

Pulping Catalysts from Lignin

by

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Abstract: Lignin, a common material in trees and woody plants, is currently a byproduct of pulp and paper production. However, joint research at the National Renewable Energy Laboratory and the Institute of Paper Science and Technology is aimed at broadening commercial uses of lignin. One project is assessing the potential of converting lignin into anthraquinone-like pulping catalysts. Anthraquinone (AQ) improves kraft pulping, but its cost, which ranges from \$4.00 to \$4.50 per pound, hinders widespread use.

Three processes for converting lignin into pulping catalysts were evaluated for their technical and economic feasibility. Preliminary results indicate that two of the processes appear viable. Amortized production costs for using lignin from kraft pulping, without intermediate conversion to vanillin and syringaldehyde, and lignin from organosolv pulping were estimated to be \$1.24 and 79 cents per pound, respectively. Comparing these two processes to competing petrochemical-based, AQ-producing methods, showed that the lignin-based routes were potentially the most cost effective.

Keywords: Lignin, pulping catalysts, anthraquinone, kraft pulping, organosolv pulping.

Lignin, the material in trees and woody plants that differentiates them from herbaceous plants, is one of the most underused renewable sources of carbon. In nature, lignin makes up as much as 30 percent of the carbon in organic matter (1). Lignin, cellulose, and hemicellulose are the three major components found in wood.

However, lignin, a byproduct of pulp and paper production, is now used primarily as in-plant fuel. Commercial operations for isolating and converting the lignin from pulp mills to other materials are limited. Joint research at the National Renewable Energy Laboratory (NREL) and the Institute of Paper Science and Technology (IPST) is aimed at broadening the commercial uses of lignin as a chemical feedstock and converting it into useful, higher value compounds such as pulping catalysts.

Anthraquinone Can Improve Kraft Pulping

Roughly 80 percent of the paper made in the United States is produced using the kraft pulping process. Wood is heated with a base and sodium sulfide, which helps separate the wood components. The kraft process produces a cellulose fraction, which is made into paper, and a fraction containing the lignin, which is burned as

fuel during recovery of the pulping chemicals. The kraft method is widely used because it rapidly separates the wood components, can utilize different types of wood, produces a strong pulp for paper manufacture, and has low chemical costs.

However, the kraft process also has a number of shortcomings. The pulp yield is relatively low and the pulp is highly colored, requiring extensive bleaching. The sodium sulfide contributes to the odor given off from kraft pulp mills. Plus, mandatory environmental safeguards and recovery of the pulping chemicals requires high capital investment.

A possible solution to several of these disadvantages was discovered in 1977 with the report that adding small amounts of anthraquinone (AQ) significantly improves the efficiency of the pulping process (2). This discovery has since become one of the most widely studied effects in paper chemistry (3). Many advantages of adding AQ to pulping processes have been reported:

- The rate of separation increases. This can result in either a faster rate of pulp production with the same amount of pulping chemicals used or lower chemical use at the same rate of production.
- The effects of AQ are seen with very low amounts. A significant increase in component separation occurs with as little as 0.01 percent by weight (based on the starting weight of the wood) of added AQ (4).

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An effect has even been observed when waste streams from AQ-catalyzed pulping reactions are recycled into subsequent pulping runs (5).

- Kraft pulp is bleached to remove residual lignin not separated during initial pulping. AQ has been suggested as a key component in the development of new processes that pulp wood for longer periods of time to remove greater amounts of lignin. In the past, such processes resulted in unacceptable decreases in the yield and strength of the pulp. In the presence of AQ, however, yield and strength are maintained even during long-term pulping runs. These new processes decrease the amount of residual lignin in the pulp and, thus, reduce the amount of bleaching needed to obtain a bright, white pulp (6).
- Kraft pulping currently uses relatively high levels of sodium sulfide. AQ can replace sodium sulfide and facilitate an evolution from high-sulfur (kraft) to low- or nonsulfur processes. Nonsulfur pulping does not have the bad odors associated with kraft pulping. The disadvantage of nonsulfur/AQ pulping is that pulp strength is reportedly lower than for simple kraft pulping. However, recent research aims to overcome this disadvantage (7).

