

creases. When, however, the amide has all been converted into a cation the velocity should decrease at the same rate as the power of activity of water or the ratio of K to the activity function of water should remain a constant. Unfortunately, the data on velocities beyond the maximum are very meager. Benrath studied the action of hydrochloric acid on acetamide up to 6 N or 6.75 molal and we studied sulfuric acid on propionamide to 11.2 molal. Table IX shows the ratio of the velocity constants to the square of the activity of water.

The constancy of the ratio of the rate constant to the square of the activity of water is striking and indicates that there may be two molecules of water involved in the hydrolysis of the amide cation. It is necessary to have more experimental data to establish definitely this point of view.

We are extending the investigation to include: (1) the action of nitrous acid on amides with varying mineral acid concentrations; (2) the hydrolysis of disubstituted amides; (3) the hydrolysis of acetamide with varying activities of water.

Summary

A study has been made of the hydrolysis of formamide, acetamide and propionamide under the influence of high concentrations of hydrochloric acid and of sulfuric acid.

Each amide has a maximum velocity of hydrolysis at one particular acid concentration. This acid concentration is not the same for both hydrochloric acid and sulfuric acid nor is it the same for different amides. The molality of hydrochloric acid is higher at maximum velocity than for sulfuric acid.

The maximum velocity is reached at about the same acidity for both acids irrespective of the amide. Formamide, however, required a higher acidity than acetamide or propionamide.

Various explanations for the maximum velocity are discussed. A new suggestion has been put forward, namely, that the decrease in the activity of water accounts for the decrease in the velocity of hydrolysis at the higher acid concentration.

HARTFORD, CONN.

RECEIVED OCTOBER 17, 1938

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,⁴ FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

The Microstructure and the Diffraction Pattern of Basswood Ash¹

BY E. A. PARKER,² W. E. PATZER³ AND GEO. J. RITTER³

In the burning of wood to ash it was found that an ash residue retaining the fine structure of the original wood could be obtained by carefully controlling a current of oxygen-ozone in the furnace.

Ash residues were prepared from basswood cross sections for determining the microstructure of the ash and the location of the ash-forming constituents. Ash retaining the structure of wood cubes was also made for comparison of its crystalline arrangement with that of ash from wood sawdust. Further, ash was prepared from acid-hydrolyzed wood sections to determine whether the hydrolysis affected the microstructure of the ash constituents.

Previous workers had made ash from thin wood sections in air at glowing furnace temperatures.

Brown⁵ believed the ash contained considerable siliceous material in the form of rodlike structures arranged parallel with the fibers. The ash structure was similar to that photographed by Ritter.⁶ Uber and Goodspeed^{7,8} concluded that the ash-forming constituents were distributed throughout the cell wall, but doubted their existence in the middle lamella.

Experimental

Microstructure of the Ash.—Wood specimens in the present study were burned carefully in a slow current of oxygen containing a small percentage of ozone which was generated by an ozonizer connected with the furnace (Fig. 1). The gas mixture was brought in direct contact with the specimen in the furnace, which was electrically heated to 300 to 325°. Excessive shrinkage of the thin wood sections during the burning was prevented by mounting each specimen on a glass object slide by means of a

(1) Presented before the Division of Cellulose Chemistry, American Chemical Society, Milwaukee, Wis., September 5-9, 1938.

(2) University of Illinois, Urbana, Illinois.

(3) Forest Products Laboratory, Madison, Wis.

(4) Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

(5) F. Brown, *Bull. Torrey Bot. Club*, **47**, 407 (1920).

(6) Geo. J. Ritter, *Rayon and Melland Textile Monthly*, **16**, [9] 98-100; [10] 58-60 (1935).

(7) F. M. Uber and T. H. Goodspeed, *Proc. Nat. Acad. Sci.*, **21**, 428 (1935).

(8) F. M. Uber and T. H. Goodspeed, *ibid.*, **22**, 463 (1936).

drop of oil consisting of equal parts of ash-free linseed oil and turpentine. The oil was then hardened in a current of the oxygen-ozone at room temperature so as to hold the specimen in place.

