ENVIRONMENTALLY FRIENDLY TECHNOLOGIES FOR THE PULP & PAPER INDUSTRY

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PREFACE

The pulp and paper industry is facing increasing pressure in terms of environmental regulations, energy usage, and profit margins; therefore, new or greatly modified technologies will be necessary to carry the industry through the twenty-first century. The innovations taking place in the industry can be classified as chemical and biological, as well as combinations of the two. These developments have occurred over approximately the last 10 to 20 years but have never been brought together in one treatment. Therefore, we decided to develop this book.

It would, of course, be impossible to cover all the new processes under development in this short treatment, so we have identified those processes that we feel have the greatest potential for future development. It should also be noted that the chapters are not "all-encompassing," as each chapter author was requested to review recent work on the processes they have developed. It can be readily noted that the chapter authors are very enthusiastic about their respective processes and often have strong opinions related to their potential. We applaud this positive approach, but readers must carefully weigh all the factors important to the success of a new technology and decide for themselves the viability of the technology in the competitive industrial arena.

We believe that we have brought together a description of some of the most important new technologies currently under development for the pulp and paper industry. Although many of these processes will probably be modified to some extent over the coming years, this book will serve as a valuable reference as to the current state of knowledge and provide the stepping stones for entry of the pulp and paper industry into the twenty-first century.

A book of this magnitude can never be accomplished without the help of many people, and we wish to acknowledge the assistance of the staffs of the Department of Forestry, University of Wisconsin, the USDA Forest Service, Forest Products Laboratory, and Biopulping International, Inc., Madison, Wisconsin. We are also most grateful to our wives, Kathryn Young and Farheen Masood, for enduring the extra time commitment necessary to make this venture successful.

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CONTENTS

Introduction: The Need for New Technologies for the Pulp and Paper Industry

MASOOD AKHTAR
and RAYMOND A. YOUNG

The pulp and paper industry is a large and growing portion of the world's economy. Pulp and paper production has increased globally, and will continue to increase in the near future. However, the industry is very capital-intensive with small profit margins, which tends to limit experimentation, development, and incorporation of new technologies into the mills. The pulp and paper industry is also under constant pressure to reduce and modify environmental emissions to air and water.

In order to keep up with the increased demand for pulp and paper and to meet increasingly stringent environmental regulations, the industry is looking towards technological improvements in the conventional pulping methods. However, it probably will eventually be necessary to shift to even newer technologies to meet industrial and consumer needs as well as the environmental requirements. In this book, the main focus is on the development of new environmentally friendly technologies (both chemical and biological) that can help solve some of the problems associated with conventional pulping technologies. The work described in this book generally represents revolutionary, rather than evolutionary, approaches to the production of pulp and paper. Descriptions and details for the new processes can be found in the individual chapters.

In the following paragraphs, we discuss the limitations of the existing conventional pulping methods and the future needs of the pulp and paper industry. Further details can be found in reports on the Technology Vision and Research Agenda 2020 prepared by the American Forest & Paper Association (November 1994), and from a workshop on Paper Industry Research Needs (Syracuse, New York, May 26–28, 1992) sponsored by the Technical Association of the Pulp and Paper Industry.

The pulp and paper industry utilizes mechanical and chemical methods to produce pulps with desired characteristics. High-yield mechanical pulping processes are electrical energy–intensive and result in paper with poor strength, poor brightness stability, and high pitch content. Often, mechanical pulps are bleached to improve the brightness, but this is costly. These disadvantages limit the use of such pulps in many grades of paper. Therefore, methods must be developed to overcome these problems. A promising alternate approach described in this book is biomechanical pulping, which reduces electrical energy requirements, improves paper strength, and reduces the pitch content. Another pitch-control fungal product (Cartapip™) has been developed in the United States and is being used commercially; the product is discussed in the biological section of the book. Pitch refers to resinous substances in wood that cause a number of problems in pulp and paper manufacture, including downtime for cleaning, breakage of paper on the paper machine, and creation of holes in the paper.

Chemical pulping methods, as compared with mechanical pulping methods, result in stronger paper but are less environmentally benign and give low yields. Chemical pulps are produced by the degradation of lignin under either acid or alkaline conditions. Acid pulping processes, such as sulfite or bisulfite, result in weaker paper as compared with the alkaline pulping processes. Therefore, the alkaline, or kraft, pulping process is by far the most important chemical pulping process practiced on an industrial scale. Some major difficulties with the kraft pulping process are the very large capital investment, the emission of reduced forms of sulfur, and the accompanying odor and high water usage. Emerging chemical and biological approaches that can alleviate many of these problems are discussed in this book.

