TABLE I—AVERAGE RESULTS OF TESTS ON VARIOUS WASTE WOODS BY DESTRUCTIVE DISTILLATION

WOOD MATERIAL TESTED	Av. wt. of measured cord Lbs.	Turpentine and light oil Gal.	Tar Gal.	Wood alcohol Gal.	Acetate of lime Lbs.	Char- coal Lbs.	Gas Cu. ft.
Douglas fir common run mill waste	3,330(a)	3.40	27.80	3.90	75.0	977	...
Douglas fir selected mill waste	4,250(b)	10.86	46.37	3.71	74.3	900	...
Douglas fir common run stump wood	3,260(b)	3.59	19.88	2.60	55.8	675	6,270
Western yellow pine common run mill waste	2,840(b)	4.91	24.80	3.25	73.4	478	6,120
Western yellow pine common run stump wood	2,620(b)	6.06	23.05	1.83	60.8	520	3,950
Western hemlock common run mill waste	3,270(c)	2.76	21.60	5.00	94.0	938	...

(a) Based on 15 half-cords.

(b) Based on 4 half-cords.

(c) Based on 5 half-cords.

larger pieces. The roots constitute 10 to 20 per cent of the total, and are for the most part rotten, except in the interior, which, in many cases, is hard and resinous. Only two of the stumps showed signs of pitch on the outside. The stumps were taken just as they occurred in the clearing of logged-off lands, and were strictly unselected, being an average sample of the common run of pine stumps for the Eastern part of the State of Washington.

WESTERN HEMLOCK COMMON RUN MILL WASTE

This material consisted chiefly of slabs, and some edgings and inside wood. It was obtained in the same manner as the Douglas fir common run mill waste.

DISCUSSION OF RESULTS

The results of the runs on the various woods are given in Table I; they show that the heaviest material is Douglas fir selected mill waste, and the lightest, Western yellow pine common run stumps. This difference is due chiefly to the fact that the former consists mostly of inside wood piled up closely with a small percentage of voids, whereas the stump wood can be piled, even after cutting into 2-ft. lengths, in a very irregular manner, with a large percentage of voids. The common run mill waste from the Douglas fir and the Western hemlock is several hundred pounds heavier than the similar material from Western yellow pine. Likewise the fir stumps are heavier than the pine stumps. In this connection it should be remembered that the yields given in Table I are based on the measured cord, as this is the method employed in the ordinary commercial handling of wood, and moreover, as it is this volume factor which limits the capacity of any distillation apparatus.

The yields of gas are available only in three cases, the greatest being for Douglas fir stumps. Although Douglas fir and hemlock mill waste were not tested for the yield of gas, it is possible that the yield may be higher in these cases than those recorded, as it is seen that the yield from the mill waste in the case of the pine is greater than that from the stumps.

CONCLUSIONS

None of the classes of the materials tested gave a higher yield of *all* the by-products than any other class of raw material. The question of *which is the most suitable class of material for distillation*, therefore, limits itself to a function of the market values of the respective by-products, the cost of obtaining the raw material, and the operating expenses.

Although one set of conditions might favor the use of one class of material to the exclusion of all others, still, conditions, such as the cost of raw material, market for charcoal, etc., might be so changed as to reverse this.

Under the present conditions, unless other factors enter into the consideration, such as the increased value of the land, due to the removal of the stumps, the order of commercial suitability for distillation is somewhat as follows:

- 1—Douglas fir selected mill waste
- 2—Douglas fir common run mill waste
- 3—Western hemlock common run mill waste
- 4—Western yellow pine common run mill waste
- 5—Western yellow pine common run stump wood
- 6—Douglas fir common run stump wood

A change in the market conditions, especially for charcoal, or a possible sale of the gas, or a possible utilization of the pyro-

lignous acid for the production of acetone,¹ or a change in the cost of raw material, may greatly change the order of the commercial value. The value of the Douglas fir selected mill waste, however, is so far advanced over that for the other raw materials tested that there is little doubt it is the most suitable for distillation.

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THE USE OF AMMONIUM HYDROXIDE FOR THE EXTRACTION OF ROSIN FROM WOOD

By H. K. BENSON AND HERBERT N. CRITES

The extraction of rosin from "light wood" in the Southern States is accomplished by first steaming the chips, next covering them with a petroleum distillate, reheating until the distillate begins to vaporize, and then withdrawing the solution of rosin. By subjecting this solution to re-distillation, the solvent is recovered first, and finally the turpentine and pine oil, leaving the rosin as a residue. The main difficulty with this method is the loss of solvent in the cycle, which, according to operators, is as high as 50 gallons per cord of wood extracted.

