Green Technology: Last Developments in Enzymes for Paper Recycling

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ABSTRACT

Application of Sustainable Development policies implies the application of green processes that reduce waste and pollution by changing patterns of production. Green processes are based on innovative ideas that generate alternatives to those technologies that can negatively affect the environment. Today, enzyme-catalyzed processes are gradually replacing chemical processes in many areas of industry because they save energy, water and chemicals, help to improve product quality, and furthermore they also give valuable environmental benefits.

Actually, the pulp and paper industry faces several problems such as a global pressure to reduce water consumption, to use more recycled fiber and to lower environmental impacts. From that point of view, the development of papermaking processes with low environmental impact finds in the use of enzymes a suitable option, especially when paper recycling is considered. Most operations of re-pulping, cleaning and processing secondary fibers involve the use of large quantities of chemical products, which makes the technology expensive and highly environmentally damaging.

Innovative ideas in enzyme production allow the commercial use of a green enzymatic biocide that replaces standard biocides in pulp & paper mills without negative effects on plant workers or the environment; a wide spectrum sterolytic product that eliminates the drawbacks caused by the very complex problem of stickies; an enzyme product that hydrolyze wet strength resins in recycling processes at paper mills and finally, a very complex enzyme formulation designed to clean and deink tissue furnish formulations containing mixed office waste, old magazines, old newsprints, box board cuttings and colored ledgers. This paper presents data obtained at tissue mills using those innovative enzyme products.

INTRODUCTION

In recent years, the concept of sustainable development has acquired important political and social attention. An important aspect of sustainable development corresponds to the application of green technologies and use of green products which contribute to sustainability by reducing environmental degradation, providing better ways of doing things while reducing impacts, and contributing to the "greening" of the society (1).

From the above point of view, biotechnology refers to the use of microorganisms (for example bacteria) or biological substances (for example enzymes) to develop new products of industrial, agricultural or therapeutic interest in order to improve the quality of human life. Today, enzymes are used for an increasing range of applications. In fact, enzyme-catalyzed processes are gradually replacing chemical processes in many areas of industry because they save energy, water and chemicals, help to improve product quality, and furthermore they also give valuable environmental benefits. These benefits are becoming more and more important at a time of increasing awareness about sustainable development, green chemistry, climate change and organic production.

Regarding the pulp & paper industry, the reduction in water consumption, the closure of water loops, the increased use of recycled fiber, the low quality of furnishes and the manufacture under alkaline/neutral conditions have considerably increased the problems of deposit formation, corrosion and odors in the papermaking process, thus affecting the productiveness of the paper machine, the life of the equipment and the quality of the final product (2).

Deposits within the paper industry can be separated into two main groups: non-biological (stickies, pitch and scale) and biological (slime), although both forms are often combined. Various enzyme products obtained by means of microbial fermentations are helping recycling paper mills to overcome the actual adverse circumstances that affect efficiency and productiveness of their paper machines. In fact, enzyme products are being innovated for slime control, for stickies control, for hydrolysis of wet strength resins and for deinking complex tissue formulations.

DEVELOPMENT OF A GREEN ENZYMATIC BIOCIDE

It has been estimated that under some circumstances, slime deposits can be responsible for up to 70% of all breaks, blockages and pump failures in pulp & papers mills (3). Biocides are routinely used for slime deposit control in paper mills. They are directed against living organisms, but frequently not restricted to "target organisms". This implies that they inevitably also can harm the health of non-target organisms such as humans or animals. Biocides contain highly hazardous substances which are potentially harmful for the skin, can cause cancer or damage the DNA, the reproductive or immune system. They can also have endocrine disrupting effects, impairing hormonal system with long-lasting harmful consequences (4-9).

Due to their hazardous properties, standard biocides are highly regulated substances worldwide. The regulatory considerations are having a profound effect for the pulp & paper industry, most notably in the United States, Canada and Western Europe. The United States Protection Agency's (EPA) product registration process is costly and time consuming. The Canadian process is comparable to that in the United States. The European Union's Biocidal Products Directive went into effect in 2000 and will eventually remove a large number of products from the market if they do not pass regulatory round-up, or producers decide to not submit them for approval. In developing regions, regulatory climates vary widely. In several countries, regulations concerning biocide use are beginning to resemble those in the US, Canada, Japan and Western Europe (10, 11).