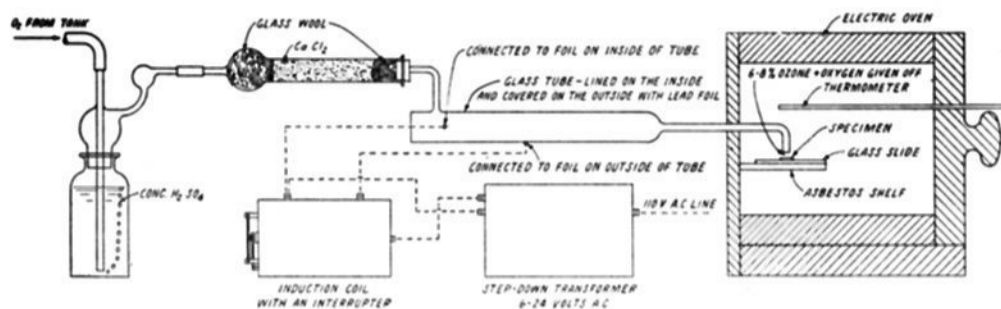
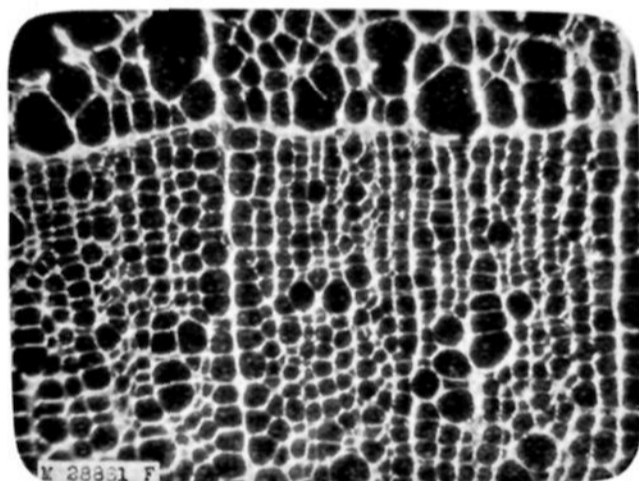


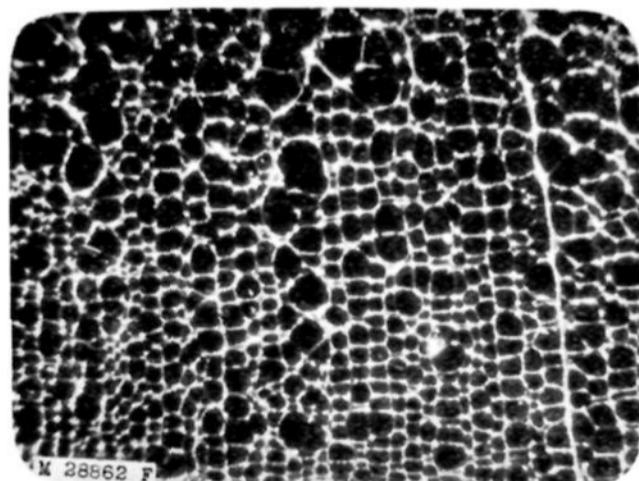
Fig. 1.—A diagram of apparatus used for ashing wood samples.

The ash from a transverse wood section 5 to 10 microns thick retained a pattern of the wood except for having thinner walls (Fig. 2a).

The ash residue from a cross section of wood treated with 35% hydrofluoric acid at 20° for seven days, then with boiling 3.0% hydrochloric acid for three hours, and finally washed with water also produced an intact pattern of the wood (Fig. 2b). Its walls were slightly thinner than those of the ash from the wood having had no acid treatment previous to burning.



(a) Ash residue from an untreated wood section (approximately 87 X).



(b) Ash residue from wood previously treated with hydrofluoric acid, hydrochloric acid and water (approximately 87 X).

Fig. 2.—Ash residues from transverse sections of wood.

The ash-forming constituents in wood appeared to be located throughout the cell wall. Although the walls of the final ash residue were thinner than those of the wood, microscopical examinations of cross sections in different

stages of burning showed a white ash residue on the surface of the entire cell wall. As the burning proceeded to completion, the ash in the secondary wall apparently shrank toward the primary wall.

When cross sections of wood 10 microns thick were burned, occasional checks were observed between some of the adjacent walls of the ash, whereas numerous checks were observed between the walls of the

ash from wood sections 5 microns thick. The numerous checks in the thinner sections confirmed the results noted by Uber and Goodspeed,⁸ whose work was confined to the thinner type of wood specimens. The many checks in the ash suggested to them that possibly no ash-forming constituents are located in the middle lamella. However, the contrast between the number of checks in the ash from the thin and the thicker wood specimens, as observed in the present study, indicates that the checks were caused by mechanical means during the sectioning of the specimens and that they became prominent during the subsequent ashing procedure.