All of these advantages may not occur simultaneously, but they can provide economic benefits to mill operators and lessen the potential for air and water pollution (3).

Making AQ From Lignin

Despite the reported advantages of AQ-catalyzed pulping, the current cost of AQ, which ranges from \$4.00 to \$4.50 per pound, hinders its general use, except under certain circumstances. For example, where wood costs are high, such as in Japan, pulping yields take on greater importance and AQ-type processes are common. As part of the NREL-IPST program, scientists have been investigating ways to prepare AQ or AQ-like pulping catalysts at a cost low enough to make it attractive for general industry use and have found lignin to be a suitable starting material (8-10).

Lignin has a number of attractive features as a raw material for AQ production. It is inexpensive (3 to 4 cents per pound when used for fuel) and is readily available as a byproduct from the paper industry. A variety of different lignin sources are available. The NREL-IPST effort is directed primarily at converting lignin from the kraft process to pulping catalysts because it is the dominant U.S. technology. The program also is investigating the use of organosolv lignin (lignin separated from wood using organic solvents) as a starting material, because it exhibits some chemical-property advantages over kraft lignin. However, its availability is much lower than kraft lignin.

The research, supported by the U.S. Department of Energy's Office of Industrial Technologies, focuses on both the scientific and economic aspects of commercializing a process that uses lignin as a feedstock. Since its inception, the program has been driven by three key factors: the process must be inexpensive, environmentally benign, and fit well with existing pulping technology. The NREL-IPST approach to the synthesis of pulping catalysts from lignin is divided into two stages: lignin processing and chemical processing.

The lignin processing stage involves selectively isolating a low-molecular-weight (LMW) fraction from lignin (11). In theory, whole lignin could be used directly in the subsequent chemical-processing stage. However, chemical reactions occur within the lignin component during and after pulping that result in a mixture of polymeric and oligomeric materials of widely differing molecular weights. From an economic perspective, using whole lignin is unattractive because it would increase chemical costs (12). It would also be difficult from an operational standpoint because of the heterogeneity of the mixture. Therefore, LMW lignins are isolated to serve as starting materials. Two methods for separating this LMW fraction have been evaluated: extraction using conventional solvents and extraction using supercritical carbon dioxide in the presence of small amounts of organic solvents (13).

The second stage of the process, chemical processing of the LMW fraction, involves two steps. First, the LMW lignin is oxidized to give a mixture of benzoquinones (intermediate chemicals whose structure makes up the core of AQ). Second, the benzoquinones are converted to pulping catalysts by adding chemicals with the appropriate number of carbons. AQ-like materials are formed during the second reaction, but the final product is a mixture of different compounds that show activity as pulping catalysts. For example, isoprene is used in the reaction because the AQ derivative obtained, dimethylantraquinone, has been shown to be twice as active as AQ in pulping studies.

Three Base Cases Were Analyzed

A key aspect of the NREL-IPST program is an ongoing technoeconomic evaluation of the various stages of the process. Three base-case scenarios were prepared as a starting point for the analysis. Two were based on the use of kraft lignin as a starting material and one was based on organosolv lignin. Once the base cases were established, it became possible to ask various "what-if" questions and probe the sensitivity of production costs as a function of different operating parameters.

The primary difference among the cases is in the lignin processing stage. In the first kraft case, LMW lignin is

isolated and then converted to pulping catalysts as outlined above. The second kraft-based approach modifies the first by eliminating the isolation of a LMW lignin fraction. Instead, the lignin is converted using known commercial technology to a crude mixture of two known compounds, vanillin and syringaldehyde (V/S). The V/S mixture is then treated with the same two-step chemical processing sequence as the first base case. This approach was evaluated because laboratory results indicated that V/S could be converted to benzoquinone more efficiently than LMW lignin. However, producing vanillin from lignin is a low-yield, expensive process that takes place under severe conditions. This base case probes whether the lower efficiency in the V/S production step can be offset by greater efficiency in the conversion to pulping catalyst.