Alternative methods to conventional biocides are being investigated for slime control. One approach is the use of specific enzymes to prevent biofilm formation or to degrade existing biofilms. For example, the US Patent No. 4370199 (12) proponed a method of killing and inhibiting the growth of microorganisms in industrial process streams by the addition of a microbial or plant dehydrogenase enzyme such as peroxidase or laccase in the presence of an oxidant. Other researchers (13, 14) were investigating enzymes for hydrolysis of the polysaccharides produced by bacteria in slime films.

A new biocide based on cell wall lytic enzyme activities was developed. In the field of microbiology, it is well known that some microorganisms are able to produce cell wall lytic enzymes that affect bacterial, fungal and yeast cells such as exo-β-1,3-glucanases, chitinases and proteases (15-19).

The enzymatic "green" biocide presents following characteristics and advantages:

- It is a biodegradable product that does not pose any risk to mill workers or to the environment.
- It is non-volatile, non-reactive and is stable during transportation.
- Totally replaces standard "chemical" biocides at paper mills.
- It shows bacteriostatic and bactericidal properties.
- It is active against gram-positive and gram-negative bacteria.
- It has residual effect; it can be applied by shock loads.
- Does not allow bacterial strains to create microbial resistance.
- It eliminates biological slime in piping and equipment doing a permanent boil-out.
- Reduces paper breaks at the PM and increases stability of the PM.
- Allows closure of mill water circuits without increasing water corrosivity.
- Reduces bad odors in the water circuits and final products.

Following cases show the results of applying the new enzymatic biocide at pulp & paper mills:

CASE 1. Bacterial control at a tissue paper mill starting the use of the enzymatic biocide.

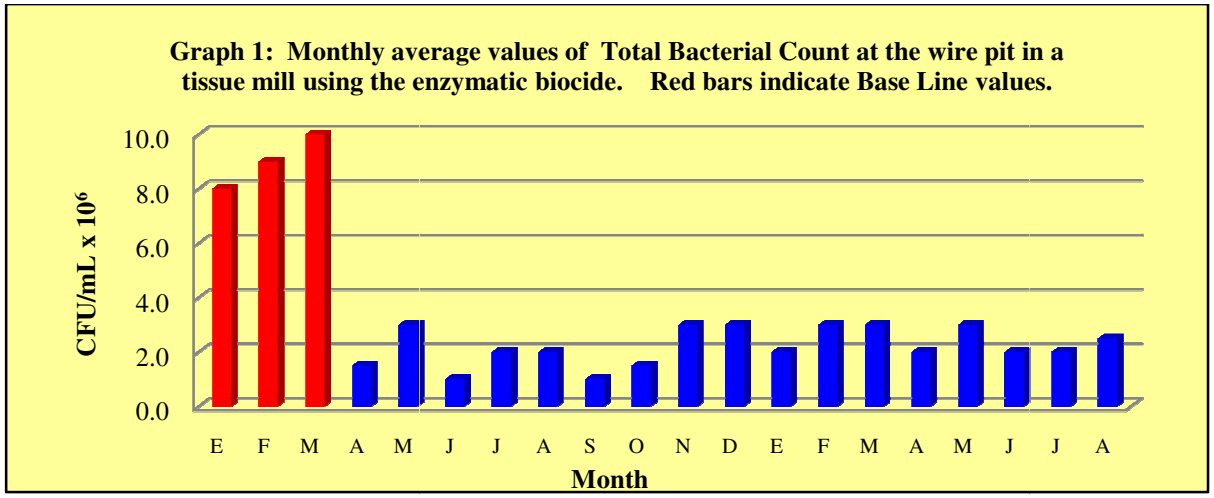
DAY	BACTERIAL COUNT AT WIRE PIT
0	60 millions CFU/g
5	15 millions CFU/g
10	4 - 5 millions CFU/g

CASE 2. Downtime reduction due to elimination of dirt and slime detachment at a paper machine by using the enzymatic biocide at a OCC mill:

