

small scale gave very poor yields of carvacrol. It is very probable, however, that satisfactory yields could be obtained from larger apparatus capable of more careful control.

CARVACROL—The calcium and barium salts of cymene sulfonic acid were made in the manner described above. The calcium salt is much more soluble than the barium. The sodium salt was prepared by decomposing a weighed amount of the barium salt with sodium carbonate in aqueous solution and evaporating to dryness after filtering off the barium carbonate.

The fusion was carried out by placing the sulfonic acid salt in a nickel dish on a sand bath and adding the alkali dissolved in a minimum amount of water, and gradually raising the temperature of the fused mass to about 300°, with constant stirring. This temperature should not be exceeded. The melt was dissolved in water, acidified, and distilled with steam. The carvacrol was extracted with ether and weighed after evaporation of the solvent. The yields of carvacrol are given in the following table:

Fusion No.	SALT Kind	Wt. Grams	ALKALI Kind	Wt. Grams	Temp. of Fusion	CARVACROL	
						Yield Gms.	% Theoretical
1	(C ₁₀ H ₁₈ .SO ₃) ₂ .Ca.2H ₂ O	10.00	KOH	30	300°	2.45	41.0
2	(C ₁₀ H ₁₈ .SO ₃) ₂ .Ca.2H ₂ O	10.00	K ₂ CO ₃	30	300°	0
3	(C ₁₀ H ₁₈ .SO ₃) ₂ .Ba.3H ₂ O	10.00	NaOH	30	350°	0
4	C ₁₀ H ₁₈ .SO ₃ .Na	7.64	KOH	30	300°	0.61	8.0
5	C ₁₀ H ₁₈ .SO ₃ .Na	7.64	NaOH	30	350°	0
6	(C ₁₀ H ₁₈ .SO ₃) ₂ .Ca.2H ₂ O	10.00	KOH	30	290°	1.10	18.4
8	C ₁₀ H ₁₈ .SO ₃ .Na	7.64	KOH	7.5	300°	0.91	18.8
9(a)	(C ₁₀ H ₁₈ .SO ₃) ₂ .Ca.2H ₂ O	10.00	KOH	8.8	300°	3.16	52.9
10(a)	(C ₁₀ H ₁₈ .SO ₃) ₂ .Ca.2H ₂ O	10.00	KOH	8.8	300°	1.68	28.9
11(a)	(C ₁₀ H ₁₈ .SO ₃) ₂ .Ca.2H ₂ O	10.00	NaOH	6.4	290°	0.74	12.4

(a) Crucible covered during the fusion.

Other fusions conducted under different conditions gave only small yields of carvacrol and served to show the great difficulty of duplicating results. This is illustrated by Fusions 9 and 10 made under identical conditions.

IDENTIFICATION OF CARVACROL—The carvacrol obtained was identified as follows: 2.5 g. of the phenol were dissolved in dilute KOH and made up to 1.5 liters. Six grams of KNO₂ were then added and after it had dissolved the solution was strongly acidified with sulfuric acid. In a short time the carvacrol nitrite rose to the surface in a flocculent condition. The nitrite crystallized very readily, using hot 50 per cent alcohol, but after several crystallizations the compound was still impure and melted at about 147°.

It was found that the nitrite was insoluble in petroleum ether and this property afforded an easy means of purification. The carvacrol nitrite was dissolved in a minimum amount of chloroform which was slowly dropped, with stirring, into a considerable volume of petroleum ether. The precipitate was finally crystallized from alcohol. The pale yellow needles melted at 153–4°. When heated slowly they melted at 150–152°.

SUMMARY

Sulfite turpentine, consisting largely of cymene, can be used for the production of carvacrol and toluene.