Various plans have been suggested to overcome this loss. Clapé proposes to use² the volatile distillate boiling between 170 and 185° C. obtained from the steaming of wood, as a solvent for rosin. The loss of this solvent is reported at less than 6 gallons per cord of wood extracted, and as it is being constantly produced in the process, no additions from external sources need be supplied. This solvent is, however, a fraction of turpentine generally permissible in commercial grades. It consequently diminishes the yield of turpentine per cord of wood, incurring a financial loss equal to or greater than that prevailing with the petroleum solvent.

To a limited extent a hot bath of some non-volatile or high-boiling material, such as molten rosin, pine tar, pine oil, etc., has been employed but has been abandoned by the commercial plants in which it had been attempted. Recently the use of alkalies such as caustic soda or soda ash has been suggested³ for the extraction of rosin. The alkali combines with the rosin acids and forms a soluble rosin soap while the turpentine and pine oil may be removed from the solution by distillation with steam. The difficulty in this method lies in the form in which rosin is finally recovered, *i. e.*, as a soap, for which apparently no great demand exists as obtained from wood by this process.

The present investigation was based upon two facts: (1) the instability of ammonium salts when heated, and (2) the completeness of recovery of ammonia as commercially carried on in the coal gas plants of this country.

EXPERIMENTAL

Powdered rosin was added to a 25 per cent solution of warm ammonium hydroxide and formed a thick, light yellow, translucent solution which became quite firm on cooling. It slowly decomposed while standing in the air and on adding heat, the ammonia was driven off, leaving rosin as a residue.

GENERAL METHOD OF PROCEDURE

The next step consisted in the use of resinous fir wood containing from 20 to 30 per cent rosin. The wood was used in

¹ THIS JOURNAL, 7 (1915), 927.

² U. S. P. application, Serial No. 875,463.

³ U. S. Department of Agriculture, Bureau of Chemistry, *Bull.* 159.

the form of chips (1 in. $\times$ $\frac{1}{8}$ in. $\times$ $\frac{1}{8}$ in.), shavings, and sawdust. The general method of procedure was to cover a weighed quantity of wood with a known quantity of ammonium hydroxide. This was heated in pressure bottles to various temperatures for several hours, and while still warm the brown syrupy liquor was poured off and the wood washed with very dilute ammonium hydroxide. The combined liquors were heated, the ammonia passing off and being regained in wash bottles containing cold water. After complete evaporation, a black, tarry mass remained, which was next treated with gasoline and filtered. The filtrate is a solution of rosin while the solid matter upon

were with chips, while in 2, sawdust, and in 3, shavings were used: 25-gram samples were used in each case.

Experiments 1 and 3 show that extraction of chips and shavings is impracticable at room temperatures while sawdust can be thus extracted. While extraction was not complete in Experiments 4, 5 and 6, the latter shows that a five per cent solution of ammonium hydroxide is equally efficient as concentrated ammonium hydroxide under the same conditions. Experiment 7 was made with sodium hydroxide for comparison. The quantity of rosin extracted in this experiment was obtained by acidifying the sodium resinate solution, drying and

TABLE I—PRELIMINARY EXTRACTION EXPERIMENTS

Exp. No.	NH ₄ OH used		CONDITIONS OF EXTRACTION		WASHING		WASH LIQUOR		PER CENT ROSIN EXTRACTED	PER CENT ROSIN NOT EXTRACTED	EFFICIENCY OF ROSIN EXTRACTION PER CENT
	Per cent	Cc.	Time Hrs.	Temp. ° C.	Time	Hrs.	Vol. Cc.	Per cent NH ₄ OH in			
1	25	150	500	18	2	6	150	3	16	12	57
2	25	200	500	18	2	6	200	3	22.8	2	92
3	25	150	500	18	2	5	100	3	12	10	54.5
4	25	90	6	100	1	2	100	5	18	5.6	76
5	3	70	7	100	1	1	80	1	18	9.05	64.5
6	5	70	7	100	1	1	80	1	21.6	5.6	79.5
7 (NaOH) 2.6		90	14	100	1	1	80	0	16	1	94

