[CONTRIBUTION FROM LIGNIN AND CELLULOSE RESEARCH, UNIVERSITY OF WASHINGTON]

Electrolytic Oxidation of Lignin

BY A. BAILEY AND H. M. BROOKS

Electrolytic oxidation of lignin produced a high yield of products susceptible to separation and identification. The reaction is significant since the yield of products is about double that of any previously known lignin reaction. The objectives of the study were to investigate the behavior of lignin in electrolytic oxidation and reduction, to determine what yields of products might be formed, to identify specific compounds produced, and to consider their possible significance in relation to lignin constitution.

Results

The following compounds were identified, in the yields noted, from the oxidation of butanol lignin at a lead cathode with a current density of 2 amperes per square decimeter with sodium hydroxide electrolyte.

Methyl ethyl ketone	23.3%
Acetone	15.2
Acetic acid	15.1
β-Resorcylic acid	7.8
Protocatechuic acid	7.6
p-Hydroxybenzoic acid	4.2
m-Toluic acid	3.9
Oxalic acid	3.1
Isobutyl methyl ketone	1.4
	81.6%

The highest yield of reduction products was about 20% although this value is not believed to represent a maximum of what might be obtained. This yield was obtained at a mercury cathode in about thirty-six hours and at a platinum cathode in a slightly longer time. The reduction products have not been fractioned and identified.

Four different lignin preparations were employed: a commercial sulfite waste liquor from western hemlock, an alkali lignin from mixed hardwoods, butanol lignin from western hemlock and methylated butanol lignin from the same source. Higher yields were obtained from the butanol lignin than from the other materials. Only the oxidation products of butanol lignin have bee identified.

Electrodes of lead, cadmium, platinum and mercury were investigated. A lead anode and a mercury cathode gave the highest yields.

The effect of a variation of e. m. f. of from 20 to 300 volts was studied. Electrolysis at high voltage is of great interest but requires further work on cell design and other features to permit control of foaming, overheating, and related problems. High voltage oxidation and reduction of lignin both depend upon a more capacious system of cooling than that employed in this study and, in addition, an effective means of eliminating foaming. Variation in anode current density from 1 to 3 amperes per square decimeter had little effect on yield and a directly inverse effect on time of reaction. At 300 volts, the temperature of the anolyte varied from 85 to 100° and the catholyte from 25 to 35°.

Reaction time was varied from twelve to ninety-six hours. Generally, anolytes became straw-colored or colorless in forty-eight hours at 60 volts and 3 amperes at a lead electrode and the catholytes in about thirty-six hours at a mercury electrode. In oxidation, the lignin was converted completely to water-soluble products, no residue was recovered upon acidification. Ether, benzene, carbon tetrachloride and chloroform failed to extract the water-soluble material completely. When extracted they were soluble in alcohol, acetone and dioxane. In reduction, the solution became light-colored and products amounting to about one fifth of the lignin were removed by appropriate solvents while substantially all of the remainder was recovered as a light tan precipitate.

An immiscible solvent was floated on the anolyte in certain oxidations to determine whether the soluble products could be protected from reoxidation. The presence of the solvent had no effect on the yield.

Reduction of butanol lignin for forty-eight hours followed by oxidation for forty-eight hours cut the yield of products in half. Reversal of the current at 20 second intervals and at 120 reversals per second (60 cycles, A. C.) produced no superior results.

Lignin was not oxidized to carbon dioxide by the process since very little carbon dioxide was evolved upon acidification of the anolytes.

Electrode efficiency was estimated to be low, although it was not considered of sufficient value nor within the scope of the present investigation to determine these efficiencies.

Both electrolytic oxidation and reduction offer unique and powerful means of *selective* oxidation and reduction by choice of appropriate anode and cathode, electrolyte, current density, temperature and similar advantages to which the process is heir. Electrolytic oxidation has the important merit, unlike inorganic oxidants, of permitting the oxidation to stop at intermediate levels, without the invariable result of obtaining a final reaction mixture consisting of unchanged lignin and carbon dioxide. The selectivity of the electrolytic reactions and the means of control available should provide an adequate basis for obtaining many intermediate oxidation and reduction products with important constitutional significance. The constitutional significance of the results obtained in this investigation is under consideration.

Experimental

Numerous variations of procedure were employed but the following is cited as typical. The electrolysis cell was constructed of 3-inch Pyrex piping.[1] The assembled, 3-compartment cell consisted of two 90° L's for ends, connected by a T. The 3 compartments were assembled with the usual gaskets and metal joint flanges, and with the compartments separated by a membrane of parchment paper. During reaction, the entire cell assembly was immersed in running water to control temperature and both anolyte and catholyte were stirred vigorously. The anode consisted of 99.9% pure lead sheet 6 × 70 × 100 mm. The cathode was a pool of mercury in a beaker 50-mm. in diameter. The distance from anode center to cathode center was about 52 cm.

Twenty grams of dry butanol lignin[2] from western hemlock (*Tsuga heterophylla* Sarg.) was dissolved in 1500 ml. of 1% sodium hydroxide solution. Half of this solution was placed in the anode compartment and half in the cathode compartment. The center compartment was filled to the same level with 1% sodium hydroxide solution.

