PRODUCTS OBTAINED BY DESTRUCTIVE DISTILLATION OF DOUGLAS FIR BARK

by

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PRODUCTS OBTAINED BY DESTRUCTIVE DISTILLATION OF DOUGLAS FIR BARK

INTRODUCTION

One of the important industries of the Pacific Northwest is lumbering and Douglas fir bark is one of the waste products produced in many sawmills of this region. Twenty-six percent of the total lumber manufactured in this country is Douglas fir. (6) At present the bark is being used only as fuel or burned to dispose of it and a better utilization of this would materially add to the prosperity of this region.

Distillation of waste wood from the sawmills of the Pacific Northwest was tried before (4) as a possible better utilization. Due to various economic reasons (2) this was not tried on a large scale. Bailey Tremper and others (28) tried to utilize this material for the production of gas for domestic use. They found that bark gave more gas than other waste.

Though the distillation of Douglas fir waste wood and sawdust (20) (23) was tried previous to the present work, no one attempted the distillation of bark alone. Considering that the bark is different from the heart wood, it would be interesting to distill bark alone and see whether the products obtained from it are any different from those reported on the distillation of Douglas fir waste wood.

During the present investigation, Douglas fir bark was distilled in an iron retort and the products obtained were examined and compared to the previously reported results.

HISTORY

Wood distillation is an ancient industry and its origin is obscure. Klar (13) mentions that the Egyptians used pyroligneous acid for embalming purposes and Macedonians practiced charcoal burning for the production of tar.

In England, the first wood distillation factory was started in 1796 to provide charcoal for the Sheffield iron industry but modern wood distillation industry has a history of only 50 years. (24) Production of charcoal was the important purpose of wood distillation for a very long time and after undergoing various vicissitudes it is still the most important product. (9) In America wood distillation took its place in the industry in 1876.

The coal tar color industry, after the discovery of Mauve by Perkin (26) created the demand for wood spirit (methanol) and acetic acid. The production of smokeless powder created the market for acetone. Hence those products assumed greater importance than the others in the wood distillation industry. With the production of acetic acid and acetone by cheaper synthetic processes, these products from wood distillation were almost driven out of the market. (10) Methanol still found use in the production of denatured alcohol. (24) Even this is now being manufactured by a synthetic process and no longer is wood

spirit uncontested in that field. (10) Now, as it was in its early days, the important product from wood distillation is charcoal and at present this industry is feasible only in those regions where there is a good demand for charcoal. (10)

Originally, tar obtained from wood distillation was used as a fuel in the process itself. Not much work was done on this tar. Even now the tar is being burned in the boilers and retorts of some wood distillation plants. Wood tar found a use in the manufacture of creosote used in the preservation of wood. Here, too, it met with competition and trouble. Due to the small amount of the wood creosote available and the constant change in the quality and grade of the product it was not very popular among the wood preserving companies. (12) Moreover, the coal tar creosote came into the field and practically displaced the wood tar creosote.

With the loss of markets for its by-products, acetic acid, acetone, methanol and the tar products, the wood distillation industry steadily declined and used only 440,000 cords of wood in 1931 against about 1.2 million in 1917. However, the industry did not decline after 1935 and in that year it looked as though the industry had become established. (10)

Threatened by its virtual extinction, the wood dis-

tillation industry became conscious of the inefficiency in its processes and applied sound chemical engineering. This activity resulted in the invention of some new and recent processes in the wood distillation industry. (26)

1. Badger-Stafford Process:

This method utilizes the heat evolved in the exothermic reaction of wood decomposition to heat the next batch of wood to the distillation temperature. The process is almost continuous and there are few moving parts in the retort. This process is in use now at the Ford plant in Dearborn, Michigan. (17)

2. Seaman Process:

This process was developed for carbonizing sawdust. It consists of a rotary cylinder into which saw dust is fed at one end and charcoal withdrawn at the other. (8)

3. Sawtelle Process:

Here the difficulties encountered in the carbonization of sawdust are eliminated by combining wood distillation and production of producer gas. This can be used only in those places where there is a demand for producer gas. (8)

4. Direct Acid Recovery Methods:

a. Suida Process:

This process recovers acid by extraction with a special tar oil. The vapours from the retorts are scrubbed by this oil and the acetic acid revovered from the extract. (19) (22)

b. Othmer Process:

This process uses some appropriate organic compound such as butyl acetate or butyl alcohol to form a constant boiling mixture with acetic acid and water. The water is removed from the acid by distilling the constant boiling mixture. (18)

c. Brewster process:

This method utilizes solvent extraction (liquid-liquid) for the recovery of acetic acid. The solvent used has greater affinity for acetic acid than has water and it is not soluble in water. The acid is recovered by distilling the solvent. (8)

All the above methods were the improved methods developed for combating the competition against the by-products of the wood distillation industry. The continued existence of this industry depends upon new and better processes of distillation and recovery of by-products, cheap and readily available raw materials, and a ready market for its present principal product, charcoal. (10) Hence the industry of wood distillation is feasible only in those places where coal is not readily available for

for fuel and metallurgical purposes.

The following table gives the growth and the condition of the wood distillation industry until 1939. (29)

TABLE NO. 1

Progress of Wood Distillation Industry

Year	Active Establishments	Wage Earners	Value of Products
1921	93	1790	$ 8,697,508.
1923	96	3034	24,661,189
1925	87	3025	17,548,315
1927	69	3002	17,830,494
1929	66	2897	19,751,805
1931	49	1615	6,892,551
1933	38	1366	4,884,344
1935	42	1918	7,410,126
1937	39	2108	8,983,273
1939	43	1770	6,843,172

In the Pacific Northwest, lumbering being the chief industry, wood distillation, as a possible source of profitably disposing of the sawmill waste, was attempted from time to time, at least on a small scale. Douglas fir being the principal species of this region, experiments were conducted on this to a large extent.

H. K. Benson (3) in 1913 conducted a number of experiments to determine the potential ways of utilizing the waste wood. He tried both steam distillation and destructive distillation. The results obtained in those experiments with regard to destructive distillation are summarized below.

"Twenty-nine thousand one hundred sixty pounds of wood yielded 12.5 gallons of turpentine, 25 gallons of light oil, 93.9 gallons of heavy tar, 1304 gallons of pyroligneous acid and 5547 pounds of charcoal (19% of the weight of the wood).

"Tar had a d_{18} of 1.068; flash point, 105; fire point, 131; free carbon, 1.18%; Engler viscosity at 100 of 1.5; fixed carbon, 3.16%; insoluble in 86° Be^1 naptha, 24.4%. Distillation of tar gave water, 4%; below 170°, 8%; 170-215°; 61%; solid pitch, 22%. The pitch had a melting point of 154 ac; free carbon, 18.23%; volatile, 68.28%; fixed carbon, 31.54%; ash, 0.18%.

"The pyroligneous acid yielded 8 to 10 gallons of methanol per 4000 pounds of wood and calcium acetate, 85 pounds."

Destructive distillation of Douglas fir was continued by Benson and his associates. (4) They experimented in 1915 on the yield of by-products from Douglas

fir (a) common run mill waste, (b) selected mill waste, and (c) common run stump wood. The results obtained in this series of experiments are summarized in the following table. (4)

TABLE NO. 2

Product Distribution

Wood Used	(A)	(B)	(C)	(D)	(E)	(F)	(G)
Mill waste	3,330	3.4	27.8	3.90	75	977	
Selected mill waste	4,250	10.86	46.37	3.71	74.3	900	
Common run stump wood	3,260	5.59	19.88	2.60	55.8	675	6270

(A) Weight of wood in pounds.

