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PULPING CATALYSTS FROM LIGNIN

The paper herein is intended for publication in a 1991 Tappi Journal spring issue dealing with emerging technology in the pulp and paper industry. The paper is rather descriptive. A more technical account can be found in the project annual reports issued by IPST or the Department of Energy. These reports are going to IPST member companies as they become available. The research is being funded by DOE and is just beginning the third year. The IPST project number and title are: 3661 SULFUR-FREE SELECTIVE PULPING PROCESS.

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PULPING CATALYSTS FROM LIGNIN

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A process is under development to provide low-cost anthraquinone catalysts from lignin which will lead to improved chemical pulping.

INTRODUCTION

The kraft pulping process has achieved wide acceptance because of its relatively rapid pulping rates, its adaptability to many types of wood feedstocks, its ability to produce a strong pulp, and its low chemical costs. However, the process has a number of shortcomings: the yield of pulp is relatively low, the pulp is highly colored, requiring extensive bleaching, the presence of the sulfur promoter leads to malodorous emissions, and there is an extremely high capital investment associated with the complex chemical recovery system and environmental processing technology.

A possible solution to several of the kraft process disadvantages was discovered in 1977. Holton reported that addition of catalytic amounts of anthraquinone (AQ) significantly promotes alkaline pulping processes. This discovery has become one of the most widely studied effects in paper chemistry in the last 13 years. There are a number of benefits associated with the use of anthraquinone, including an increase in pulping rates, higher pulp yields, a decrease in the amount of the alkali in the process, and adaptability with existing kraft technology. Of course, all of these benefits may not be realized simultaneously. Importantly, the pulp properties are quite similar to kraft, except for a small decrease in tear strength.

Despite the reported advantages of anthraquinone catalyzed pulping, the current cost of AQ (about $4.50/lb) hinders its general use, except under certain circumstances. Where wood costs are high, such as in Japan, pulping yields take on greater importance and AQ-type processes are common. Anthraquinone is also used to give "relief" from a bottleneck, such as a deficiency in recovery furnace capacity.

ANTHRAQUINONE PULPING CATALYSTS FROM LIGNIN

We have been investigating ways to prepare anthraquinone at a cost low enough to make it attractive for general industry use and have found lignin to be a
suitable starting material. Lignin has a number of attractive features as a raw material for anthraquinone production. First, lignin is inexpensive; it is readily available as a by-product from the paper industry. Its cost is normally calculated as its fuel value which is $0.03-0.04/lb. Second, a successful synthesis of anthraquinone from lignin will give a new, higher value-added product to the industry. Third, a mixture of lignin and anthraquinone could probably be used as a pulping promoter without purification and, hence, could be used on site and save several costly processing steps.

In the last two years, our research, supported by the Office of Industrial Technology of the U.S. Department of Energy, has focused on both the scientific and economic aspects of commercialization of an AQ-from-lignin process. Our approach for the synthesis of anthraquinone from lignin has been divided into two large stages, lignin processing and chemical processing.

The lignin processing stage involves selectively isolating a low-molecular-weight fraction from a lignin source. Lignin is a complex high molecular weight biopolymer which is fragmented during pulping. However, condensation reactions, which occur during pulping, reconnect some of the fragments to give new polymeric and oligomeric materials of widely differing molecular weights. In theory, this crude mixture could be used directly in the subsequent chemical processing stage without separation of a low-molecular-weight fraction. However, our economic evaluation has indicated that this approach is unattractive because of expected non-productive consumptions of chemicals. In addition, chemical processing of the whole lignin would probably be difficult from an operational standpoint because of the heterogeneity of the mixture. Therefore, low-molecular-weight lignins must be isolated to serve as starting materials. Two methods for separation of this low-molecular-weight fraction have been evaluated: lignin extraction using supercritical carbon dioxide in the presence of small amounts of organic solvents and just using conventional solvents.

The second stage of the process involves chemical processing of the low-molecular-weight fraction and contains two critical chemical steps (Figure 1). In the first step, the low-molecular-weight lignin is oxidized with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones. This step attempts to retain the aromatic rings of the lignin while oxidizing away the side chains and cleaving the bonds between monomer units. The aliphatic lignin side chains are not needed and, in fact, will cause problems in subsequent steps in the process. The degree of methoxy-substitution depends on the source of the lignin. Softwoods will give mostly monomethoxybenzoquinone, while hardwoods give a mixture of mono and dimethoxybenzoquinone.
Figure 1. Chemical steps in the conversion of lignin to anthraquinone.

In the second step of the chemical processing sequence, the benzoquinones are converted into nonaromatic anthraquinone precursors by treatment with a diene, using the well-known Diels-Alder reaction. Final conversion of these precursors to anthraquinone derivatives (e.g., 2) occurs by loss of methanol and hydrogen, either during reaction or in a separate step. The aromatization step may be unnecessary; partially aromatic anthraquinone also functions as a pulping catalyst by in situ conversion to anthraquinone.