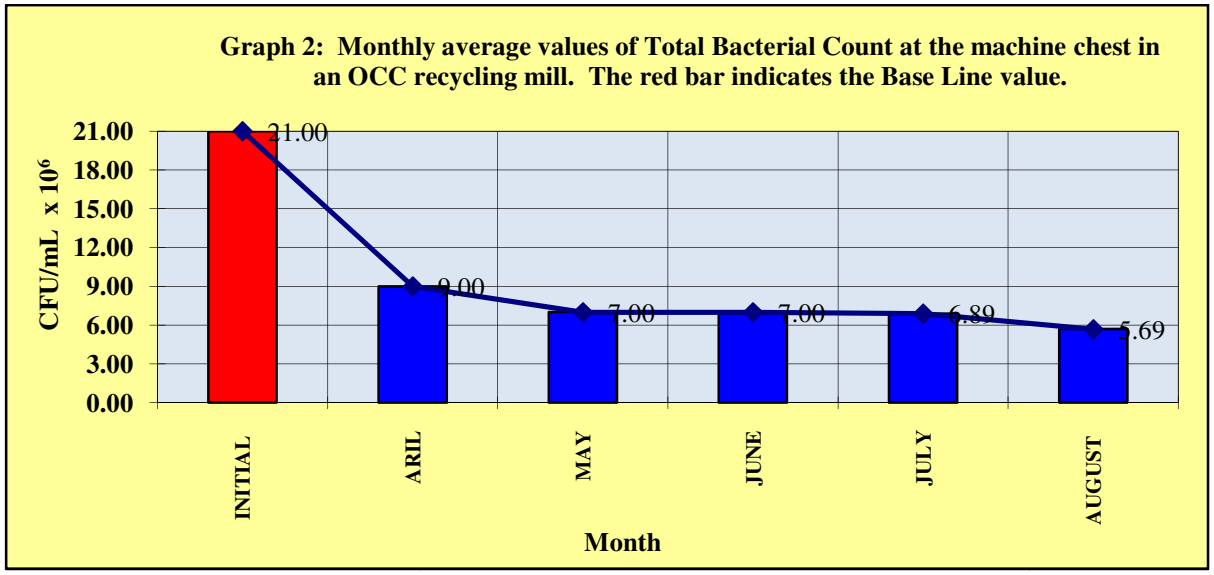
A Downtime reduction due to elimination of dirt detachment:
Reduction from 5,6 h/day to 0,4 h/day on PM 1 (Reduction 93 %)
Reduction from 2,7 h/day to 0,2 h/day on PM 2 (Reduction 92 %)

B Downtime reduction due to elimination of slime detachment:
Reduction from 0,5 h/day to 0,1 h/day on PM 1 (Reduction 74 %)
Reduction from 0,8 hr/day to 0,3 hr/day on PM 2 (Reduction 70 %)

CASE 3. Bacterial counts at the wire pit in a tissue mill using the enzymatic biocide. .



CASE 4. Bacterial count at the machine chest of an OCC recycling mill using the enzymatic biocide. .



DEVELOPMENT OF A WIDE SPECTRUM ENZYMATIC PRODUCT FOR STICKIES CONTROL

In the classic book "Recycled Fiber and Deinking", Dr. Hans-Joachim Putz (20) points out that the presence of stickies corresponds with the major challenge in the processing and use of recycled fiber. Some researchers proposed the use of enzymes for stickies hydrolysis back in 1997-99 (21, 22). Actually, the use of esterases for stickies control is a successful industrial application (23-24).

In a very appropriate analysis, Dr. Theresa Philips (25) points out that advantages of enzymes as chemical methods for removal of stickies have, historically, not been 100% satisfactory. However, one limitation of enzymes is that certain esterases might only be effective against certain types of esters, which turns out to be a major disadvantage due to the complex nature of stickies in mill water systems. Some esterases are able to hydrolyze a wide spectrum of substrates, but others result it strictly specific particular substrates (26).

The extreme complexity of stickies in pulp & paper mills has been well documented (20, 27-30). In fact, stickies can be considered a complex mix of waxes, tackifiers, PE, hot melts, styrene butadiene, polybutene, PVAc, acrylics, starch and fibers. Furthermore, MacNeil *et. al.* (31) in a study carried out at three paper mills on different continents, with each having a different source of recycled paper as raw material, reported that short-term variations in extractable stickies in the incoming raw material were quite extreme, with differences of 100% being seen within hours.