(B) Turpentine and light oil in gallons.

(C) Tar (retort tar and still tar) in gallons.

(D) Wood alcohol in gallons.

(E) Acetate of lime in pounds.

(F) Charcoal - 80 to 70% fixed carbon and 1 to 2% ash - in pounds.

(G) Gas in cubic feet.

It is difficult to calculate the above results in percentages of the weight of the wood used, because the results are given in gallons and the density of the different fractions is not given. However, the weight

of the charcoal can be calculated in percentage of the weight of the wood used and the results are given below.

TABLE NO. 3

Yield of Charcoal from Douglas fir waste

Wood Used	Percent weight of charcoal
Sawmill waste	29.35
Selected mill waste	21.15
Common run stump wood	20.65

At about the same time, Bailey Tremper (28) reported the use of Douglas fir sawmill waste on a commercial scale, for the production of illuminating gas. It was reported that a factory in Auburn, Washington successfully produced the illuminating gas on a commercial scale and here are the conclusions reached in that report:

"1. From Douglas fir forest wood (wood cut from live trees, seasoned and fairly resinous) 25,000 cubic feet of gas with a calorific value of 482 B.T.U. per cubic foot is obtained per cord of 3700 pounds. Nineteen hundred cubic feet of this gas has a heating value of 538 B.T.U.

"2. From Douglas fir mill waste 18,000 cubic feet of gas with a calorific value of 475 B.T.U. is obtained per cord of 3300 pounds.

"3. Enough tar is obtained to pay for the cost of the wood at the plant.

"4. Exothermic character of the reaction favors low fuel consumption.

"5. Water gas can be produced satisfactorily from charcoal at a rate of 1000 cubic feet per 25 pounds of charcoal.

"6. Wood gas and charcoal are especially available for metallurgical operations at mines located far from fuel supplies other than wood."

In order to produce larger amounts of gas, which was the principal product in the above venture, high temperatures were used. Temperatures of 1400 to 1600°F. were employed. It was also found that bark was essential in the wood to be employed for this purpose because it produced more gas. Of the 25,000 cubic feet of gas produced by a cord of forest wood, bark in it alone produced 17,000 cubic feet of the gas with a calorific value of 494 B.T.U., the maximum value being 567 B.T.U. Higher temperatures were also necessary, especially in the case of bark, to reduce the amount of carbon dioxide in the final product. The by-products were tar and charcoal. The charcoal obtained was of a lower grade where there was bark in the original charge of wood. Seven hundred to 800 pounds of charcoal were obtained per cord of wood.

In 1927, W. L. Benschlein (2) wrote a paper in which the possibilities of carbonizing west coast soft wood sawdust was discussed. He came to the "inevitable conclusion that destructive distillation of soft wood mill waste is not too optimistic even though large quantities of the raw material may be had at a very low cost." The reasons listed were:

1. Low yield of merchantable by-products such as acetic acid and methanol. (This point may not be of great interest at present.)

2. Small size of charcoal. It was contended that the small size charcoal had not much fuel value unless it was briquetted.

3. Market.

Later developments show that charcoal is the principal product of any destructive distillation operation.

As the competition of synthetic products increased, efforts were made to obtain other by-products and find better uses for the tar. In that direction, Morrell and Egloff (16) performed some experiments to investigate the possibility of producing motor fuels from the tar. They conducted the tests on tars obtained by destructively distilling various species of wood including Douglas fir. A brief summary of the results obtained by them on Douglas fir are reported below.

Calculated annual waste of Douglas fir:

7.5 billion board feet

or

2.5 million cords

or

4.2 million tons

From this, they estimated that the following could be produced: (*)

8,500,000 gallons of turpentine and light oil

70,000,000 gallons of tar

9,780,000 gallons of wood alcohol

187,500,000 pounds of acetate of lime

2,440,000,000 pounds of charcoal

(*) these figures based on the results obtained by Benson and associates. (4)

From their present work (16) they estimated that they could produce the following:

1. 23,300,000 gallons of motor oil equal in anti-knock properties to benzene.

2. 6,000,000 gallons of low boiling tar acids and phenols for antiseptic and disinfectant and other uses.

3. 125,000 tons of high grade coke.

4. 1,180,000 cubic feet of gas would be produced in the cracking operation.

Conditions of cracking the tar and the yields are given below:

Conditions of the experiment.

Pressures - 75, 100, 120 pounds per square inch.

Temperatures - 393 to 405°C.

Yields

Tar acid free motor oil based on dry wood - 26%

With recycling the yield was - - - - - - - - 30%

Tar acids (for use as disinfectants)- - - - 19%

(Acids obtained by extracting the oil with sodium hydroxide.)

Other products derivable from pressure distillation of tar:

Light oil solvents - - - - - - - - - - - - - 4.7%

Turpentine substitute- - - - - - - - - - - -17.0%

Pine oil equivalent- - - - - - - - - - - - -20.0%

Pressure distillate- - - - - - - - - - - - -36.0%

Tar acids- - - - - - - - - - - - - - - - - - -22.3%

In 1945, the Oregon Forest Products Laboratory published a series of papers (20) (21) (25) on the experiments done on the carbonization of Douglas fir sawdust in a rotary kiln. These experiments were conducted to examine the possibility of utilizing the sawdust available on the west coast. The results are summarized below.

TABLE NO. 4

Weight and Heat Balance

Product	Input	Output
<u>Weight Balance</u>	%	%
Wood	32.2	
Moisture	17.3	
Air	44.7	
Water in air	0.7	
Portland gas	5.1	
Charcoal		8.1
Kiln gas		64.3
Water in kiln gas		2.2
Condensate		25.4
<u>Heat Balance</u>		
Wood	74.0	
Portland gas	25.7	
S. H. of air	0.1	
Latent heat in air	0.2	
Charcoal		29.2
Kiln gas		50.8
Moisture latent heat		6.2
Tar		4.0
Radiation		9.8

Temperatures employed were from 480 to 1180°F. Retention time of the batch was 20 to 70 minutes. A process for making briquettes was discussed (21) and the composition of tars obtained in the distillation determined. (25)

Later experiments on the rotary kiln in the Oregon Forest Products Laboratory were reported by J. D. Ross and the results are summarized below. (23)

Potential usable Douglas fir waste available for use - 4,895,210 units of 200 cubic feet each. (7)

Wast wood not utilized (18.5%) - 900,000 units (30)

TABLE NO. 5

Data on Hu Rotary Retort

Speed of rotation	3 rpm.
Temperature, feed end	350°F.
Temperature, discharge end	1250°F.
Feed - 100 pounds dry wood material per hour	
Retention time	25 minutes

Yield of the products:

Product	%
Pyroligneous acid, soluble tars, etc.	38
Gas	35
Charcoal	23
Settled tar	4
	100

Charcoal: Proximate analysis:

Fixed carbon	88.6
V.C.M.	9.5
Ash	1.9

Gas analysis:	% by Vol.
Carbon monoxide	33.6
Nitrogen	19.8
Methane	16.7
Carbon dioxide	10.9
Ethane	6.3
Hydrogen	5.8
Oxygen	3.6
Illuminants	3.3

Calorific value of the gas - - - - - - - - - - - - 420 B.T.U. per cubic feet

The paper mentions the construction of a pilot plant to study economics of the operation.