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THE EFFECT OF INCOMPLETE DISTILLATION ON THE YIELD OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF BIRCH

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OBJECT OF TESTS

In most hardwood distillation plants a certain amount of the wood comes out of the retorts after distillation as "brands" or "bones," that is, pieces incompletely charred. When a plant finds it necessary for economic reasons to use wood that has been insufficiently seasoned or wood excessively wet with rain or snow, it is difficult to complete the distillation in the required 24 hours. Under such conditions the amount of brands is likely to be large, amounting to as much as 8 or 10 per cent of the charge. Usually the brands are redistilled, although they are not considered as new raw material. There is no agreement among operators as to what yields are obtained by distilling the wood in two stages, that is, whether there is actually any gain or loss in products by this procedure. To the knowledge of the author, the literature reveals no data on this point. A few experiments were therefore made to determine just what effect incomplete distillation had on the yield of products in the destructive distillation of hardwood and how yields from stopping the distillation and then redistilling the residue compared with the yields from a single operation.

EXPERIMENTAL PROCEDURE

Yellow birch cord wood reduced to pieces about 2½ in. by 2½ in. by 16 in., not very well seasoned, was distilled in a semi-commercial laboratory retort holding about 50 lbs. of wood. The temperature in the empty retort was raised to about 340° C. and a specially constructed basket containing the wood was then quickly introduced. The start of the distillation was then similar to the start of a commercial distillation where a new charge is placed in a retort immediately after drawing out the hot charcoal from a run that has just been completed. The distillations were carried on according to the best practice of temperature control, that is, regulating the fire so that the rate of rise of temperature in the retort was decidedly decreased after the tar began to be formed. One run was made in which the distillation was normally carried to completion. In two other runs the fire was turned off when it was obvious from the amount of distillate, temperature, etc., that the distillation was not complete. Different stopping points were selected for the different runs. As the distillation had not reached the point of marked exothermic reaction in these runs it was checked very quickly after the fire was turned off.

After cooling to room temperature the retort was opened and all brands were separated from charcoal. Any stick which was brown in color, or which could not be readily fractured by a moderate blow with a hammer, was considered a brand. All the brands from incomplete distillations were allowed to remain out of doors during a heavy rain until they had absorbed water to about 3½ per cent of the dry weight and were then completely distilled as if they were normal wood.

The crude pyroligneous acid liquor from each run was weighed, measured and separated in a clear acid and settled tar, and the clear acid liquor was then analyzed for total acid (calculated as acetic), acetic acid, formic acid, wood alcohol and dissolved tar.

RESULTS

The results of the tests in percentage of the dry weight of wood distilled are given in Table I. Runs 2 and 3 which were made on fresh wood and Run 4 which was made on the brands obtained in Runs 2 and 3 have been combined by calculation to show the total yields obtained by the complete distillation of the original wood. The yields from this calculation and the yields from Run 1 indicate the effect of a two-stage distillation compared to a single normal operation.

TABLE I—YIELD FROM THE DISTILLATION OF BIRCHWOOD AT DIFFERENT STAGES OF COMPLETION(a)

Run No.	Char-coal	Brands	Tar		Total	Acetic Acid	Formic Acid	Wood Alcohol
			Settled	Dissolved	tar			
1 Complete distillation...	42.30	0	5.52	5.28	10.80	5.52	4.92	0.44
2 Wood incomplete.....	17.66	48.00	1.93	2.91	4.84	4.53	3.92	0.48
3 Wood incomplete.....	10.77	62.96	0.87	1.73	2.60	3.44	2.99	0.36
4 Brands from 2 and 3 completely distilled...	54.50	0	4.99	4.29	9.28	2.96	2.56	0.30
Runs 2, 3, and 4 as one run.....	44.49	0	4.17	4.69	8.86	5.59	4.86	0.59

(a) The yields are given in per cent of the dry weight of the wood or brands distilled.

As will be noted, the distillation in two steps gives from 20 to 25 per cent less tar.

The yield of acetic acid is about 2.4 per cent lower for the double operation. The total acid, calculated as acetic, is practically the same. This is due to the fact that while the acetic acid yield is somewhat lower the yield of formic acid is about 30 per cent higher for the two-step operation. The distillation in two steps gives about 4 per cent more charcoal and 2.8 per cent more alcohol. Considering all the products it is apparent that, except for the tar, there is no appreciable loss or gain in valuable products recovered when brands are redistilled.