TABLE II—EXTRACTION OF RESINOUS CHIPS

Exp. No.	CONDITIONS OF EXTRACTION		WASHING		WASH LIQUOR		Per cent rosin extracted in liquor		Per cent humus extracted in liquor		Per cent rosin not extracted		EFFICIENCY OF ROSIN EXTRACTION PER CENT
	Liquor used Cc.	Time Hrs.	Time	Hrs.	Vol. Cc.	Per cent NH ₄ OH in	1st	Wash	1st	Wash	1st	Wash	
1	100	3	1	3	80	5	16.9	1.5	7.7	6.9	7.4		71
2	175	8	1	3	90	1	19.7		21.0		2.2		90
3	200	6	1	3	90	1	15.8		14.9		2.0		89
4	200	5	1	3	60	1	16.4	1.0	10.4	2.2	0.8		95.6

the filter paper consists of portions of the wood which are also soluble in ammonium hydroxide and which for convenience will be designated as "humus." Upon evaporation of the gasoline, a residue of rosin of fine golden color remains. To ascertain the efficiency of extraction, the extracted chips were dried, finely ground in a Grumbaugh mill and extracted with ether in a Soxhlet apparatus.

PRELIMINARY EXPERIMENTS

In Table I are given the results obtained from the preliminary experiments. The efficiency of extraction is found by dividing

FIG. 1—EFFECT OF TEMPERATURE ON EXTRACTION

the amount of rosin extracted by the sum of the quantity extracted plus that not extracted. Owing to the manner in which rosin is distributed in Douglas fir, it is difficult to get samples with uniform rosin content. This fact accounts in part for variations in total rosin content. Experiments 1, 4, 5, 6 and 7

weighing the rosin thus obtained. Fineness of wood, higher temperatures (involving closed vessels under pressure), and sufficient volume of liquor are consequently necessary factors for efficient extraction.

EFFECT OF TEMPERATURE ON EXTRACTION

A series of seven extractions was undertaken and carried out under the same set of conditions with the exception of temperature. A concentration of 5 per cent ammonium hydroxide was used. The efficiency of extraction is shown in Fig. 1, from which it is observed that rapid extraction begins at 40° to 50° C. and reaches its maximum at 70° C.

EFFECT OF VOLUME OF LIQUOR AND TIME OF EXTRACTION

To ascertain the effect of the volume of ammonium hydroxide solution and the period of time of extraction, a number of extractions were made, the results of which are given in Table II. Twenty-five grams of chips, a 5 per cent solution of ammonium hydroxide and a temperature of 70° C. for extraction and washing were used in each case. In Experiments 2 and 3 the percentage of rosin and of humus in the wash liquor were not determined, but only the total quantity of each in the combined extraction and wash liquors.

In Experiment 1, with a short period of extraction and a small volume of extracting liquor, poor extraction was obtained. While only a small amount of rosin is obtained by washing, the quantity of humus is nearly as great as in extraction. In Experiments 2 and 3 the effect of 2 hours' heating is found to be very slight on the yield of rosin, but high on humus. Maximum rosin and minimum humus extraction are obtained in Experiment 4, in which the minimum period of heating and volume of wash liquor are employed.

USE OF HUMUS

While this investigation did not include a study of the humus, the dry powdery form in which it is separated from the rosin makes it adaptable to such uses as have been suggested by Cram¹ for the humus obtained in the soda process for wood pulp.

CONCLUSIONS

I—When resinous wood is treated with a five per cent solution of ammonium hydroxide equal to eight times the weight of the

¹ THIS JOURNAL, 6 (1914), 896.

wood at 70° C. for five hours, nearly complete extraction of rosin occurs.

II—From the general properties of ammonia and its complete recovery in gas works, it is believed that nearly complete extraction of rosin from wood may be made and complete recovery of ammonia obtained.

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DISCOLORATION OF MAPLE IN THE KILN

By ROY C. JUDD

In kiln-drying green frozen maple lumber, a brown stain or discoloration occurs unless the most favorable conditions are maintained. An investigation of the causes and of the nature of the discoloration was made. Irving W. Bailey¹ states that some sap staining is due to an enzyme. To substantiate this view, Mr. Bailey states that the action can be arrested by simply dipping the lumber in hot water.

To study the possibility that this action is due to some enzyme, such as an oxydase, several small blocks of maple were given various preliminary treatments, and then placed in an oven where the humidity exceeded 90 per cent. The temperature was maintained at 90° C. for from one to three hours. The preliminary treatments were made as follows:

- 1—Dipping in water at 90° C.
- 2—Soaking in boiling water for 1, 2, 5, 60, and 200-minute periods.
- 3—Steaming at 100° C. for 5, 60, and 200-minute periods.
- 4—Heating in a drying oven at 105° C. for 10 min., 30 min., 1 hr., 2 hrs., 10 hrs., and 20 hours.
- 5—Previous treatment with solutions of germicides:

- a—Zinc chloride
- b—Mercuric chloride
- c—Sodium fluoride
- d—Phenol
- e—Arsenious oxide
- f—Hydrogen peroxide
- g—Sodium carbonate

Discoloration appeared in every case when these samples were finally subjected to the unfavorable conditions of a warm humid atmosphere. The stain was formed on the surface first, but, on remaining for a longer period in the moist air, the stain appeared throughout the specimen. The possibility of the discoloration being caused by an enzyme was disproven because at least some of the above treatments would have destroyed the enzyme. If dipping maple in hot water prevents subsequent staining in the kiln, it is not because the enzymes are destroyed but because the heated wood dries more readily.