More work on the tar was recently reported. Goos and Reiter (9) reported the perfection of processes for the production of "new products from wood carbonization." They reported that under the present conditions charcoal was the principal product of wood distillation and to make the industry paying, greater attention should be paid to the production of by-products from tar. The processes were

perfected for the production of the following products from tar.

1. Guaiacol
2. Cresol
3. Butyrolactone
4. Acetol acetate
5. Butyric acid
6. Crotonic acid
7. Maltol (3-oxy-2-methyl-(4) pyrone)
8. 2-hydroxy-3 methyl-$\Delta 2$ cyclopentenone.
9. 2,6 dimethoxy phenol
10. Tiglaldehyde
11. Methyl isopropyl ketone
12. Methyl ethyl ketone
13. Methyl furyl ketone
14. 4-ethyl guaiacol

The following table gives a summary of the results obtained in previous wood distillation experiments.

TABLE NO. 6

Product Distribution

Product	(A) %	(B) %	(C) %
Charcoal	33.6	36.0	29.0
Acetic acid	3.87	4.2	- -
Methanol	2.54	2.0	- -
Tar and oils	6.67	12.2	7.0
Non-condensible gas	24.4	21.7	19.0
Water and loss	28.92	23.9	45 *

* including the acid and methanol

(A) Reference (15) calculations based on oven dry wood.

(B) Calculations based on the oven dry wood.
Reference (9)

(C) Reference (16)

Not much work was done on bark alone. The only experiments done on bark were in 1925. Hilding Bergstroem (5) conducted experiments on the carbonization of bark and his results are summarized below.

"Experiments were conducted with bark and pure wood from spruce, red fir and birch, in a retort (35-l.) heated indirectly by gas. The volatile combustion products were taken out at the top of the retort and condensed at first in a copper and then in a glass cooler. The incondensable gas was measured and analyzed. The carbonization lasted for 3 to 6 hours at maximum temperatures of 400 to 500°C at the bottom and 450 to 500°C at the top of the retort. The results show that bark gives a somewhat higher output of charcoal and tar and a little less of wood acid, acetic acid and methanol than does the corresponding wood. Spruce wood particularly was very difficultly carbonizable."

Experimental Procedure

The material used in this work was Douglas fir bark. The bark was sawed into small pieces of about 1" x 1" x 1" by a small band saw. Some of the pieces were larger and smaller than the above size. A weighed quantity (about 2½ to 3 pounds) of these bark chips was put into an iron retort. (A) The arrangement of the carbonizing apparatus was as shown in Figure 1. The iron retort was heated by a muffle furnace, which could be heated to a safety limit of 1850°F. The muffle furnace was connected through a 16 ohm rheostat (F) to both 110 and 220 volt terminals. There was an automatic time switch (E) in the circuit and this enabled control of current through the furnace. This time switch, together with the rheostat and the possibility of utilizing two mains, 110 and 220 volts, made it possible to control the temperature of the furnace and the speed of heating the charge of bark in the retort. A series of condensing equipment (B) was connected to the retort to condense the vapors coming out of the retort and separate tar and pyroligneous acid from the non-condensable gas. The retort was provided with a thermocouple well and an iron-constantan couple (T) which was connected to an automatic potentiometer recorder. (D) The non-condensable gas was passed through a wet test meter (C) and the

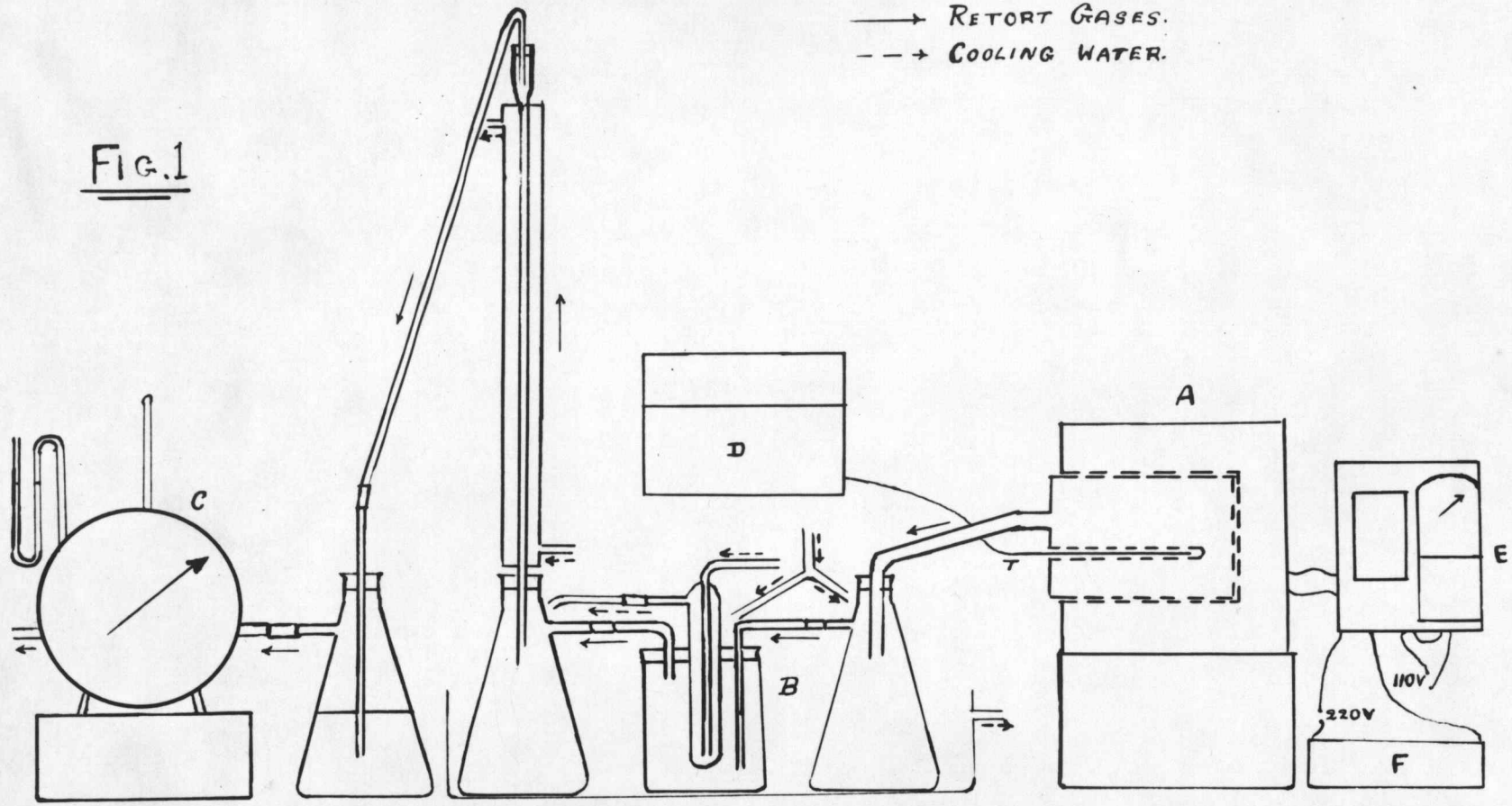


FIG.1

volume of the gas recorded. The flow of the materials is also shown in Figure 1.