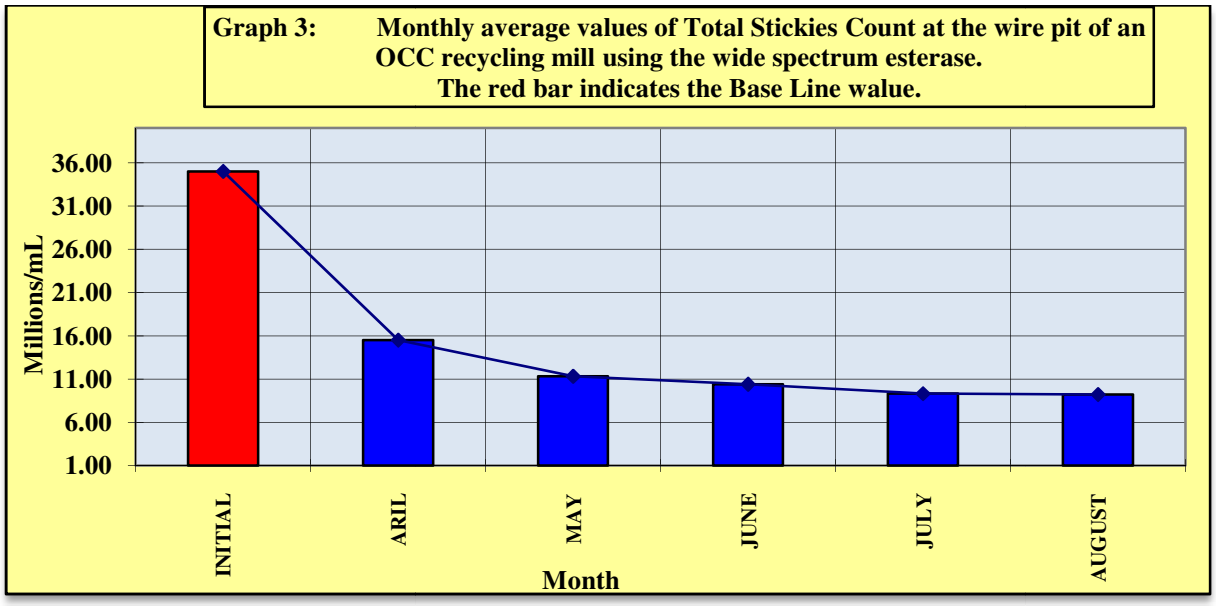
It shall be clear that a complex problem requires a "complex" solution: the esterase enzyme family includes different classes of esterolytic enzymes, including between others, carboxylesterases, true lipases, and various types of phospholipases that can be commonly obtained by bacterial fermentations (32).

Some strains are able to produce esterases that hydrolyze complex polymers such as poly(ethylene terephthalate) (33, 34), polyester polyurethane (35), poly(vinyl alcohol), p-nitrophenyl esters, 2-naphthyl acetate, and phenyl acetate (36), methacrylate polymers (37), vinyl acetate (38, 39), and the endocrine disrupting chemical DEHP [di-(2-ethylhexyl)-phthalate] (40).

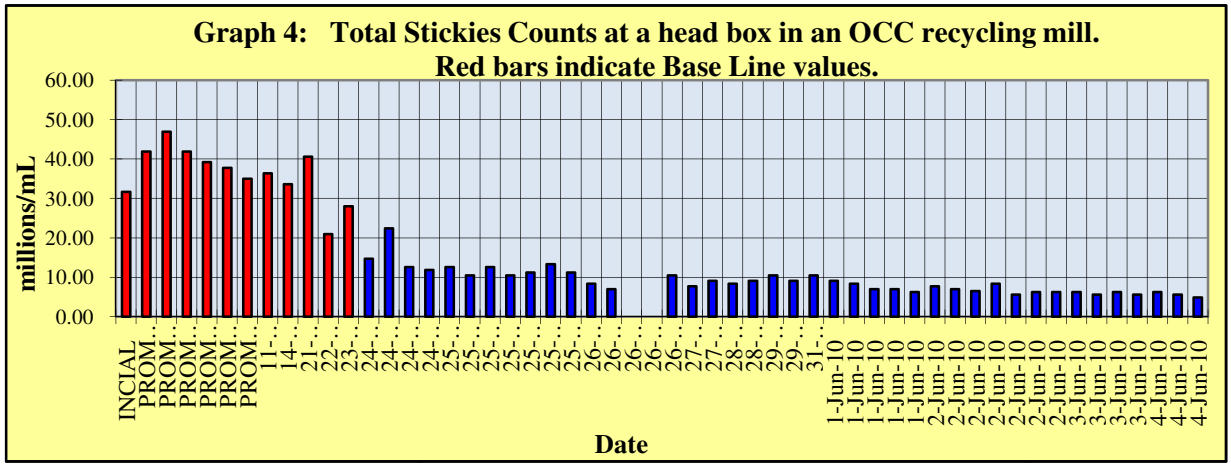
A wide spectrum sterolytic product containing various enzyme activities was developed to control the stickies problem at pulp & paper mills using recycled fiber. The enzyme product shows following characteristics:

- It is a non-hazardous, biodegradable substance that does not affect mill workers, nor the environment.
- It is a NON-GMO derived product, no multi-copy, instead containing a wide spectrum of esterase activities.
- It is a wide spectrum product for a very complex problem, reducing stickies counts by more than 70 %.
- Allows tissue formulators to use low quality furnishes, such as envelopes. Allowing 10 % envelopes in formulations.
- Increases life span of wires and felts by reducing cleaning operations with organic solvents.

Following graphics show performance of the wide spectrum sterolytic product controlling stickies at paper mills:



CASE 2. An OCC mill started the use of wide spectrum enzymatic product for stickies control. The violet lines show the base line values.



DEVELOPMENT OF AN ENZYMATIC PRODUCT FOR WET STRENGTH RESINS HYDROLYSIS

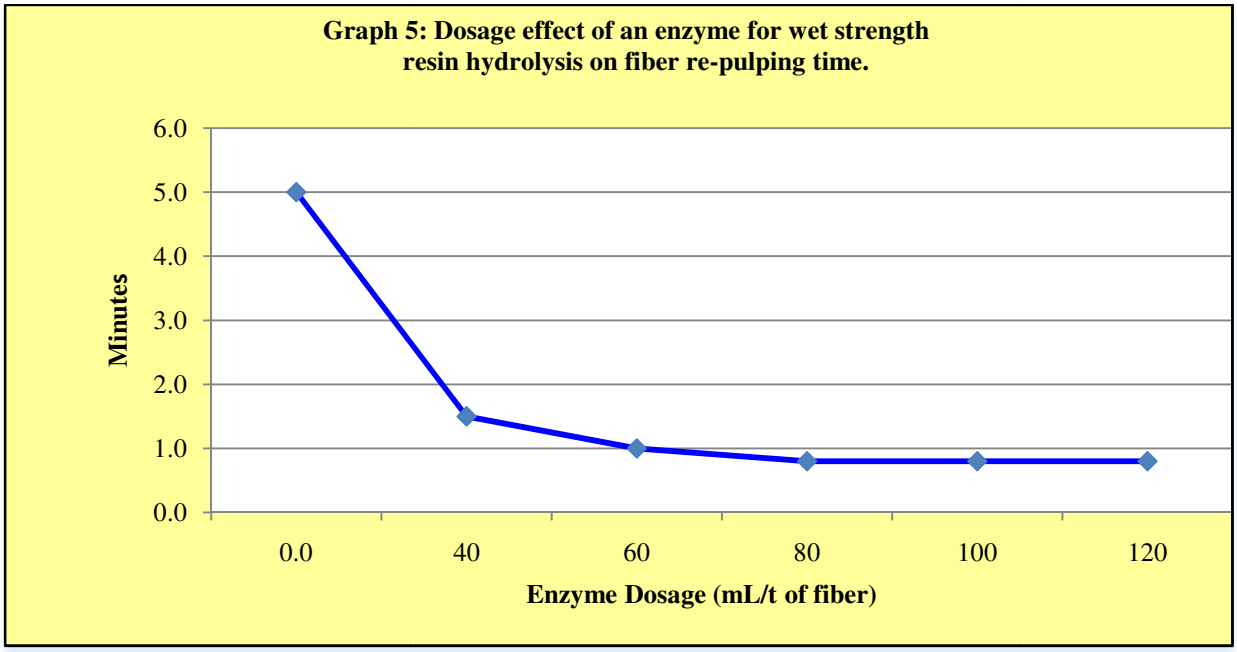
Polyamides are widely used in the paper industry as wet strength agents. However, when recycling polyamide resin-treated fibers, such materials are very difficult to repulp because of the structural stability of the polyamide chain. Polyamides used as wet strength agents in paper and paperboard products are commonly derived from adipic acid and diethylenetriamine followed by a cross-linking with epichlorohydrin.