AMOUNT AND ORDER OF FORMATION OF PRODUCTS AT DIFFERENT STAGES OF DISTILLATION

An examination of the yield data obtained by stopping the distillation in order to make brands gives an indication of the order in which the products are formed in the destructive distillation of hardwood. The yields of each product in the incomplete runs calculated in percentage of the total obtained in a single distillation are given in Table II. When the same data are shown graphically, the percentage of total production being given as one axis against the per cent of wood left as brands as the other, the results presented are of both scientific and practical interest.

TABLE II—PROPORTION OF TOTAL PRODUCTION WHEN DIFFERENT AMOUNTS OF BRANDS ARE LEFT IN THE RETORT(a)

Run No.	Char-coal	Brands	Tar		Total	Total Acid	Acetic Acid	Formic Acid	Wood Alcohol
			Settled	Dissolved					
1... 100.0	0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2... 41.75	48.00	34.9	55.1	44.8	82.0	79.7	100.0	62.8	62.8
3... 25.48	62.96	15.7	32.7	24.1	62.3	60.7	81.7	37.1	37.1

(a) The yield from a single complete distillation (Run 1) is taken as 100 per cent.

From a scientific standpoint the data are of interest in throwing some light on the order and amount of the different products formed at different stages in the

distillation. The acids are the first of the valuable products to be formed¹ and it is especially interesting to note that the formic acid is formed more rapidly than the acetic. The total amount of formic acid is obtained when more than 45 per cent of the wood is left as brands. The charcoal curve does not begin at 100 per cent brands because a stick was not considered charcoal until it had increased in carbon content to such an extent that it could be readily fractured by a moderate blow with a hammer. The tars do not begin to come over until after there is some charcoal in the retort. The dissolved tar (tar soluble in the pyroligneous acid) comes over before the oily tar which settles out of the pyroligneous acid. The wood alcohol is the last valuable product to begin to be formed but it starts just prior to the appearance of the oily tar. This fact is of special interest in view of the experiments on temperature control.² It shows why the point when settled tar begins to come is of value in determining when to begin to practice control, that is, because the alcohol precedes the tar in order of formation. It also shows why it is not detrimental to the yields to push the distillation rapidly at the start, the reason being that only a small amount of the acid and none of the alcohol is formed during the first part of the distillation.

The practical application of the curve lies in the fact that it shows the losses in valuable products when the distillation is at any degree of completion. It may be noted that even with 10 per cent brands, which may be considered the maximum usually obtained in the commercial plant, the loss of alcohol is only 5.0 per cent and acetate 2.5 per cent. The charcoal loss is, of course, high, being about 12.5 per cent.

SUMMARY

Semi-commercial laboratory distillations were made with birch in which the distillation was stopped before completion. The brands obtained were redistilled. The results showed that the combined effect of the distillation in two steps gave practically the same yields of valuable products as when the distillation was completed in one step.

Considering the maximum yield of brands allowable in a commercial plant as 10 per cent of the original charge the data show that the loss of products is only 5.0 per cent wood alcohol and 2.5 per cent acetate of lime when the distillation is stopped at that point.

Analysis of the data is of interest from a scientific standpoint in showing the order in which the products are formed in the destructive distillation process. The acids are the first of the valuable products to be formed. The formic acid is formed more rapidly than acetic acid, the total yield of formic acid being obtained when about half of the wood remained as brands. The tar soluble in the pyroligneous acid is the next volatile product to be formed. This is followed by the oily tar which settles out of the pyroligneous acid. Wood alcohol is the last of the valuable products to begin to be formed but precedes the oily tar in order of formation. This fact is of special interest in view of experiments

¹ Gas is actually the first product formed.

² THIS JOURNAL, 7 (1915), 663.

in temperature control which showed that in order to obtain the maximum yield of wood alcohol it was very necessary to control the distillation just before the tar began to be formed.