The organosolv case uses lignin produced by solvent fractionation of lignocellulose, followed by the two-step chemical conversion into pulping catalysts. Isolating a LMW fraction is not necessary in this case because organosolv lignin tends to be lower in molecular weight than kraft lignin.

The analysis, which is commonly known as preliminary chemical-process design, involves a number of steps:

- Drawing a flow diagram for each base case,
- Calculating the material balance,
- Calculating the energy balance,
- Estimating equipment sizes,
- Estimating capital costs,
- Estimating operating costs,
- Evaluating the economics and potential profitability,
- Defining and evaluating variations of the base cases, and
- Developing conclusions and recommendations.

The degree of detail in each step can vary considerably, usually depending on the availability and quality of basic process-chemistry information. Approximate, short-cut design and costing methods are used because they conserve time and are more than adequate to identify areas for further research or more detailed calculations.

Results Favor Processes That Use Non-V/S Kraft Lignin and Organosolv Lignin

The initial evaluation of the three base cases was performed using several key technical assumptions (table B-1), which are based on small-scale laboratory research. The analysis, conducted Arthur J. Power and Associates, was based on a hypothetical, new production plant and facilities located in the southeastern United States during the third quarter of 1994, which could produce 19.3 million pounds of pulping catalysts per year. Capital costs were based on process design, material and energy balances, and major equipment specifications. Raw

material and operating costs were based on technical specifications and current input costs.

The initial economic evaluation gave several interesting conclusions. First, the base case producing pulping catalysts from an intermediate V/S mixture did not compare favorably with the other two processes, because of a high projected amortized production cost of slightly greater than \$4 per pound (figure B-1). In contrast, both the kraft case (without the intermediate V/S step) and the organosolv case appear viable, with amortized production costs of \$1.24 and 79 cents per pound, respectively (tables B-2 and B-3).

An analysis was also made of competing methods that could be used to make AQ to see how a lignin-based route would fit into the market. Five petrochemical-based processes--using styrene, naphthalene, benzene, phthalic anhydride, and anthracene--were identified from the open and patent literature. All five are, or have been, used for commercial AQ synthesis and were judged to be the most serious competitors to the lignin-based process. The analysis calculated total raw material costs for each process, with estimated values for utilities, operating costs, and capital charges based on similar processes. The usual detailed work on preliminary process designs, capital and operating cost estimates, and profitability calculations was not done. The approximate results, however, are good enough to rank the processes on potential sales price (figure B-2). The lignin-to-AQ route was potentially the most cost effective of all those analyzed.

Further Technical Refinements Yield Additional Progress

A number of lignin processing techniques to separate the LMW fractions have been examined. Recent results indicate that simple solvent extraction of either kraft or organosolv lignin provides significant amounts of LMW material that can be converted to benzoquinones in the chemical processing stage. Supercritical fluid extraction, using carbon dioxide and a small amount of organic solvent, has been used to remove LMW lignin from pulping liquor (13). While the selectivity for LMW lignin was good, the yield was low.

A number of oxidizing agents have been studied for use in the first step of the chemical processing stage. Initially, hydrogen peroxide was examined. It has a number of attractive features; it is inexpensive, environmentally benign, and well established in the chemical and paper industries. However, early research generated low yields of benzoquinones. In contrast, more recent work indicates that both kraft LMW and organosolv lignin can be oxidized to benzoquinones using hydrogen peroxide and a catalyst.