After the run, the condensing system was disconnected and the material taken out for further analysis.

Analytical Procedure

The following scheme of analysis was employed.

Pyroligneous acid:

The amount of acetic acid, acetone, methanol and dissolved tar was estimated as follows:

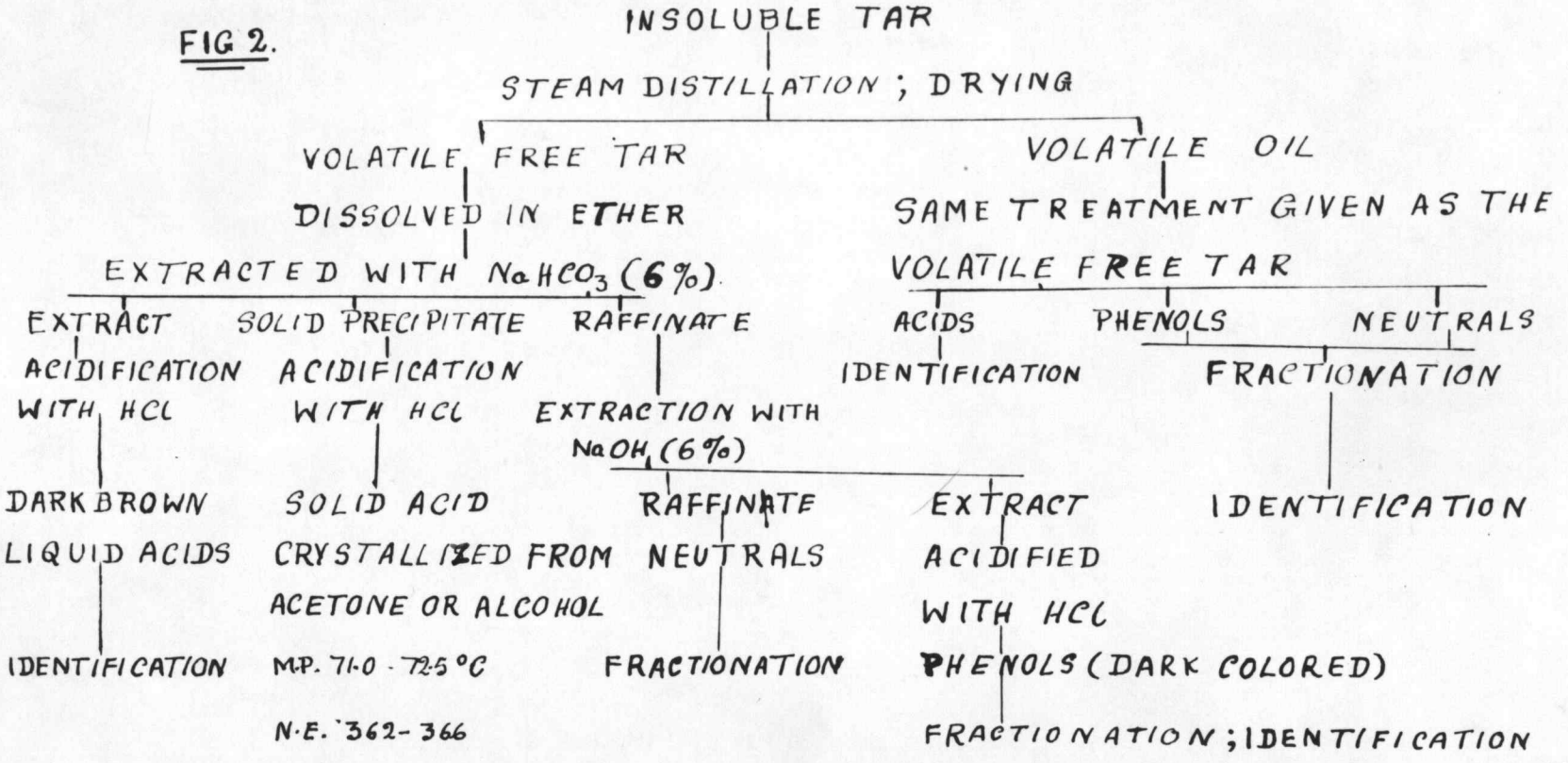
Acetic acid was determined by titration against standard alkali (sodium hydroxide) using a Beckmann pH meter for the determination of the end point. A distilled sample of the pyroligneous acid was used for the determination. (14)

The acetone content was determined by Messinger's method. (11)

The methanol in the pyroligneous acid was determined by the estimation of methoxyl groups using the modified Zeisel's method. (27)

The test sample used in the determination of acetone and methanol was prepared by neutralizing the distilled pyroligneous acid with sodium hydroxide and redistilling it. The tar left in the distillation flask was assumed to be the dissolved tar and its amount was found by determining the weight of the distilling flask before and

FIG 2.


INSOLUBLE TAR
STEAM DISTILLATION ; DRYING
VOLATILE FREE TAR
DISSOLVED IN ETHER
EXTRACTED WITH NaHCO3 (6%)
VOLATILE OIL
SAME TREATMENT GIVEN AS THE VOLATILE FREE TAR
EXTRACT
SOLID PRECIPITATE
RAFFINATE
ACIDS
PHENOLS
NEUTRALS
ACIDIFICATION WITH HCL
ACIDIFICATION WITH HCL
EXTRACTION WITH NaOH (6%)
IDENTIFICATION
FRACTIONATION
DARK BROWN LIQUID ACIDS
SOLID ACID CRYSTALLIZED FROM ACETONE OR ALCOHOL
RAFFINATE NEUTRALS
EXTRACT ACIDIFIED WITH HCL
IDENTIFICATION
IDENTIFICATION
M.P. 71.0 - 72.5 °C
N.E. 362-366
FRACTIONATION
PHENOLS (DARK COLORED)
FRACTIONATION ; IDENTIFICATION

after the experiment.

Tar

The condensate on standing separated into two fractions, pyroligneous acid and insoluble tar. In all the runs, the tar obtained was lighter than the acid and floated on the latter. The two fractions were separated by decantation and siphoning.

The pyroligneous acid so obtained was treated as described above.

The insoluble tar was subjected to the treatment given in Figure 2.

The insoluble tar was first steam distilled to separate it into volatile and non-volatile fractions. The distillate, which contained a light brown oil, was extracted with ethyl ether and the ether solution was dried over anhydrous sodium sulphate overnight and the ether distilled off to obtain the volatile fraction of the insoluble tar.

The non-volatile tar was dried by distilling off the water under a vacuum obtained by the water aspirator. The moisture free non-volatile tar and the volatile oil so obtained were used for further analysis.