SUMMARY OF RECENT RESULTS

Progress has been made in each of the areas mentioned above since our initial disclosure of the preparation and activity of AQ catalysts derived from lignin. The most important activities are summarized briefly below.

Process Economics - The single most important determining factor in the final cost of anthraquinone prepared from lignin is the overall yield of the chemical processing steps. An economic evaluation determined that the anthraquinone cost drops exponentially with increasing overall yield. Because of the strong dependence of anthraquinone price on chemical yield, the contribution of the preliminary lignin processing stage to the overall cost is not significantly different regardless of whether a supercritical fluid extraction or conventional solvent extraction is employed. Another conclusion of the economic evaluation is that the AQ cost drops significantly as the scale of the operation increases. Under optimum conditions, the cost of AQ could be as low as $1.00/lb. More realistically, a cost between $1.25 and $1.75/lb has been projected.

An economic evaluation also compared the lignin based route to AQ to other competing routes which are primarily based on fossil fuel-derived starting materials. Five alternative commercial or near-commercial routes were con-
sidered. Assuming satisfactory progress in research and development, the lignin route was potentially the most cost-effective anthraquinone process available.

Lignin Processing - A number of lignin processing techniques have been examined. Both supercritical fluid extraction and solvent extraction hold the promise of providing the necessary low-molecular-weight lignin fraction necessary for conversion to anthraquinone. Supercritical fluid extraction, involving carbon dioxide and 15-25% added organic solvent, has been used to remove the low-molecular-weight lignin which remains in the aqueous phase following acid precipitation of the high-molecular-weight lignin from a pulping liquor. While the selectivity for low-molecular-weight lignin is good, the yield has been low.

Recent results indicate that simple organic solvent extraction of organosolv lignins provides significant amounts of low-molecular-weight material. Organosolv lignin has a number of interesting characteristics when considered as a starting material for this process. Structurally, it resembles native lignin more closely than other types of lignin, such as kraft. This property is important since organosolv lignin retains certain functional groups that could make subsequent chemical processing easier. Organosolv lignin also appears to contain a higher proportion of the low-molecular-weight fraction needed for anthraquinone synthesis.

An economic evaluation led to the conclusion that an organosolv operation of sufficient scale, taking credit for the sale of pulp produced, could provide lignin for anthraquinone synthesis at no net cost. Residual lignin from an auxiliary organosolv mill could readily be altered and fed into an existing standard alkaline pulping process.

Chemical Processing: Oxidation of Lignin and Lignin Models - A number of oxidizing agents have been evaluated for suitability in the first step of the chemical processing stage. Because of the structural complexity of lignin, initial work was performed on compounds that model lignin's behavior. Fremy salt is an excellent oxidant for the production of benzoquinones from phenols which bear lignin-like functional groups; however, the reagent does not appear suitable for a large industrial process.

Hydrogen peroxide oxidation of certain lignin models to give benzoquinones has been optimized to give yields of 80-90%. However, a large excess of oxidant is needed for good yields, thereby reducing its cost-effectiveness. Also, the yields of benzoquinones from H\textsubscript{2}O\textsubscript{2} treatment of isolated lignins have been discouragingly low. These drawbacks have led to the examination of other oxidants.

Nitrogen dioxide, a readily available material, has been shown to be an effective oxidant for lignin models. The procedure, which is still being investigated, involves treating the substrate at room temperature with NO\textsubscript{2}/O\textsubscript{2} in an alcohol solvent. The yields of dimethoxybenzoquinone with simple lignin models are often above 80% and with an extracted lignin in the 20-40% range.
In addition, inexpensive oxygen has been successfully used as an oxidant in the presence of catalytic amounts of certain transition metal complexes. Yields of benzoquinones from the oxidation of lignin models as high as 85% have been realized under mild conditions.

**Chemical Processing: Diene Addition** - The second step in the process, addition of a diene to the benzoquinone mixture to give anthraquinone precursors, has been demonstrated for each of the benzoquinones expected from lignin oxidation. The yields of these reactions can be high, especially for formation of one ring. However, the formation of two rings simultaneously (benzoquinone directly to an anthraquinone) is a more difficult task; the intermediate naphthaquinone structures react very slowly under standard conditions. Recent encouraging results, using catalysis to assist the diene addition and a novel diene addition reaction carried out in water, suggest that a direct one-step conversion of benzoquinones to anthraquinones, without isolation of non-aromatic precursors, is possible. We now suspect that the Diels-Alder step will not be a significant contributor to the overall process cost.

**FUTURE DIRECTIONS**

We have demonstrated the feasibility of each step in the overall process under certain cost constraints. The objective of our present research is to develop and optimize our lignin extraction and chemical conversion efficiencies to further lower the cost of pulping catalysts from lignin. The research will move the successful results of the laboratory research to larger scale.

Development of a cost effective soda/AQ process will greatly reduce the air emissions typically associated with present processes and simplify chemical recovery and environmental processing. If catalyst cost can be kept low, an anthraquinone process offers opportunities to improve productivity, conserve raw materials, and save significant amounts of energy.

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LITERATURE CITED