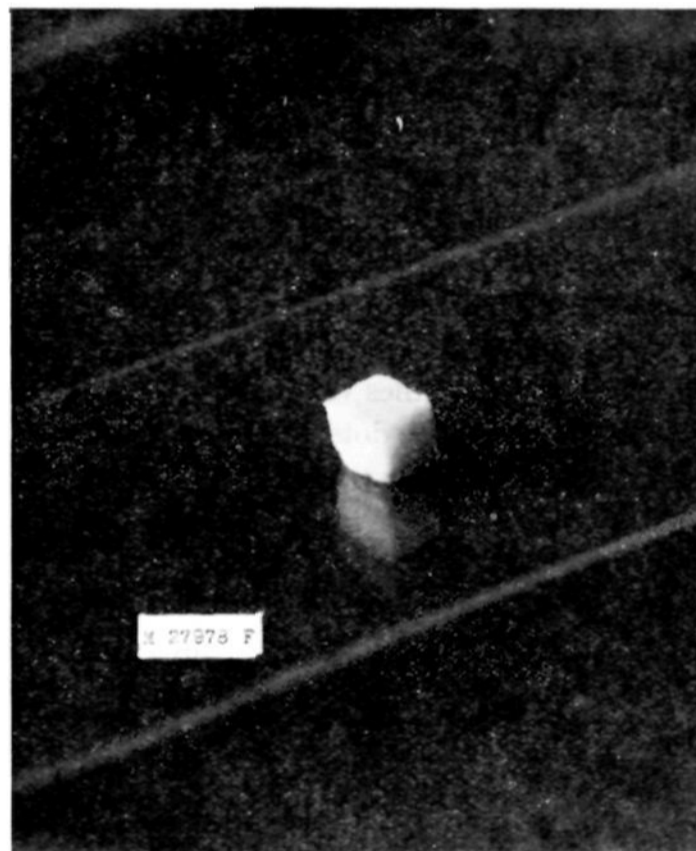


Fig. 3.—Ash residue from a wood cube.

Crystal Arrangement of the Ash.—The well-preserved structure of the ash obtained from a wood cube 3 mm. on edge (Fig. 3), suggested that the crystalline ash constituents might have a preferred orientation. Accordingly, a photographic pattern of the ash cube was made by

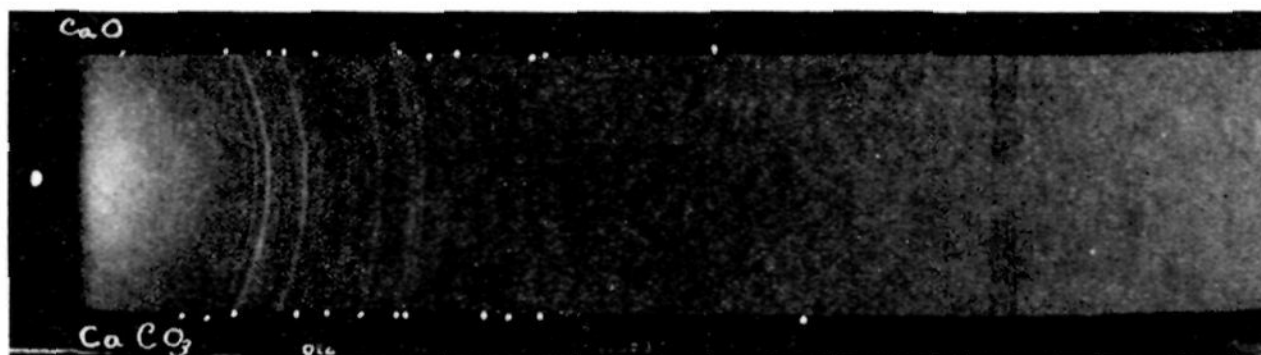


Fig. 4.—Diffraction pattern produced by ash from basswood sawdust. Lines produced by calcium oxide checked at top of pattern; lines produced by calcium carbonate checked at bottom of pattern.

passing an X-ray beam through the block perpendicular to the long axis of the fibers. The diffraction pattern, which was recorded on a flat film, indicated random arrangement of the ash crystals, the same as the arrangement of ash from sawdust of the same wood sample.

In order to facilitate the identification of the ash constituents recorded on the film, an X-ray pattern was made under the conditions employed for making reference patterns of known compounds. In this case a circular camera having a 6.4 cm. radius was used in conjunction with a fine-structure tube having a copper target, operating on 36 p. k. v. and 23 m. a. The pattern (Fig. 4) obtained under these conditions was compared with reference patterns of constituents found, in general, in wood ash. The comparison indicated that the oxide and the carbonate of calcium produced all the lines recorded. The oxide lines are checked on the top and the carbonate lines on the bottom of Fig. 4 by means of the white dots.

Why other ash constituents are not recorded on the pattern is not known. One reason advanced is that any ash constituent, other than the two of calcium, is present in too small a percentage to produce diffraction lines. Another reason is that the lattice spacing of some of the constituents might have been destroyed by a partial fusing during the preparation of the ash.

We offer these reasons with no definite proof of their accuracy.

Summary

The ash residue obtained from the burning of wood forms intact skeletons of the original wood. An ash residue of a transverse wood section has walls considerably thinner than those of the original wood section. As the organic material of the cell wall burns, a lateral shrinkage of the ash cell wall occurs, the ash in the secondary layer being drawn toward the middle lamella.

It is believed that the occasional checks between two adjacent cell walls of the ash are caused by the sectioning of the wood and are no indication of the absence of ash in the middle lamella.

Ash residues from transverse wood sections indicate that the ash-forming minerals in wood are located in both the cell wall and the middle lamella.

Small blocks of the ash residue retain the shape of the original wood.

X-ray diffraction patterns of ash cubes indicate a random arrangement of the ash crystals.

By a comparison of the diffraction pattern of the ash with those of known compounds, it has been shown definitely that the carbonate and the oxide of calcium produced the only visible diffraction lines.

MADISON, WISCONSIN

RECEIVED OCTOBER 17, 1938