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**Back to the Future: How Current Pulp-Bleaching Research  
Will Influence Future Furnish Resources**

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# **Back to the Future: How Current Pulp-Bleaching Research Will Influence Future Furnish Resources**

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## **Abstract:**

Current pulp-bleaching research studies are primarily directed towards reducing the capital and operating costs of modern kraft pulp manufacturing facilities. Many of these developing technologies will alter the nature of pulp carbohydrates, and this will ultimately impact the properties of virgin and recycled fiber. In addition, the development of the next generation of paper fillers and fiber modification technologies promise to modify the furnishes available for recycling purposes. Finally, the rapid developments in the field of genetic modification of trees will dramatically impact the basic properties of hardwood and softwood fibers. These new technologies will present new opportunities and challenges to modern pulp recycling operations. This seminar takes a look at the future horizon to determine how these emerging technologies will impact recycling trends and operations.

## **Introduction:**

Although the production of kraft bleached pulp has changed more in the last decade than in the previous thirty years, the revolution is far from complete. A brief review of the literature indicates that the bleaching revolution of the last decade has dramatically changed pulping technologies. As summarized by Singh<sup>i</sup>, pulp bleaching operations in the early part of the past millennium were primarily centered on chlorine. Changes in environmental regulations and societal pressures have dramatically altered the bleaching

landscape. The early 1990's saw two competing bleaching technologies; a variety of researchers proposed the replacement of chlorine with Totally Chlorine Free (TCF) bleaching chemicals (i.e., O, Z, P, A, etc) whereas Elemental Chlorine Free (ECF) was championed by many others. In the U.S.A., EPA's promulgated Cluster Rules<sup>ii</sup> approved the use of ECF bleaching technologies, while other parts of the globe saw increased industrial application of TCF bleaching technologies.

In the late 1990's, several research groups began to publish articles documenting problems in achieving high brightness and brightness stability for TCF bleached pulps. A study by Chirat and La Chapelle<sup>iii</sup> examined the brightness stability of softwood and hardwood kraft and bisulfite industrial pulps subjected to hydrogen peroxide- and ozone-based ECF and TCF bleaching sequences and then exposed to heat or light. Based on these studies, the authors concluded that TCF bleached pulps generally experience higher brightness reversion upon heat or light exposure than do ECF pulps. The pulp ketone content was shown to negatively influence brightness stability upon heat exposure and even more so if aldehyde groups in C1 or C6 positions were present. In addition, for a given degree of brightness reversion, light exposure results in lower pulp degradation than does heat exposure, which suggests separate mechanisms at work. Other researchers have supported the overall reversion trends of ECF and TCF pulps.<sup>iv</sup>

Of perhaps greater interest to recycling efforts are the strength properties of ECF and TCF bleached pulps. This issue has been extensively studied and reported. A recent article by Sjoström<sup>v</sup> examined the strength properties of pine and birch kraft pulps that were bleached with sequences containing peracetic acid, performic acid, Caro's acid or chlorine dioxide. The chemical, fiber and paper properties of the pulps were determined after each bleaching stage in order to find out in which stage differences between the pulps appear. Correlations between the pulps and pulp properties were studied using multivariate analysis. According to these results, the bonding and strength properties of unbeaten ECF bleached pulps were higher than those of TCF bleached pulps. The TCF pine pulps were very similar to each other, whereas the TCF(Pfa) birch pulp differed from the other pulps in having lower strength. The TCF(Pfa) pulps also had lower surface

lignin contents than the other pulps studied. In both pine and birch pulps, higher paper strength properties could be obtained with high carboxyl group content, but the carboxyl group content alone could not explain the differences between the pulps. On the other hand, the ECF pulps had both longer fibers and fewer fiber deformations, which could partly explain their higher strength. After beating for 2000 revs in a PFI mill, the strength properties of the TCF pulps were inferior to those of the ECF pulp. In the case of the pine pulp, this was probably due to the higher zero-span strength and the better bonding properties of the ECF fibers, while the difference between the birch pulps was mainly in the bonding properties. Bleaching to 85% brightness instead of 89%, by using less peracid in bleaching, brought the strength properties closer to those of the ECF pulp, but the same level could not be reached. Studies by Seisto et al.<sup>vi</sup> came to the same conclusion as Sjostrom.

Lumiainen<sup>vii</sup> employed an industrial-scale refining technique on a series of eleven ECF and seven TCF bleached Scandinavian softwood kraft pulps to determine the refining behavior of chlorine-free pulps. Compared to chlorine bleached pulps, the ECF pulps had slightly lower brightness and required significantly more refining energy. Although it was necessary to refine the ECF pulps to slightly higher freeness values, the pulps exhibited strength properties comparable to those of chlorine-bleached pulps. The TCF pulps were significantly lower in brightness than chlorine bleached pulps and required more refining energy. The TCF pulps required refining to significantly higher freeness values and exhibited lower strength properties than either the ECF or chlorine-bleached pulps.

Despite these reports, other authors have reported that TCF pulps provide strength properties comparable to ECF pulps. One such example was the mill data published from the Franklin VA mill,<sup>viii</sup> that produced bleached SW kraft pulp from an ozone-based process. Clearly these results, and others, suggest that the strength properties of TCF vs. ECF pulps are dependent on a variety of parameters including pulping and bleaching technologies employed.