Present methods for repulping fibrous materials containing polyamide wet strength resins require extreme conditions such as a pH of 10 or greater and temperatures of 160° F. or more, or they require the presence of strong oxidizing agents. Repulping fibers at high pH and high temperature is unsatisfactory for several reasons. Because papermaking machines are generally operated at a neutral or near neutral pH, if repulped fibers prepared at high pH are used to prepare recycled papers, a pH adjustment with acids would be required. High pH can cause damage to the repulped fiber and furthermore any adjustment of pH requires an additional step in the repulping method, which is undesirable from an operational standpoint. Elevated temperatures are undesirable because they add increased energy costs to the method. Other methods for repulping polyamide treated papers require the use of strong oxidizing agents to degrade the polyamides. Generally these other methods do not require the extreme operating

conditions of high pH and high temperature, but such strong oxidizing agents may cause the formation and production of undesirable byproducts. As a result of the difficulties encountered in repulping papers containing polyamide wet strength agents, these papers are often not recycled.

In 1993, the US Patent No. 5330619 (41) proposed a method for treating paper or paperboard containing polyamide resin as a wet strength agent with an enzyme to hydrolyze the resin and thereby improve repulping of the fibrous materials. More recently, Heumann *et. al.* (42),and Guebitz & Cavaco-Paulo (43) proposed the use of microbial enzymes for hydrolyzing polyethyleneterephthalate and polyamide fibres.

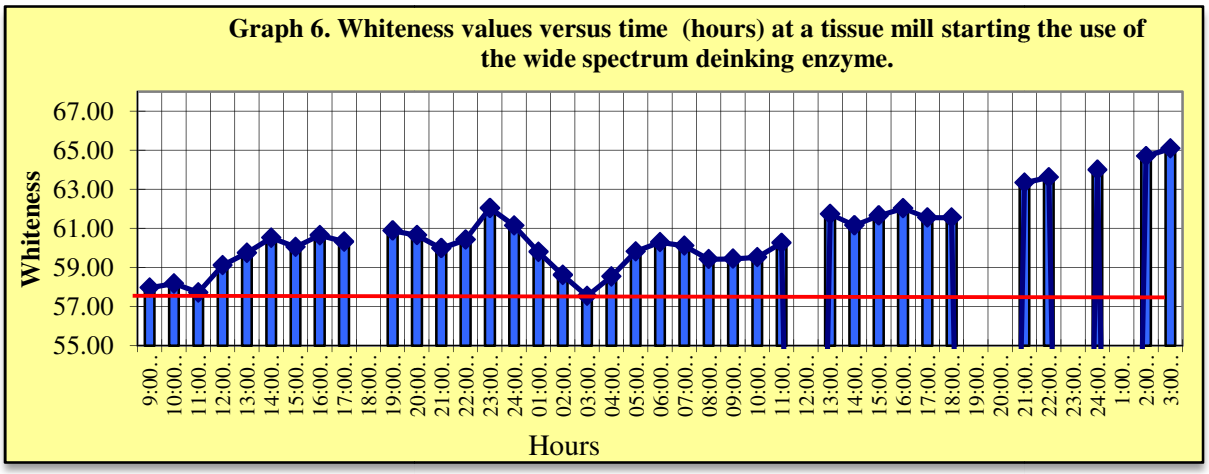
Very recently, an enzyme product for wet strength resin hydrolysis was marketed for pulp & paper mills recycling secondary fibers. The product hydrolyzes the wet strength resins reducing the structural stability of the polymer allowing fibers to be repulped with a minimum amount of energy. The graph No. 5 shows the performance of the enzyme product on re-pulping of recycled papers contaminated with wet strength resins.