Table B-1--Technical assumptions used for evaluating the three base cases

Case		
Kraft lignin	Kraft lignin through V/S intermediates	Organosolv lignin
Lignin supplied from seven kraft mills that have a pulp output of 1,500 tons per day. Ten percent of the lignin fraction was diverted from fuel use to production of pulping catalysts. ¹	Lignin supplied from seven kraft mills that have a pulp output of 1,500 tons per day. Ten percent of the lignin fraction was diverted from fuel use to production of pulping catalysts. ¹	Lignin collected as part of normal pulping operation
	V/S produced in 15 percent chemical yield	
Oxidation to benzoquinone has 20 percent chemical yield	V/S converted to benzoquinone in 80 percent chemical yield	Oxidation to benzoquinones has 40 percent chemical yield
Isoprene reaction has 80 percent chemical yield	Isoprene reaction has 90 percent chemical yield	Isoprene reaction has 50 percent chemical yield

¹Diverting 10 percent of the lignin fraction from fuel use will still leave enough lignin available to burn in the chemical-recovery furnace.

Figure B-1

Kraft and Organosolv Cases Appear Viable

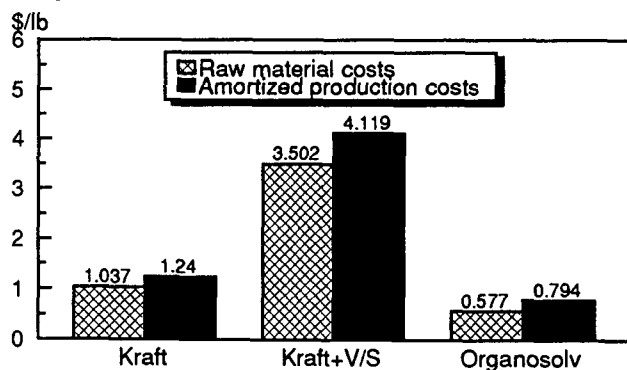
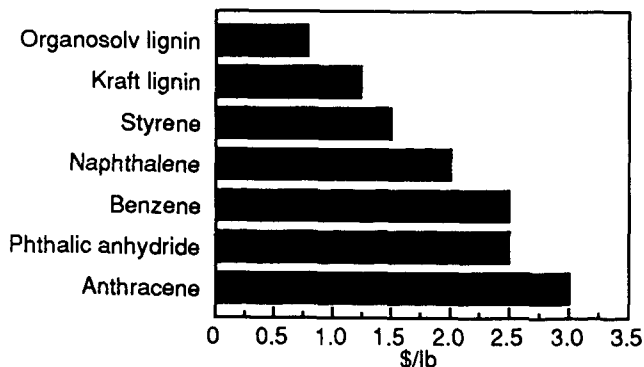


Figure B-2

Estimated Production Costs Lowest for Lignin-Based Processes



Another promising oxidizing agent is nitrogen dioxide. In the presence of oxygen, nitrogen dioxide effectively oxidizes about 60 percent of LMW hardwood lignin to benzoquinones. A third possibility was recently developed that directly oxidizes whole lignin without prior extraction of the LMW fraction. Samples of whole lignin were treated with metal salts in the presence of a base and then oxidized with nitrogen dioxide and oxygen. This increased the yield of benzoquinones. Additional research is underway to improve the method and develop milder and more efficient conditions for oxidation.

The second chemical processing step (adding isoprene) also can be improved with proper catalysts. Catalyzed reactions, as well as reactions carried out in water or mixtures of water and organic solvents, produce a number of materials, including dimethylantraquinone, with good conversion of the starting benzoquinone. Analysis of these mixtures shows the presence of up to 25 percent dimethylantraquinone.

Research Continues

The research undertaken thus far has demonstrated the feasibility of each step in the overall process under certain cost constraints on a small scale in the laboratory. The objective of present research is to develop and optimize lignin extraction and chemical conversion efficiencies to further lower the cost of pulping catalysts made from lignin. The program also is moving to demonstrate the

Table B-2--Costs of producing pulping catalysts from kraft LMW lignin in a hypothetical, new 19.3-million-pound production plant and facilities in the southeastern United States, third quarter 1994