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THE INFLUENCE OF MOISTURE ON THE YIELD OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF HARDWOOD

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OBJECT OF WORK

In the destructive distillation of hardwood it has been considered for a long time the best practice to season the wood for at least 12 months before using it. The reason for this practice lies chiefly in the increase in operating expenses, due to an excessive dilution of the crude liquor. It is also the opinion of some operators that besides increasing the volume of liquor, green wood gives lower yields of products than dry, especially of acid. Other operators do not hold this view. In discussing the importance of using seasoned wood Klar¹ says "the yields of acetate of lime are inversely proportional to the water content of the wood carbonized—while the yield of alcohol is increased if changed at all."

There exists then no agreement among operators as to the influence of an excess of moisture on the yields. Many plants are now using wood with a higher moisture content than formerly because of changes in economic conditions of wood supply.

In making commercial experiments and demonstrations in controlling the distillation in order to secure the maximum yield of products, it became apparent that former experiments in controlling dry wood should be extended to determine the influence of moisture under controlled conditions.

In view of these conditions and the possible influence of moisture in temperature control, the experiments described in this paper were made. The tests also included a study of the effect of moisture under conditions comparable with uncontrolled as well as controlled plant conditions.

EXPERIMENTAL PROCEDURE

DISTILLATION—As it was thought that different species might be affected differently, the three standard distillation species, beech, yellow birch and hard maple, were studied separately. The material was ordinary cord wood from a commercial plant containing wood seasoned for about 18 months and wood seasoned from 4 to 6 months.

The tests were all made in a laboratory retort² holding about 50 lbs. of wood. In all previous work in the same retort it was the usual practice to start the distillation from a cold retort. By this method any excess moisture present was always distilled over before it could play any part in the destructive distillation reaction and no effect of moisture could be noted. In these tests the empty retort was first heated to

what would correspond to the end temperature of a commercial distillation, at which time a specially constructed basket containing the wood was quickly introduced into the retort. In this way the distillations were comparable to continuous daily plant practice. Destructive distillation had always commenced in parts of the charge, while the water in another part continued to distil over.

Uncontrolled and controlled distillations were made for both green and seasoned wood of the three species. In former laboratory tests, in which the importance of control features was established, the procedure was based on the temperature-percentage distillate relation. In continuous plant practice it is not possible to determine the proportion of the total distillate at any stage of the distillation, so it was thought important to determine if the time-temperature relation would not serve as well. There seems to be no doubt but that it can, as the curves drawn for these relations were found in these tests to be quite parallel. In uncontrolled distillation the maximum fire was kept under the retort until the tar-point was well established and the fire was then checked so that the distillation was completed largely by means of the exothermic reaction. In the controlled runs, as soon as the first indications of tar were noted in the distillate, the fire was checked and the firing so regulated that after that point the rate of rise in temperature was appreciably lower than in the uncontrolled runs.

ANALYSES—The yields of settled tar and charcoal were determined by actual measurement. The yields of acetic and formic acids, dissolved tar and wood alcohol were determined by analysis of the clear pyroligneous acid.

For acid and dissolved tar determinations 100 cc. of pyroligneous acid were distilled until no further distillate came over and the temperature, measured in the residue, reached 140° C. The residual tar was then washed with 50 cc. of water and the distillate added to the first, the distillation being stopped when the temperature in the residue reached 150° C. The residue was dissolved tar.

A 25 cc. portion of the distillate was titrated with normal NaOH to give total acid, calculated as acetic. Another 25 cc. portion was diluted with 100 cc. water and placed on the steam bath with an excess of mercuric oxide and allowed to remain for about 2 hours, or until it was evident that there was no further reduction of the oxide. The flask was shaken occasionally. The whole was then distilled from phosphoric acid. Titration of the distillate with *N*/10 NaOH gave acetic acid. The difference between the total acid and acetic acid determinations was taken as the formic acid, the formic being oxidized by the mercuric oxide. Phenolphthalein was the indicator in both titrations.

Wood alcohol was determined by distilling from a 500 cc. sample of the pyroligneous acid. The distillate was made alkaline with strong NaOH and 65 per cent distilled from it. After again being sure that the distillate was alkaline a third distillation of 60 per cent was made. About 2 cc. of H₂SO₄ were added to

¹ "Technologie der Holzverkohlung," 1910 edition, p. 77.

² Forest Service Bulletin 129, and This JOURNAL, 7 (1915), 663.