce consumption of traditional chemicals. "Enzymes participate in the delignification process and if previously we applied 10 kg per ton of pulp, now we have reduced it to 8. The great tendency is to use these agents in the prebleaching stage, so as to progressively reduce the application of conventional chemicals to the process. Enzymes are harmless products, free from the effects caused by the already common brightening agents, especially in interferences with handling and treatment of effluents", declares Wanderlei Eduardo Peron, senior environmental specialist of the company.

Reduction in chlorine dioxide consumption is also among the goals of VCP and the company will start presenting its reduction results to the academic community still in April. "We are working on reduction in dioxide consumption by means of enzyme application. There is a certain development in Brazil, but many enzymes are still imported and for this reason we are working with universities,

research institutes and within the scope of industry on a pilot scale", says Paulo Gaia, General Manager of Jacaré Unit of VCP. For him, the industrial application of this technology will be already possible within the next two years.

Leandro Coelho Dalvi, specialist of the Environment area of Cenibra—a company who does not use any enzyme in the process up to the present date—says that this may be the future of improvements in the area. "It is a tendency, as previously they could not be applied at ambient temperatures above 60°C, whereas at present they can already endure temperatures above 70°C, which is close to the situation existing in our fibre line. And we are paying careful attention to everything that may reduce costs and environmental impacts".

Another executive highlighting biotechnology as promising in the area is Oscar Volpini, Technical Support Manager for the Paper Area of Basf. "The chemical sector requires renewable sources of raw material", he says, citing some examples of changes occurring at present: "biotechnology for fuel production from biomass; the famous biorefineries in the papermaking jargon; ionic-liquids in pulp obtention, a process that will revolutionise cooking and chemical recovery; and enzymes and mediators for a bleaching process free from chlorine and oxidating substances."

CONTINUOUS CHANGES

In addition to the studies of enzymes, the traditional pulp manufacturing chemistry is also undergoing transitions. Still with regard to bleaching, using chemicals of the phosphine family as bleaching agents is also a novelty, according to Colodette. The product for this purpose was patented in Canada as biphosphine. Other products, as peracetic acid, cannot yet be used on a large scale, on account of their high cost.

At pulping, Colodette tells that surfactants are being used, which help the cooking liquor to penetrate the chips. "There are many new products being tested and each producing company has one of its own. In the dispersing agent area there is a very large range of products, as the molecules

undergo a gradual change, most of them composed of ethoxylated alcohols.”

In the recovery area, Alfredo Mokfien-ski, pulp specialist, highlights auto-causticising and the black liquor fractionation in the kraft process, tools perfectly fitting into the sector's great concern to be environmentally correct. “With auto-causticising the black liquor burned along with sodium methaborate results in less sodium carbonate and more soda, the latter being essential to the pulping process”. He explains that this reduces the residues and simplifies the process, reducing the environmental liabilities.

The process begins to popularise and many pulp and paper mills are conducting and confirming this new stoichiometry, in accordance with the technical article: *Auto-causticising of black liquor for kraft-anthraquinone pulp production by using sodium methaborate*, published in the present edition of *OPapel*. According to the study, the auto-causticising process is based on using sodium methaborate to produce disodic borate ($\text{Na}_2\text{B}_2\text{O}_7$) and trisodic borate (Na_3BO_3) in the recovery boiler, which are then hydrolysed to produce sodium hydroxide directly in the dissolving tank. The article also reads that auto-causticising may partially make up for the need of sodium hydroxide in the kraft process, providing an easy method to increase the causticising capacity, without installing new equipment at the mills as a result of it.

PAPER IN MUTATION

If pulp manufacturing changes occur at an accelerated rhythm, the paper area does not owe the pulp one anything at all, having likewise a great variety of ways to be explored. At the chemical machine cleaning, the “boil out” process, with enzyme application, is one more field that is gaining adherents.

As the paper manufacturing process is wet, the fibrous suspension processed tends to form mainly organic deposits, which may generate colonies of bacteria and fungi, a slime potentially causing discontinuities in machine production. This cleaning requires intense circulation of a water solution with strong-base chemicals or solvents. “Paper

machines must be always shutdown for system cleaning and nowadays there are enzymes managing to replace the chemical agent at this stage”, says Sidney Kitazono Carvalho, specialist in Application – Pulp and Paper Division of Buckman.

A company already applying enzymes to the “boil out” process is VCP. According to Sérgio Borges de Almeida, the company's Paper Process Technology coordinator, water and reagent saving is great. “When just the traditional chemical agent is used, the final pH of the system is very high, about 12.5. By using enzymes it decreases to approximately 8, which is closer to the necessary value for the paper production to be able to be resumed, which affords us water and time saving, besides reducing chemical consumption. In this case of ours, it dropped to half the previous amount.” But the enzyme price is considerably higher and Almeida says that the optimum concentration must be always striven for, in order to obtain cleaning efficiency along with gains in the effluent volume to be treated.

The company is also developing the same line of studies with enzymes in stock refining, which may reduce power consumption. “The project is still rather embryonic, but these enzymes may carry out a first fibre treatment, favouring fibrillation and hydration conditions and contributing to an efficient and more energy-saving refining process”, anticipates the VCP coordinator.

Also at IP there were many changes in the process. As acid sizing was abandoned in 2000, a proportion of 15% to 20% of mineral filler consisting of kaolin – under the circumstances the only chemically compatible one – was not added any longer to the stock. Now, like practically at all paper plants, the company practises alkaline sizing, thus having made viable using calcium carbonate (CaCO_3) produced inside the plant itself. “This practice reduces the use of natural resources, like kaolin, which may be directed to more specific uses. The precipitated calcium carbonate plants have also an important function at present, because they apply carbonic gas to the production, eliminating emissions of CO_2 that would go to the

atmosphere. Then the resulting calcium carbonate is applied to the stock or the paper web according to the demand for the product”, says Peron.

Thus, it was also possible to obtain better paper characteristics, among which the lasting preservation of brightness. Let's take, by way of example, that old letter or document that has become yellow. This is just a phenomenon that the alkaline sizing technology and carbonate application prevent from happening. “Now the manufactured paper is expected to take centuries to grow old”, says the environmental specialist of IP. He also tells that among the benefits obtained by changing to alkaline sizing is the elimination of the use of aluminium sulphate, previously indispensable in the acid sizing process to fix the resin to the fibres. “At present the acid process fell out of use in the great majority of the paper manufacturing systems, especially the writing and printing grades, a further reflection of the advance in terms of additives.”

As far as the coating area is concerned, Almeida, from VCP, reports that there is much to be done in search for a lower use of chemicals. The company is also working on latex replacement with starch in the colour formulation for coated paper. “We want to abandon the line of products that may be exhaustible, such as latex, which is obtained from petroleum, and go over to renewable raw materials.”

Volpini, manager of Basf, believes in this change. The company is finishing the latex development based on renewable raw materials, reducing its dependence on monomers derived at present from petroleum. “The technology is rather similar to Ecobras, a biodegradable plastic considered to be one of the ten greatest innovations of the decade by the magazine *Exame*, as well as by the American company Monitor Consultancy”, he declares.

Regarding chemical applications to paper manufacturing, Volpini also mentions changes in wet strength resins, at present free from formaldehyde. “Furthermore, the new chemical base polyvinyl amine, used at dry strength agents, allows higher strength quality to the paper grades produced from recycled fibres, or greater secondary fibre participation in their production.”