Non-volatile tar

The tar was soluble in ethyl ether. The ether

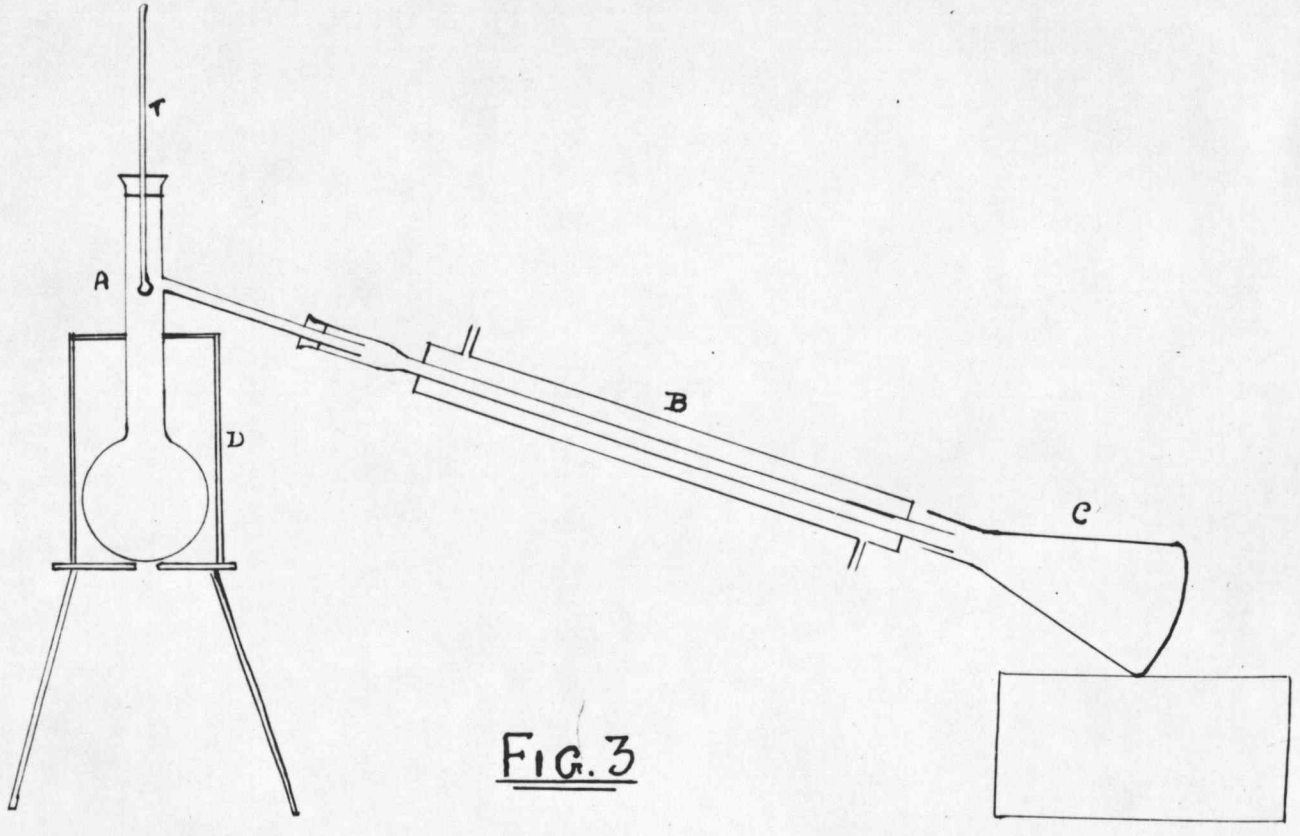


FIG. 3

solution was filtered to remove fine charcoal powder which could have come into the condensate along with the vapors coming out of the retort. The tar was extracted successively with sodium bicarbonate (6%) solution and sodium hydroxide (6%) solution. The extractions were done with fresh solutions each time till the extract was fairly colorless. The substances not extracted by either of the above solutions were assumed to be the neutrals.

The materials extracted by sodium bicarbonate were designated acids and those by sodium hydroxide phenols.

The acids, phenols and neutrals so obtained were subjected to fractionation in an ordinary distillation flask (A) (Figure 3) protected from radiation losses by an asbestos covering (D). The system had a condenser (B) and a thermometer (T) to indicate the temperatures. Previously weighed Erlenmeyer flasks were used to collect the distillate. (C) The boiling range of these fractions of the non-volatile tar was determined and attempts were made to identify these fractions by preparing derivatives and testing other properties. No pure crystalline derivatives were actually obtained perhaps due to the impurities in the sample. With the material available it was not possible to obtain pure components from these fractions.

Volatile oil from tar

This oil obtained by the steam distillation of the

insoluble tar was subjected to the same treatment as the non-volatile portion.

Charcoal

A.S.T.M. methods were followed (1) to determine the following on the charcoal obtained from the distillation of the bark.

1. Volatile combustible matter.
2. True specific gravity.
3. Apparent density.
4. Ash content.
5. Moisture.
6. Fixed carbon.

Moisture in the bark used was determined by the standard method. (31)

Presentation of Data

Carbonization

The following table gives the temperature-time relation of the various carbonization experiments. The time taken for the attainment of the various temperature, the final temperature in each carbonization run and the total time taken by each run are given in the table.

TABLE NO. 7

Time-Temperature Data

Exp.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	C.	D.
1.	1-45	470	—	—	—	—	—	—	—	—	—	—	(720)	6.0
2.	1-30	333	2-20	452	5-30	770	6-30	816	—	—	—	—	815	6.50
3.	1-30	285	2-40	520	3-00	575	6-00	770	6-30	780	7-30	815	815	7.50
4.	3-05	333	6-50	710	7-30	735	7-50	770	8-50	795	—	—	795	8.835
5.	0-30	220	1-15	310	1-30	333	6-10	740	6-45	770	7-00	780	780	7-0
6.	2-00	498	3-20	601	4-00	625	7-25	740	7-45	770	—	—	770	7.75
7.	0-45	220	1-35	330	2-10	470	2-35	545	7-00	735	7-35	770	770	7.50
8.	0-30	220	2-10	430	2-50	600	3-50	633	4-50	680	6-30	745	745	6.5
9.	0-15	180	4-25	500	4-50	540	8-45	800	—	—	—	—	800	8.75
10.	0-45	220	2-30	400	3-05	460	10-10	820	—	—	—	—	820	10.17
11.	0-35	240	0-55	380	1-15	565	1-35	790	1-45	880	2-00	870	870	2-00
12.	0-25	170	0-45	300	1-05	460	1-25	590	1-45	785	2-05	885	885	2-25
13.	0-20	100	1-00	310	1-20	490	1-40	615	2-00	800	2-20	870	870	2-33
14.	0-15	90	0-45	225	1-15	355	1-45	575	2-15	790	2-30	910	910	2.50

A. Time in hours and minutes.

B. Temperature in degrees Fahrenheit.

C. Final temperature in degrees Fahrenheit.

D. Total time in hours

In the above table the experiments can be divided into two groups. Experiments 1 to 10 were comparatively slow and experiments 11 to 14 were very much faster and consumed only one-fourth of the time.

The following table gives the product recovery from the various experiments.

TABLE NO. 8

Product Recovery

Exp.	Bark gms.	Moisture %	A	B	C	D	E
1.	969	9.6	474	—	—	6.00	(745)
2.	1310	17.4	531	—	45	6.50	815
3.	1040	31.8	397	—	42	7.50	815
4.	1063	11.5	437	443	43	8.835	795
5.	1127	17.1	464	456	45	7-00	780
6.	1124	10.25	459	475	41	7.75	770
7.	1022	10.0	458.5	435	38.7	7.50	770
8.	1053	9.26	453	463	41.8	6.50	745
9.	1033	14.35	440	420	31.0	8.75	800
10.	1136.5	17.8	430	548	44.5	10.17	870

TABLE NO. 8 (Cont.)