Item	Units used per year	Cost per unit	Total annual cost	Annual cost per pound of production
	Pounds	Dollars	Thousand dollars	Dollars
Production costs:				
Raw materials--				
LMW lignin 1/	57,592,000	0.180	10,367	0.537
Methanol	13,520,000	0.100	1,352	0.070
Oxygen	1,237,000	0.025	31	0.002
Nitric oxide	3,552,000	0.300	1,066	0.055
Isoprene	25,264,000	0.285	7,200	0.373
Total raw material costs			20,015	1.037
Utilities--				
	Kilowatt hours			
Electric power	787,200	0.035	28	
	Million pounds			
Steam 2/	110,900	3.900	433	
	Million gallons			
Cooling water	1,344,000	0.060	81	
Total utility costs			542	0.028
Operating costs and expenses--				
	Workers			
Operating labor	12	28,700	344	
Foremen	4	32,500	130	
Supervisor	1	40,000	40	
Direct overhead 3/			325	
Maintenance 4/			275	
General plant overhead 5/			513	
Insurance and property taxes 6/			132	
Total operating costs and expenses			1,760	0.091
Total cash cost of production			22,317	1.156
Annual capital charges 7/			1,610	0.083
Total amortized manufacturing cost			23,927	1.240

1/ Cost of 18 cents per pound based on the fuel value of the contained organics in the kraft black liquor plus processing costs. 2/ 150 pounds-per-square-inch gauge. 3/ 45 percent of operating labor costs plus supervision (foremen and supervisor) costs. 4/ 4 percent of inside-battery-limit costs. 5/ 65 percent of operating costs. 6/ 1.5 percent of total fixed investment (\$8,794,000). 7/ 15 percent of total utilized investment (\$10,735,600) per year.

Table B-3--Costs of producing pulping catalysts from organosolv lignin in a hypothetical, new 19.3-million-pound production plant and facilities in the southeastern United States, third quarter 1994

Item	Units used per year	Cost per unit	Total annual cost	Annual cost per pound of production
	Pounds	Dollars	Thousand dollars	Dollars
Production costs:				
Raw materials--				
LMW lignin 1/	69,552,000	0.016	1,113	0.058
Methanol	16,232,000	0.100	1,623	0.084
Oxygen	1,341,000	0.025	34	0.002
Nitric oxide	3,856,000	0.300	1,157	0.060
Isoprene	25,264,000	0.285	7,200	0.373
Total raw material costs			11,127	0.577
Utilities--				
	Kilowatt hours			
Electric power	787,200	0.035	28	
	Million pounds			
Steam 2/	110,900	3.900	433	
	Million gallons			
Cooling water	1,344,000	0.060	81	
Total utility costs			542	0.028
Operating costs and expenses--				
	Workers			
Operating labor	12	28,700	344	
Foremen	4	32,500	130	
Supervisor	1	40,000	40	
Direct overhead 3/			325	
Maintenance 4/			275	
General plant overhead 5/			513	
Insurance and property taxes 6/			132	
Total operating costs and expenses			1,759	0.091
Total cash cost of production			13,427	0.696
Annual capital charges 7/			1,901	0.099
Total amortized manufacturing cost			15,329	0.794

1/ Cost of 1.6 cents per pound based on purchase of wood chips at \$60 per dry ton and sale of byproduct cellulose pulp at \$300 per ton. 2/ 150 pounds-per-square-inch gauge. 3/ 45 percent of operating labor costs plus supervision (foreman and supervisor) costs. 4/ 4 percent of inside-batter-limit costs. 5/ 65 percent of operating costs. 6/ 1.5 percent of total fixed investment (\$8,780,000). 7/ 15 percent of total utilized investment (\$12,675,000) per year.

successful results of the laboratory research on a larger scale, with the goal of producing between 1.0 and 1.5 pounds of an active pulping catalyst mixture. An important component of the near-term work will be testing the catalyst mixtures under actual pulping conditions.

Preparation of AQ and other pulping catalysts from lignin looks to be a promising new direction for lignin use. However, it is only one possible material that potentially can be produced from lignin. In the future, the NREL-IPST program may be expanded to evaluate the production of other lignin-derived, high-value chemicals.

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