Delignification methods as currently practiced in conventional kraft and soda pulping processes are not very specific for lignin removal. Research is needed to develop methods for greater lignin selectively during the cooking. Further research is also necessary to make sulfur-free pulping a reality. Most of the processes described in the book are based on sulfur-free delignification mechanisms. Several chapters are also devoted to the bleach plant, where there is a critical need to reduce the use of large amounts of chemicals.

It is predicted that the major virgin raw material for paper will continue to be wood. However, recovered fibers will have a much greater role than they do today and alternative agro-based plant fibers will be increasingly viewed as a component of fiber supply. Wood pulping will continue to be dominated by chemical processes, but there will be an increasing improvement in the environmental compatibility of pulping and bleaching operations. The dominating pulping technology is still expected to be the kraft pulping process, but there will be a trend toward increased use of processes, such as those described in this book, that do not utilize reduced sulfur compounds. New bleach plants will result in improved environmental compatibility through the use of technologies such as reduced water usage, extended use of oxygen-based chemicals, and other alternatives. Several chapters in this book describe the rapidly changing technology of pulp bleaching.

It is clear that there are significant problems associated with the current conventional pulping processes, and evolutionary steps in technology have greatly improved the viability of these processes; however, it may be necessary to move to radically different technologies to meet more stringent requirements of the next century. Some of the more viable alternatives currently available or under development today are described in this book. It is hoped that this information will provide a stepping-stone to new developments in the pulp and paper industry in the twenty-first century.

PART ONE
Chemical Applications to Pulp and Paper Processing

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1 Developments in Organosolv Pulping—An Overview

HERBERT L. HERGERT

INTRODUCTION

Beginning in the 1950s the kraft process was selected for new pulp mills much more frequently than other chemical pulping processes, such as acid bisulfite, neutral sulfite, alkali-anthraquinone, and so on, so that it is now the dominant wood pulping process throughout the world. It is the most economic of the major chemical pulping processes, and the pulp produced has the best strength properties. Furthermore, all of the engineered components of the process have been time-tested. This is particularly important to the pulp and paper industry, which is conservative toward risk taking because of the high capital investment in manufacturing equipment and the relatively low return on equity.

There are a number of drawbacks to the kraft process, however, not the least of which is the obnoxious odor associated with even the most advanced mills. Even more serious is the problem associated with size. New kraft mills must have a production capacity of 1,000 tons per day or more to be economic, and this, of course, requires a tremendous capital investment. In some countries—Germany, for example—safety considerations have forbidden the installation of the Tomlinson-type recovery furnace used in almost all kraft mills because of the fear of kraft smelt explosions. Bleached kraft pulp mills have been targeted by environmentalists because of their use of chlorine, chlorine dioxide, or other chlorine-containing chemicals. Substitution of nonchlorine bleach sequences has not been easy because of the resistance of the residual lignin in kraft unbleached pulp to the use of nonchlorine bleaching agents utilized to reach requisite levels of whiteness and cleanliness.

For these reasons and others, there has been renewed interest in recent years in trying to find alternatives to the kraft system that will yield pulp with kraftlike strength properties but without the environmental drawbacks. One of the major areas of activity is "organosolv" pulping, that is, the process of using organic solvents to aid in the removal of lignin from wood. The question may well be asked: Why

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organic solvents? Even the least expensive organic solvent is substantially more expensive than the water used as the only solvent in all current commercial processes. Nevertheless, there has been a major expansion in organosolv research and development activity during the past decade, with more than 600 papers being published and/or presented at technical meetings.

The pioneering work on organosolv pulping began with the discovery in 1931 by Kleinert and Tayanthal (1931, 1932) that wood could be pulped with mixtures of ethanol and water at elevated temperatures and pressure. A few subsequent investigations during the following 30 years showed that a rather wide array of organic solvents could be used with or without the addition of acidic catalysts such as mineral acids, acidic salts, sulfur dioxide, chlorine, and so on. Summarizing the situation in 1965, Rydholm (1965) in his classic pulping text noted "the cost of the solvent though the inevitable losses has made these processes unattractive for industrial purposes, especially as, in general, they offer no advantage in pulp yield or quality over the conventional processes."

Rydholm's assessment continued to prevail for another decade until the confluence of two major societal changes impacted the pulp and paper industry. First, environmental regulations imposed the need for massive reduction in emissions and effluents. Second, the oil "shock" of the middle 1970s imposed a new discipline on energy-inefficient mills. The price (and value) of pulp doubled between 1973 and 1977. Predictions were made that crude oil prices in the 1980s would be more than ten to fifteen times greater than they were in the 1960s. Wood was once again hailed as having the potential for yielding chemicals and liquid fuels independent of the rapidly escalating price of petroleum. Hydrolysis of wood could yield sugars fermentable to ethanol, a liquid fuel. Researchers, however, turned to the use of cellulolytic enzymes for processing rather than the inefficiencies of mineral acid hydrolysis practiced during World War II. The trouble, as it turned out, was that woody materials had to be delignified for enzymatic hydrolysis to proceed at economic rates. Thus, various schemes for a "biorefinery" inevitably involved the use of a delignification scheme or the use of already delignified pulp that might otherwise be used for papermaking. This delignification often involved organosolv procedures.