Product Recovery

Exp.	Bark gms.	Moisture %	A.	B.	C.	D.	E.
11.	1200	8.26	509	500	42.7	2-00	870
12.	1222	8.26	558	508.5	39.1	2.25	885
13.	1274.5	14.43	478	566.6	58.1	2.33	870
14.	1310	10.42	493	566.8	69.5	2.50	910

A. Charcoal in grams

B. Condensate in grams.

C. Gas (non-condensable in cubic feet)

D. Total time of the run in hours

E. Maximum and final temperature of each run in degrees Fahrenheit.

In the following table the percentage distribution of the products recovered is given. The basis is the weight of the oven dry bark.

TABLE NO. 9

Percentage Product Distribution

(Basis: Oven dry bark)

Exp.	Charcoal %	Dondensate %	Gas %
1.	54.3	-----	---
2.	49.1	-----	---

TABLE NO. 9

Percentage Product Distribution

(Basis: Oven dry bark)

Exp.	Charcoal %	Condensate %	Gas %
3.	56.0	- - -	- -
4.	46.6	33.95	19.5
5.	49.7	29.5	20.8
6.	45.5	35.78	18.72
7.	49.8	35.98	14.22
8.	47.4	37.28	14.78
9.	49.7	30.7	19.6
10.	46.1	36.98	16.92
11.	46.3	36.48	17.32
12.	49.7	36.58	13.72
13.	43.3	35.6	21.1
14.	42.0	36.6	21.4

From the above table, the average product distribution is calculated and the results are given in the following table. In calculating the average values, experiments 1 to 10 are taken as one group and experiments 11 to 14 are taken as the other group. Percentages are based upon the weight of oven dry bark.

TABLE NO. 10

Average Product Distribution

(Basis: Weight of oven dry bark)

Exps.	Charcoal %	Condensate %	Gas %
4 to 10	47.83	34.4	17.77
11 to 14	45.30	36.31	18.4

A sample calculation of the material balance is given below. The calculation is for run number 6. The retort and the condensing equipment were leak proof in all the experiments except 1, in which the gasket on the retort was not satisfactory. Thus no loss has been reported in the following calculation.

TABLE NO. 11

Sample calculation of material balance

Run 6

Bark charged into the retort - - - - - - - - 1124 gms.

% moisture in the bark - - - - - - - - - - - 10.25

Charcoal obtained- - - - - - - - - - - - - - - 459.0 gms.

Condensate obtained- - - - - - - - - - - - - - 475.0 gms.

% charcoal (based on the wt. of bark)- - - - - 40.8

% condensate (based on the wt. of bark) - - - 42.4

% gas (41 cubic feet) (based on the wt. of bark) - - - - - - - - - - - - - - - - - - 16.8

TABLE NO. 11 (Cont.)

Sample Calculation of Material Balance

Run 6

Total- - - - - - 100.00

Weight of oven dry bark- - - - -1010 gms.

% charcoal based on the wt. of oven dry bark 45.5

% condensate based on the wt. of oven dry bark- - - - - - - - - - - - - - - - - - - 35.78

% non-condensable gas based on the wt. of oven dry bark - - - - - - - - - - - - - - 18.72

Total- - - - - - 100.0

Analysis of the pyroligneous acid

The results obtained by analyzing pyroligneous acid as indicated before are given in the following table. In obtaining these results, the acid of several runs was mixed and analyzed.

TABLE NO. 12

Composition of the Pyroligneous acid

(% wt. of oven dry bark)

Expts.	Acetic Acid %	Methanol %	Acetone %	Dissolved Tar %
4,5,6	0.781	- - -	0.57	3.28
11,12	0.648	0.348	0.357	3.06
13,14	0,8859	0.4117	0.3639	1.824

Analysis of Insoluble Tar

As indicated before, the insoluble tar was steam distilled and dried, thus separating it into two fractions, volatile oils and the non-volatile tar. The percentage of the two fractions in the insoluble tar and their percentage weight of the oven dry bark are given in the following table.

TABLE NO. 13

Composition of Settled Tar

Expts.	Non-volatile tar		Volatile oil	
	A.	B.	A.	B.
11,12	10.99	79.80	2.765	20.2
13,14	9.874	76.82	2.983	23.18

A - % wt. of oven dry bark

B - % wt. of the insoluble tar

After separating the insoluble tar into volatile oil and non-volatile tar, each of these two fractions was further separated into acids (extracted by 6% sodium bicarbonate), phenols (extracted by 6% sodium hydroxide), and neutrals by successively extracting the fractions with 6% sodium bicarbonate and 6% sodium hydroxide. The material remaining unextracted was assumed to be the neutrals.

The following table gives the composition of the non-volatile tar. The table gives the percentage weight of the various components of the tar fraction and oven dry weight of wood.

TABLE NO. 14

Composition of Non-volatile tar

Experiments 13 and 14

	% wt. of non-volatile tar.	% wt. of oven dry bark.
6% sodium bicarbonate solubles (acids) - - -	13.22	1.305
6% sodium hydroxide solubles (phenols) - -	54.87	5.419
Neutrals - - - - - - - - -	31.92	3.152

While extracting with the sodium hydroxide a solid was obtained which was not soluble in either the ether solution of the tar or the sodium hydroxide. The material was separated by filtration and analyzed separately. It was solubls in alcohol, acetone and ligroin. The material was crystallized from both alcohol (95%) and acetone. The melting point and neutral equivalent were determined. The material gave no evidence of unsaturation with either potassium permanganate or bromine. The results are tabulated below.

TABLE NO. 15

Melting point and neutral equivalent

of the solid acids

M.P. (C)	N.E.
72.5	362 (crystallized from alcohol)
71.0	366 (crystallized from acetone)

This nearly corresponds to a C_{24} acid. Lignoceric acid (C_{23} H_{47}Cooh) has a M.P. of 81 °C and neutral equivalent of 368.5. The acids obtained here may be a mixture of fatty acids of this order.

The volatile oil was also subjected to the same treatment as the non-volatile tar. The results obtained are given in the following table.

TABLE NO. 16

Composition of volatile oil obtained by

steam distilling insoluble tar

	% wt. of volatile fraction of tar	% wt. of oven dry bark
Expts. 11, 12		
Sodium bicarbonate (6%)		
solubles (acids)- - - - -	4.742	0.1237
Sodium hydroxide (6%)		
solubles (phenols) - - -	53.46	1.478
Neutrals- - - - - - - - - -	41.81	1.156

TABLE NO. 16 (Cont.)

Composition of volatile oil obtained by steam distilling insoluble tar

	% wt. of volatile fraction of tar	% wt. of oven dry bark
Expts. 13, 14		
Sodium bicarbonate (6%)		
solubles (acids)- - - -	11.58	0.346
Sodium hydroxide (6%)		
solubles (phenols)- - -	39.83	1.180
Neutrals - - - - - - - - -	48.60	1.450

In the above table it would be noted that the percentage of phenols obtained in the runs 11 and 12 is higher than that obtained in runs 13 and 14. In the first case more extractions were made. In no case, however, was it possible to obtain a clear extract at the end, even though seven extractions, with fresh solution of sodium hydroxide each time, were made in the case of volatile oil from runs 13 and 14 and more in the case of runs 11 and 12. After the third extraction in each case, a colloidal solution, colored bright yellow, was obtained as the extract. The colloidal solution broke down when acidified with dilute hydrochloric acid. When the acidified solution was extracted with ether and

the ether distilled off, a clear, brown oil was obtained. This was assumed to be the phenols from volatile oil.