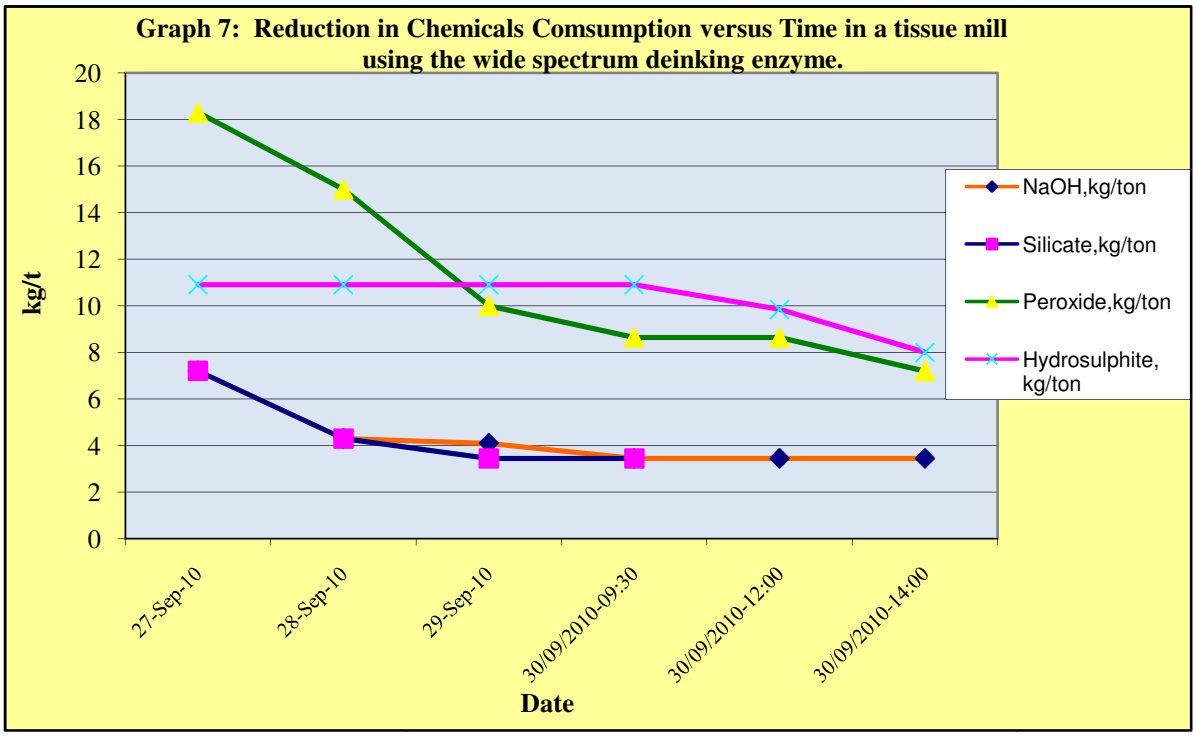
DEVELOPMENT OF A DEINKING ENZYME FOR COMPLEX TISSUE FORMULATIONS

Several researches were developed in the 90's on enzymatic deinking (44-48). More recently deinking technology was based on cellulases for the most challenging problem of non-impact inks (xerox and toner). It is now clear that cellulases are a very good alternative for deinking fibers contaminated with xerox and toner inks (49,50), however there is not a single tissue formulation based on 100% white paper with non-impact inks, instead tissue formulations may also contain old magazines, old newsprints, box board cuttings, colored ledgers and computer print outs.

A deinking enzyme for such complex formulations requires a wide spectrum of enzyme activities. A complex deinking product was developed in order to be used at tissue mills. The graph No. 6 shows the effect of the deinking enzymatic product on whiteness values in the final product at a tissue mill.



The deinking performance of the product allows users to reduce or replace hazardous chemicals that are normally used for deinking such as caustic soda, peroxide and hydrosulphite. The graph No. 7 shows the reduction in chemicals dosage at a tissue mill using the wide spectrum enzymatic product for deinking.



CONCLUSIONS

New enzyme technologies for paper recycling are providing various advantages for the pulp & paper mills which certainly impact the process economics and the efficiency inside the product life-cycle by allowing paper products to be recycled at a lower cost and with less process difficulties. Enzyme applications at paper mills simplify process chemistry, allowing less chemicals to be used, thus producing lower anionic trash, lower COD and also lower inventories of chemical products. Furthermore, the enzyme technologies provide new tools for those paper mills looking for environmental excellence awards and/or eco-labels.

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