An e. m. f. of 60 volts was applied which caused a passage of 3 amperes. As the current increased, a small amount of solution from the center compartment was withdrawn and replaced with water, maintaining the current approximately constant at 3 amperes. The center compartment served the important functions of controlling current, preventing undue heating, preventing foaming and providing a visual check on undesirable migration. The temperature of the electrolyte was 30 to 35°, and the time of electrolysis was forty-eight hours. Both anolyte and catholyte became straw-colored in this time, the latter more rapidly, and produced maximum yields of products.

Anolytes and catholytes were acidified and extracted with ether, the volume of each reduced under a 34-plate column, re-extracted, and rough yields determined. The aqueous solution of anolyte was then evaporated to dryness and the solids left were extracted with acetone. Eight or ten cycles of grinding the solids and re-extracting with acetone were necessary to recover all soluble material.

Anolyte–ether extracts from a number of identical electrolyses were combined and fractioned directly (without bicarbonate extraction, etc.) in efficient columns of small size of the helices and twisted-screen types. Low pressure distillation was employed on fractions not sufficiently volatile to ascend the columns. Molecular distillation was used on the fractions of lowest volatility. A pressure of 10^{-6} mm. of mercury at the distilling gap was established by means of a three-stage, four-compartment oil diffusion pump using Octoil-S. Anolyte–acetone extracts were treated separately and similarly.

Identification of Products

1. **Ethyl Methyl Ketone.**—The 2,4-dinitrophenylhydrazone melted at 113.1° and the semicarbazone at 134.3°.
2. **Acetone.**—The 2,4-dinitrophenylhydrazone melted at 126° and the *p*-nitrophenylhydrazone at 147.2°.
3. **Acetic Acid.**—The *p*-nitrobenzyl ester melted at 75–76° and the *p*-phenylphenacyl ester at 109.5°.
4. **β-Resorcylic Acid.**—The *p*-nitrobenzyl ester melted at 187–188°. When methylated with dimethyl sulfate and alkali and purified, yielded acid, m. p. 106.0–106.3° (2,4-dimethoxybenzoic acid, m. p. 108°).
5. **Protocatechuic Acid.**—The *p*-nitrobenzyl ester melted at 186°, the amide at 209–210° and the anilide at 164°.
6. ***p*-Hydroxybenzoic Acid.**—The *p*-nitrobenzyl ester melted at 180–181° and the *p*-phenylphenacyl ester at 238.5°.
7. ***m*-Toluic Acid.**—The S-benzylthiuronium ester melted at 162.6° and the *p*-bromophenacyl ester at 107°.
8. **Oxalic Acid.**—Sublimed below 100°, the *p*-phenylphenacyl ester melted at 164° and the S-benzylthiuronium ester at 192–193°.
9. **Isobutyl Methyl Ketone.**—The semicarbazone melted at 130.0–130.5° and the 2,4-dinitrophenylhydrazone at 131°.

Summary

Lignin was electrolytically oxidized and reduced. Oxidation products were obtained in good yield and identified as ketones and acids.

SEATTLE 5, WASHINGTON RECEIVED SEPTEMBER 24, 1945

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(1) Corning Glass Works, Pyrex Brand Piping and Heat Exchangers, Bulletin 814, Corning, N. Y., 1940.

(2) A. Bailey, *Paper Trade J.*, **111**, 63–6 (1940); *Tech. Assoc. Papers*, **24**, 608–11 (1941), entitled "Preparation and Properties of Butanol Lignin."

[CONTRIBUTION FROM THE MINER LABORATORIES]

Diglycerol by a New Ether Synthesis[1]

BY H. J. WRIGHT[2] AND R. N. DU PUIS

Diglycerol has been prepared by a new series of reactions between glycerol, calcium hydroxide or calcium oxide, and carbon dioxide. The course of these reactions, which may be carried out to yield diglycerol with substantial absence of higher polyglycerols, has not been definitely established. Theories concerning the mechanism of the reactions have been devised from experimental data and are presented in the following discussion.

The reactions between an alcohol, calcium oxide or calcium hydroxide, and carbon dioxide to yield the ether of the alcohol have never been reported in the literature so far as we are aware. It was thought, therefore, that although such a reaction has been applied only to glycerol in the Laboratory and the data are admittedly incomplete, publication of the procedures used and results obtained might be of interest to workers in related fields.

Reactions between glycerol and calcium hydroxide to form calcium glyceroxides have been studied previously.[3,4] Briefly, it has been found that heating calcium oxide or calcium hydroxide with glycerol results in formation of calcium monoglyceroxide, I, $Ca[C_3H_5(OH)O_2]$ or calcium diglyceroxide, II, $Ca[C_3H_5(OH)_2O]_2$ and water.

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(1) This research was sponsored by the Association of American Soap and Glycerine Producers, Inc.

(2) Present address: 700 Desnoyer Street, Kaukauna, Wisconsin.

(3) Grün and Bockisch, *Ber.*, **41**, 3476 (1908).

(4) Wheeler, *Chem. News*, **142**, 241–243 (1931).