The complete product analysis of the runs 13 and 14 are given in the following tables.

TABLE NO. 17

Products obtained in runs 13 and 14

A. Preliminary Analysis

Charcoal - - - - - - - - - - - 37.55%

Condensate - - - - - - - - - - 43.80%

Gas (by difference)- - - - - 18.65%

The above percentages are based upon the weight of the wet bark.

% Charcoal based on the oven dry weight of the bark - - - - - - - - - - - - - - - - 42.9

% Condensate based on the oven dry bark 35.92

% Non-condensable gas based on the oven dry weight of the bark - - - - - - 21.18

B. Complete analysis

TABLE NO. 18

The percentages reported in the following table are percentages weight of the oven dry bark.

Product Recovery

Product	Percent
Charcoal	42.9
Non-condensable gas	21.18
Acetic acid	0.8859
Acetone	0.3639
Methanol	0.4117
Non-Volatile Tar	
Acids	1.3050
Phenols	5.4190
Neutrals	3.1520
Volatile oil from insoluble tar	
Acids	0.346
Phenols	1.180
Neutrals	1.450
Dissolved tar	1.824
Total	80.4175
Water and loss (by difference)	19.5825
Total	100.0000

The charcoal obtained was analyzed as indicated before and the results tabulated below.

TABLE NO. 19

Analysis of Charcoal

	Composite sample Expts. 1 to 10	Composite sample Expts. 11 to 14
Moisture (%) - - - - - -	1.65	2.359
Ash (%) - - - - - - - -	1.373	1.185
Volatile Combustible material (%) - - - -	16.82	17.1
Apparent density - - -	0.1501	0.1274
True specific gravity-	1.088	1.32
% fixed carbon - - - -	80.15	79.356

Further analysis of the fractions from volatile oil and non-volatile tar

The acids, phenols and neutrals obtained from the volatile oil and the non-volatile tar were analyzed further in an effort to separate them into different components. The fractions were first subjected to ordinary atmospheric distillation in an apparatus shown in Figure 3. Depending on the boiling points of the various components of the fractions, various cuts were obtained from the fractions. In most of the cases the liquids boiled over the entire range making it difficult to prepare pure components. This made the preparation of derivatives very difficult.

The acids, phenols and neutrals obtained from the

volatile oil were easier to deal with. The results obtained in this case are given first.

Volatile oil: Acids

The acids were distilled in a small distillation flask. Almost all of the liquid distilled over at a temperature of about 152 to 153°C. The liquid so obtained had very pungent odor. It was soluble in ether and alcohol. It decolorized and acidified potassium permanganate. It was not saturated as indicated by potassium permanganate and bromine in carbon tetrachloride. It did not reduce Fehlings solution. Neutral equivalent determination was run on the acid and was 131. This corresponds to a C_7 acid.

Volatile oil from tar: Phenols

The phenols were distilled in a distillation flask as shown in Figure 3 and the following separation was made.

TABLE NO. 20

Phenols from Volatile fraction from tar

Distilling range	% of liquid distilling
Below 120°C	10.08
120 to 208°C	73.4
Residue	5.175
Loss	11.42
Total	100.07

The phenols distilling in the range 120 to 208°C which constitute the bulk of the mixture were yellow in the beginning but soon darkened to dark brown.

The residue was dark, shining pitch.

Volatile oils from tar: Neutrals

Distillation similar to that done on the phenols was conducted in this case also and the results are given below.

TABLE NO. 21

Neutrals from volatile fraction from tar

Distilling range	% Distilling
Distilling below 110°C	1.656
110 to 150°C	4.910
150 to 200°C	42.650
200 to 240°C	27.100
Residue	6.310
Loss	17.400
Total	100.02

The color of the liquid varied from light yellow to dark yellow and brown, the color darkening as the boiling point increased. The residue was a dark brown colored liquid. The fractions were soluble in ether and alcohol. They did not darken on standing.

Non-volatile tar: Phenols

The phenols obtained from the non-volatile fraction of the tar were subjected to the same treatment as those from volatile oils. The results are tabulated below.

TABLE NO. 22

Phenols from non-volatile tar

Distilling range	% liquid distilled
Below 100°C	18.1
100 to 210°C	14.1
210 to 250°C	20.95
Residue	23.22
Loss	23.60
Total	99.97

The phenols though light colored in the beginning soon turned into dark brown. There was evolution of gases during the distillation at higher temperatures perhaps due to decomposition. The residue obtained was a dark solid.

Identification

Several attempts were made to test the properties of these various cuts and to prepare the derivatives. But in no case a pure, crystalline derivative could be obtained. It could be due to the fact that the components were not obtained in a sufficiently pure condition.

DISCUSSION

Not much work had been done on the destructive distillation of bark and no work at all on the distillation of Douglas fir bark, so it is difficult to compare the present work with any done previously. The distillation of Douglas fir wastewood (4) and the destructive distillation of Douglas fir sawdust (20), (23) are the only ones with which the results obtained in this work can be compared with some advantage. The work done (5) by Hilding Bergstroem on the destructive distillation of barks will be of some use in comparing the results of this work, though he does not say anything about Douglas fir.

One other impediment in the comparison of the results obtained in this work and others is the units in which these various results are reported. H. K. Benson (4) reported the yields of all the by-products in gallons and neither the density of these products nor their water content are known. Hence these results cannot be satisfactorily compared with the present ones. Only in the case of charcoal, the results can be compared in percentages but even here they cannot be reported on the percentage weight of the oven dry wood as the moisture content of the wood used in the previous experiments was not given.

The report on the destructive distillation of (20) (23) Douglas fir sawdust does not give the yields of by-products like acetic acid, methanol, acetone and the like, but the yields of charcoal, tar and non-condensable gas are given and they can be compared with the results of the present work.

The results obtained with regard to the destructive distillation of some other woods can be compared to the present results. (15) (9) (16). But in some of these cases the exact species is not given and most of the yields are from hard woods. Tables 23, 24, and 25 show the previously reported results and the results of the present investigation.

Comparison of product distribution in the destructive distillation of Douglas fir

The following table shows the comparison between the results obtained by H. K. Benson on Douglas fir waste wood (4) and those of the present work. The yields of charcoal and acetic acid are calculated in percentage of the weight of the wood used from the data given in Benson's paper. In that paper, charcoal was given in pounds and the acetic acid in pounds of calcium acetate. For the purpose of the present calculation the purity of the calcium acetate was assumed to be 80%.

TABLE NO. 23

Product distribution in the destructive distillation of Douglas fir

Product	Mill waste (3,300 lbs)	Selected mill waste (4,250 lbs.)	Common run stump wood (3,260 lbs.)	Bark*
1. % wt. of charcoal	29.35	21.5	20.65	46.6
2. Tar in gals - - -	27.80	46.37	19.88	13.3%
3. Acetone and methanol in gals - - -	3.9	3.71	2.6	0.74%
4. Acetic acid in percentage wt. of wood	0.683	0.532	0.52	0.77
5. Non-condensable gas in cubic feet	- - -	- - -	6270	18.04%

* Results were reported in the percentage weight of the oven dry bark and the values represented the average for the entire number of experiments.