The predicted never-ending escalation of oil prices in the 1980s did not materialize. Interest in wood as a raw material for liquid fuels has abated. The value of pulp, whether as a marketable commodity or as a component of paper, is significantly greater than that of methanol or ethanol. The latter is derivable at lower cost from natural gas or fermentation of glucose from corn starch or sucrose from sugarcane. Research is now primarily directed toward production of pulp with competitive strength properties at yields higher than derived from existing commercial processes. Much interest in the past decade has, therefore, been redirected to organosolv techniques that could avoid odorous emissions or toxic effluents, that is, environmentally benign processes (Laxen, 1987).

Recent work on organosolv pulping has received considerable attention from the worldwide technical press (Anders, 1987; Aravamuthan et al., 1989; *Asia Pacific Pulp Pap.*, 1991; Aziz et al., 1988; Aziz and Sarkanen, 1989; Felsch, 1990; Franzreb, 1989; Fuller, 1989; Doshi and Associates, Inc., 1987; Integrated Paper Sciences, Inc., 1989; *Chemical Week*, 1984; Fleming, 1985; Johansson et al., 1987b; Kramer, 1988; Minton, 1992; Onisko, 1989; Sano, 1991; Sarkanen, 1983; Sarkanen, 1990; Schenck, 1990; Schliephake, 1990; Surewicz, 1988; Surewicz, 1990; *Asia Pacific Pulp Pap.*, 1991; Gavrilescu and Obrocea, 1991; Hergert, 1993; Hergert and Pye, 1992; Jameel, 1992; Judt, 1995; Liebergott and van Lierop, 1992; McDonough, 1993; Ray et al., 1991; Rozmarin and Malutan, 1993; Rutkowski, 1993; Sakai, 1994; Schroeter, 1994; Stockburger, 1993; Teder and Olm, 1992; Young, 1993; Young, 1994). In general, it has been concluded that there is need for smaller-sized pulp mills, especially in third world countries, that would have the same economy of capital and operating costs as new large-scale kraft mills. Odor-free mills are needed in western Europe and North America to meet current environmental concerns. Organosolv pulping processes, it is hoped, can meet these goals. Research emphasis has shifted from retrofitting existing mills to capacity expansions at already operating mill sites. In the last few years much work has been devoted to the pulping of annual crop residues—for example, straw, kenaf, sugarcane, bagasse, and so on—because societal pressures have dictated a decrease in the harvesting of forests, much of which are publicly owned (Young, 1996). The pulp and paper industry's view has been aptly summarized by Minton (1992): "It is unlikely that any one solvent process will be the ultimate 'kraft replacement.' But in the next ten years, we need to keep moving toward pulping processes in quality and cost for the product being made. Solvent pulps may be an important step toward that goal." A number of well-researched and piloted projects have been publicized, but a successfully operating commercial plant is needed to confirm the claims of the research community and to convince an interested but generally skeptical industrial pulp and paper establishment.

DIFFERENTIATION OF ORGANOSOLV PROCESSES

Wood, as is well known, consists of an intimate mixture of (1) 42 to 52% cellulose, a glucose polymer with a molecular weight of about 2,000,000; (2) 25 to 32% hemicellulose, based primarily on xylose in hardwoods and mannose and glucose in conifers and having a molecular weight of 20,000 to 30,000; (3) 20 to 30% lignin, an aromatic, three-dimensional polymer with apparent infinite molecular weight; and (4) 1.5 to 6% acetic acid in the form of acetyl groups attached to the hemicelluloses. The latter, though small in amount, is particularly important in many organosolv pulping schemes. Lignin is covalently bonded with xylans in the case of hardwoods, and with galactoglucomannans in softwoods, probably through glucuronic acid linkages. Even though mechanically cleavable to a relatively low molecular weight, lignin is not soluble in water. Therefore, lignin removal in commercial water-based pulping systems requires: (1) strong alkali to break phenolic ether linkages to yield alkali-soluble phenolate products and hydrosulfide ions to prevent lignin recondensation (kraft process), or (2) sulfur dioxide and bisulfite ions to sulfonate alpha and gamma hydroxyl groups and cleave ether linkages to give water-soluble lignosulfonates (sulfite processes). In either case, such lignins isolated from process