From today's perspective, it is interesting to observe the merging of these two technologies (i.e., ECF and TCF). Preliminary publications by Chirat et al.<sup>ix</sup> and Homer et al.<sup>x</sup> demonstrated that the use of a D/Z or Z/D stage offered unique opportunities to decrease bleaching costs and provide pulps with improved strength properties.<sup>xi</sup> This technology has now left the laboratory and is being employed at several kraft bleach plants.<sup>xii, xiii</sup>

Coupled to these substantial changes in bleaching technologies, pulp manufacturers have significantly modified kraft pulping protocols providing improved fiber strength properties after the cook. The outcome of these advances in technology indicate that the strength and optical properties of kraft fibers have changed substantially over the past decade and these changes have and will continue to impact the quality of recycled fiber.

Despite these changes in pulp manufacturing technologies, even greater changes are projected into the future. Advances in forest genetics, fiber modification, and filler technologies are projected to significantly alter the primary furnish used for recycling efforts. These changes are being driven by industry needs. Research directed to address these challenges in the U.S.A. is being supported, in part, by the U.S. Department of Energy's Office of Industrial Technologies in a research and development program called "Industries of the Future." The program creates partnerships between industry, government, and supporting laboratories and institutions to accelerate the research, development, and deployment of new technologies. These technologies are aimed at cutting energy use, minimizing environmental impacts, and improving productivity in industry. Industry drives the process by creating a strategic vision of the future and technology roadmaps that establish more detailed R&D priorities. OIT serves as a facilitator by encouraging industry to undertake long-term technology planning and by cost-sharing research. This past summer the U.S. Department of Energy's Office of Industrial Technologies hosted the Technology Summit in the Forest Industry (see [http://www.oit.doe.gov/forest/visions\\_summit.shtml](http://www.oit.doe.gov/forest/visions_summit.shtml)). The objective of this meeting was to review and revise research and development goals in the pulp and paper industry to

better address industrial needs. This summit identified six technology platforms of importance to the industry, including:

- Higher Value Raw Material Supply
- Significantly Reduced Manufacturing Costs
- Technologically Advanced Workforce
- Environmental Performance
- Energy Performance
- New Forest Based Materials

One of the sub components of the Significantly Reduced Manufacturing Costs platform was directed at Fiber Engineering. Currently, pulping, bleaching, and refining operations produce both beneficial structural changes and unwanted, harmful changes in the structure of the fiber. The creation of new genetic fiber modification, enzymatic/microchemistry based modification and microsurgery/micromechanics based mechanical modification technologies were identified as the most promising approach for creating only beneficial changes in the fiber structure. Also, the acceleration of the development of advanced fillers was identified as a means of reducing paper manufacturing costs significantly.

Of the many competing technologies that could address the Fiber Engineering objectives, the panel selected the following four research focus areas:

1. **Fiber Modification: Modification of Fibers and Fiber Surface with additives or enzymes to provide new properties that would (1) enhance fiber bonding, (2) use less fiber to provide desired product attributes, and (3) lead to new product lines.** This recommended research area cuts across all the product lines of paper and board. This research area represents a mixture of basic research and process development.

2. **Cell Wall Polymer Biosynthesis:** Identify molecular mechanisms regulating cell wall polymer biosynthesis, especially cellulose and hemicellulose formation, with the expectation that this understanding would lead to the control and impact of cellulose and hemicellulose on fiber properties. This recommended research area cuts across all the product lines.
3. **Micromechanical Modeling of the Fiber Cell Wall:** Develop and validate a micromechanical model that predicts the properties of the fiber as a function of composition, geometry and architecture. Such a model should provide guidance and opportunities to bio-engineer desirable fiber properties. This title represents both fundamental research and knowledge generation for deeper understanding the micromechanical behavior of the cell wall as a function of its physical and chemical composition. It is not a pure theoretical derivation, because the model needs to be verified with experimental data, the generation of which requires good experiments and analysis.
4. **Alternative Refining Methods:** Develop alternative refining methods that optimize energy transfer to the fiber to enhance and control fiber quality in order to control specific structural modifications in cell wall and improve energy efficiency. This recommended research area cuts across all product lines and covers both mechanical pulping and low consistency refining of chemical pulp fibers.

The working committee concluded their discussions by stating “the recommended research areas by the Fiber Engineering Team are very central to the competitive future of the whole industry. As pointed out earlier, they are linked to the material efficiency of the papermaking, to the economics of the papermaking and to delivery of new product attributes to the final product. They also do not require any radical changes into the actual papermaking equipment or into the converting industry or final product use environment.”



With regard to fibrous fillers, the working committee acknowledged the role that fillers have to lower manufacturing cost and enhance some paper properties, such as graphics. They also indicated that the practical filler content of paper has been reached and that traditional thinking needs to be challenged with “out-of-the-box” approaches based upon fundamental research yielding new sheets structures with significant increases in filler contents are needed. A technology gap filling analysis suggested that fillers engineered to behave more like fibers (i.e., having an aspect ratio of at least 3:1) and having surface adhesion capabilities, will permit better retention of the fillers and reduce the negative impact on sheet strength and paper machine runability. This will enable greater use of these materials in the sheet, thereby permitting greater substitution of fillers for the more expensive fiber component. Successful implementation will see the non-fiber content of paper rising 50-100% over current norms, and paper manufacturing costs decreasing by 20-30%.

#### **Conclusion:**

Over the past few decades, researchers at pulp and paper mills, industrial labs, assorted universities and pulp and paper research organizations have redefined many of the core pulping and bleaching technologies employed in the industry. In this new millennium, new expectations and challenges have developed and as these issues are addressed new technologies will be developed that will improve physical properties and lead to increased applications of the worlds leading renewable, natural resources. These changes in fiber resource will benefit and challenge many recycling operations.

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