The percentages in the case of previously reported results were on the basis of wet wood whose moisture content was not given.

Comparison of product distribution in the destructive distillation of Douglas fir sawdust with the results obtained from bark

The following table gives the comparison between the products obtained by the destructive distillation of Douglas fir sawdust (20) (23) and the results obtained in the present work. As no information is available on the yield of acetic acid and the other by-products in the case of the former, the comparison is on the yields of charcoal, condensate and the gas.

TABLE NO. 24

Product Recovery

Material Distilled	Char-coal %	Settled tar %	Pyroli-gneous acid. %	Gas %
1. Sawdust (23) *	27.1	4.71	26.99	41.2
2. Sawdust (20)'	9.8			80.4
3. Bark (present work)	46.6	13.30	22.06	18.04

* The percentages were calculated on the basis of the weight of oven dry sawdust, from the results given in the paper. It was assumed that the moisture in the sawdust was 15%, as indirectly indicated in the original paper. (23)

' Here the percentages are calculated on the basis of

oven dry sawdust. Moisture in the sawdust was 17.3% as given in the paper. (20) Tar and pyroligneous acid were combined as separate values were not available.

Comparison of product distribution in the destructive distillation of Douglas fir bark with that obtained with regard to other woods

The following table gives the comparison of the product distribution obtained in the case of bark with that obtained in the case of the destructive distillation of other woods.

TABLE NO. 25

Product Recovery

Product	A(15) %	B (9) %	C(16) %	D* %
Charcoal - - - -	33.6	36.0	29.0	46.6
Acetic acid- - -	3.87	4.2	- - -	0.77
Methanol - - - -	2.54	2.0	- - -	0.38
Acetone- - - - -	- - -	- - -	- - -	0.36
Tar and oils - -	6.67	12.2	7.0	13.30
Non-condensable gases- - - -	24.4	21.7	19.0	18.04
Water and loss	28.92	23.9	45.0 #	20.55

*percentages based on the weight of oven dry wood.

includes the pyroligneous acid

D - Present work.

From the foregoing tables the following conclusions can be drawn.

1. The yield of charcoal in the destructive distillation of Douglas fir bark is definitely more than that obtained in the previous distillations of Douglas fir waste wood (4), Douglas fir sawdust (20) (23) and all other woods. (15) (9) (16)

2. The volatile combustible material in the charcoal obtained from bark is about 18% as compared to 9.5% in sawdust charcoal (23) and 17.5% in the case of another reported wood. (9)

3. The yields of acetic acid, methanol and acetone are slightly more than those reported on Douglas fir wood but very much less than those reported for hard woods.

4. The yield of tar is definitely greater in the case of bark than in the case of other reported results on Douglas fir wood and it is of the same order as that obtained from other woods.

5. The yield of non-condensable gases is of the same order as that obtained from other woods but very much less than that obtained when Douglas fir sawdust was distilled.

The comparisons cannot be drawn further because of lack of additional data.

The yields of acetic acid, methanol and acetone in the

case of the destructive distillation of bark are not very high or even equal to those obtained with species of hard wood, even though they are higher than those reported previously on Douglas fir, but this consideration with regard to present day wood distillation is not very important because of the low yield and the low value of these products in the market where cheap synthetic products are available. (26)

The yield of tar is similar to that obtained in the previous experiments on woods other than Douglas fir. (26) (9) (16) The tar was separated into volatile and non-volatile tar by steam distillation and each of these into acids, phenols and neutrals. The volatile fractions were easier to deal with than the non-volatile tar. The former was clear brown liquid while the non-volatile tar was a dark mass, which softened about 60 to 70°C.

The separation of these acids, phenols and neutrals into various components by atmospheric distillation showed that most of them distilled over the entire range thus making it almost impossible to get pure fractions from the comparitively small amount of the material available. Hence the preparation of derivatives and identification was very difficult.

The phenolic fractions of both volatile oils (obtained by steam distilling insoluble tar) and non-volatile tar

gave clear oils an atmospheric distillation but these oils turned dark on standing.

The neutral fraction from volatile oils when subjected to a similar distillation gave light yellow oils which did not become dark on standing.

The acids and neutrals from non-volatile tar are mixtures of solids and liquids.

The charcoal obtained from bark has a volatile combustible matter and fixed carbon comparable to that obtained from other woods, though it has more V.C.M. than the charcoal from Douglas fir sawdust. Sawdust was subjected to very much higher temperatures (1250°F) as compared to the maximum in the present investigation which was only 910°F. Higher temperatures give charcoal with less volatile combustible material and higher fixed carbon. (11a)

The results of the present investigation very nearly bear out the conclusions reached by Hilding Bergstroem (5) that bark gives a higher output of charcoal and tar and lower output of acetic acid and methanol.

It can be seen from table 10 that the yield of charcoal is somewhat lower and the yields of condensate and non-condensable gases are somewhat higher, when the charge is rapidly distilled. One more consideration in this regard is that the temperatures employed in runs 4 to 10 are lower than that employed in runs 11 to 14. The average

temperature for the former runs was 790°F and that for the latter was 884°F. This will affect the final yields of the products, in destructive distillation. It was reported that yield of non-condensable gas was higher and that of charcoal lower when higher temperatures were employed. (11a)

SUMMARY

Several destructive distillations were conducted on Douglas fir bark. The temperatures employed were from 745° to 910°F. The time taken by each run varied from 2 to 10 hours. The distillations were run at atmospheric pressure.

The amounts of crude products obtained were as below:

Expts. 4 to 10 - Charcoal, 47.83%; condensate, 34.4%; non-condensable gas, 17.77%

Expts. 11 to 14 - Charcoal, 45.3%; condensate, 36.31%; non-condensable gas, 18.4%.

The pyroligneous acid contained 0.77% acetic acid; 0.38% methanol; 0.36% acetone and 2.72% dissolved tar, based on the weight of oven dry bark. These were average yields.

The insoluble tar had a steam non-volatile content equal to 78.31% (10.4% based on the weight of oven dry bark) and steam volatile oil content equal to 21.69% (2.874% based on the weight of oven dry bark).

The two fractions of the insoluble tar were separated into acids, phenols and neutrals by successively extracting the ether solution of the fractions with 6% sodium bicarbonate and 6% sodium hydroxide and assuming the unextracted material as neutrals. The yields from steam

non-volatile tar: Acids, 13.22%; phenols, 54.87%; and neutrals, 31.92%. The yields from steam volatile oil: Acids, 11.58%; phenols, 39.83%; and neutrals, 48.6%. The results were obtained on the composite tar from runs 13 and 14.

The acids, phenols and neutrals thus obtained were further separated into different fractions by atmospheric distillation in an ordinary distillation flask. The fractions distilled over the entire range, from 100 to 250°C, making it difficult to isolate pure components and to prepare derivative for identification purposes.

In the sodium hydroxide extractive a solid acid was obtained which had a melting point of 71 to 72.5°C and a neutral equivalent equal to 362 to 366. This corresponds to a predominantly C_{24} acid mixture.

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