A series of experiments were carried on in an autoclave. Pieces of fresh green maple were given the following treatments:

- 1—Enough of a 3 per cent solution of hydrogen peroxide was added to cover the sample. The air was pumped out and the temperature of 75° C. maintained.
- 2—An atmosphere of sulfur dioxide was supplied and the temperature kept at 80° C.
- 3—An atmosphere of carbon dioxide was added and the temperature maintained at 80° C.
- 4—The air was removed and live steam passed through continuously.
- 5—An NH₄OH solution was placed in the autoclave and the air exhausted. The temperature was kept at 75° C.
- 6—A little water was added and air was left in. A temperature of 80° C. was maintained.

The duration of the above experiments was from two to four hours. The results of these experiments showed that discoloration did not appear in the presence of hydrogen peroxide, carbon dioxide, sulfur dioxide, nor with steam in the absence of air. In an atmosphere of air saturated with moisture and also

in the experiment with ammonium hydroxide, discoloration was very appreciable.

Three sets of experiments were carried on simultaneously. Pieces of maple were placed in flasks containing distilled water. Air was continuously bubbled through one and carbon dioxide and sulfur dioxide, respectively, through the other two. The initial temperature of 40° C. was maintained for one hour. Then the temperature was raised 10° at one-hour intervals till the temperature of boiling water was obtained. At the end of the process the pieces of maple in the flasks through which carbon dioxide or sulfur dioxide had been passed were even lighter colored than the original, while the maple in the flasks through which air had been passed was very badly discolored. The first evidence of discoloration appeared at about 60° C. and became more pronounced as the temperature was raised. Several experiments indicated that weak solutions of organic or mineral acids prevent discoloration. Some experiments were carried out on a small scale in laboratory drying ovens. It was found that no staining took place when the humidity of the air in immediate contact with the drying wood was kept low. The investigation seems to indicate that the staining is probably of a physical chemical nature and is independent of enzymes.

This paper is not intended to cover the subject of kiln-drying but is written for the purpose of showing that it is possible with conditions well under control to dry green maple lumber artificially and still retain its natural color. The conditions that prevail in a commercial kiln for drying lumber are not as easily controlled as those in a small laboratory apparatus. The section of timber physics in the Forest Products Laboratory has worked out its application in a dry kiln. The only available means of overcoming this difficulty in commercial practice is by the use of a low temperature (120° to 130° F.) and a low humidity (60 per cent or less) in the dry kilns. Fortunately, maple is a wood which does not check easily and hence these low humidities are quite practicable on a commercial scale.

I wish to express my appreciation of the suggestions and interest contributed by Mr. H. D. Tiemann, in Charge, Section of Timber Physics, and a specialist in kiln-drying, and Dr. S. F. Acree, Chief of the Section of Derived Products, who suggested the studies of the chemical and enzymic phases of this problem.

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MANUFACTURE OF ETHYL ALCOHOL FROM WOOD WASTE—II. THE HYDROLYSIS OF WHITE SPRUCE

By F. W. KRESSMANN

A paper¹ presented at the Forty-Ninth Meeting of this Society at Cincinnati, described (1) the scope of the work, (2) the apparatus used, (3) the method of procedure, and in addition gave the results obtained from a series of preliminary experiments on white spruce. Since the above work was done the yeasting operations and fermentation conditions have been standardized so that duplicate and comparable data have been made possible.

The yeast used is a pure culture strain of *Saccharomyces cerevisiae*, isolated from a yeast used in a Hungarian distillery, producing alcohol from beet sugar molasses. It is well adapted to the fermentation of sugar solutions obtained from the hydrolysis of wood, although the addition of nitrogenous food is necessary. This yeast nutrient is a mixture of ammonium sulfate and malt sprouts. The details of yeast propagation and the preparation of the mash for fermentation along with other details of the present work will be given later in the form of a professional paper of the United States Department of Agriculture. In all cases, 7,500 cc. of a solution having a gravity

¹ *Botanical Gazette*, 50, 142-147, No. 2, August, 1910.

¹ *THIS JOURNAL* 6 (1914), 625.