

THE UNIVERSITY OF MINNESOTA

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Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Adolph Christopher Bakken for the degree of Master of Science. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

Charles S. Mann
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Date June 5 1923

THE UNIVERSITY OF MINNESOTA
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of
Committee on Examination

This is to certify that we the
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School, have given Adolph Christopher Bakken
final oral examination for the degree of
Master of Science

We recommend that the degree of
Master of Science
be conferred upon the candidate.

Charles A. Mann
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Date June 5, 1923

THE CHEMICAL ANALYSIS OF STRAW TAR

A Thesis

Submitted to the Graduate Faculty
of the
University of Minnesota

by

Adolph Christopher Bakken.

In partial fulfillment of the requirements
for the
degree of
Master of Science

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THE CHEMICAL ANALYSIS OF STRAW TAR

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Introduction

Recently a process has been developed for the destructive distillation of straw, primarily for the production of vegetable carbon. Some of the by-products are combustible gases, pyroligneous acid and straw tar. Each ton of straw produces about ten gallons of tar. This tar accumulates rapidly, so it is necessary to find some method of disposal, particularly a profitable one if possible. In order to determine the usefulness of this tar it seemed necessary to determine its composition, which is the prime object of this thesis. This tar has never been given in literature, nor have any methods of analysis been suggested, so these methods had to be developed from methods applied to other known tars.

The tar used for this work was supplied by the Manufactures Chemical Company, St. Paul Park, Minnesota. This tar in common with other low temperature tars is a black oily fluid having a density greater than water (1.0588 at 15.4°). It has a strong empyreumatic or burnt odor, its viscosity is less than that of coke-oven tar or gas-works tar, and it has no odor of ammonia or naphthalene. The original tar contains considerable amounts of water, and it is therefore necessary to dehydrate the tar before any examination can be made. On distillation, a lustrous black pitch is obtained which is very brittle and has a conchoidal fracture. These characteristics are similar to those of coal tar pitches.

Distillation of Tar for Analysis

A special cast iron still was used having a capacity of two gallons, heated by a circular pipe burner around the sides of the still that could be moved up or down. By this arrangement, excessive foaming could be avoided. Heat could also be applied from the bottom by using Bunsen burners. Figure I shows the type of still used for this distillation.

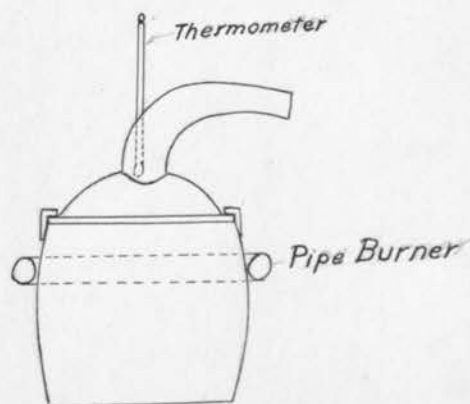


Fig. No 1

Four different samples of crude tar were distilled, the temperature being gradually increased until the point of pitch was reached which was 293° . Similar distillates resulting from these four distillations were mixed together, and the water layer was separated from the tar oils by means of a large separatory funnel. This water fraction was called pyroligneous acid, and the tar remaining was called partially de-

hydrated tar. Table I shows the number of grams of crude tar used for each sample, the amount of pyroligneous acid, the amount of tar oils and the amount of pitch resulting from the four distillations.

Table I.

Sample	Crude Tar	Pyro-ligneous Acid	Tar Oils	Pitch
I	5000 gms.	1958.6 gms.	1221.5 gms.	1919.1 gms.
II	5000 "	1280.5 "	1910.6 "	1808.9 "
III	2944 "	993.3 "	754.0 "	1196.7 "
IV	<u>4472 "</u>	<u>471.1 "</u>	<u>2215.7 "</u>	<u>1785.2 "</u>
Total	17416.0"	4703.5 "	6001.8 "	6710.7 "

From Table I the per cent by weight was determined for the different components of straw tar:

Pyroligneous acid	27.0%
Dehydrated tar oils	28.8%
Pitch	44.2%

The pyroligneous acid contains acetic acid, formic acid, phenols, acetone, methyl alcohol, pyridene, aldehydes and water. The pyroligneous acid of the tar portion was separately analyzed. The nearly completely dehydrated tar oils contain carboxylic acids, tar acids, nitrogen bases, neutral oils and some water.

On distillation of the 6001.8 grams of the tar oils, in the same still there was obtained 467.2 grams of watery distillate (pyroligneous acid), 5479.5 grams of tar oils and

522.3 grams of pitch.

The tar oils were fractionated using the same laboratory still. In this fractionation, the first three fractions contained small amounts of water which were separated by means of a separatory funnel. The heat was gradually increased until the temperature of 299° was reached, the temperature at which pitch was obtained. The fractions were cut at temperatures indicated in Table II, which also represents the amounts of each fraction.

After this fractionation no more water remained in the tar oils. It is, of course, possible that some of the water and pitch obtained in the latter distillation resulted from the breaking down of some of the tar constituents. This could not be avoided, as the only method of dehydration^{available} was applied.

The tar oil fractions were combined and again refractionated using a two liter pyrex distilling flask. During this distillation it was easier to control the temperature, and closer cuts on fractions could be made. During this distillation it was found that no water came over with the tar oils, which indicated the tar was completely dehydrated.

Table III shows the weight and specific gravity of each fraction, also the temperature at which the fraction was cut. The specific gravity determinations were made with a Westphal balance at 25°C.

Table II

Fraction	Range of Temperature	Weight of Tar Oils
1	0°- 130°	242.5 grams
2	130°- 177°	551.0 "
3	177°- 180°	198.5 "
4	180°- 197.5°	483.5 "
5	197.5°- 205°	485.5 "
6	203.5°- 206°	194.0 "
7	206°- 210.5°	230.5 "
8	210.5°- 220°	490.8 "
9	215°- 220°	137.0 "
10	220°- 230°	353.0 "
11	230°- 240°	401.5 "
12	240°- 250°	392.5 "
13	250°- 269°	85.0 "
14	269°- 275°	138.0 "
15	275°- 280°	100.0 "
16	280°- 285°	164.5 "
17	285°- 300°	<u>112.5</u> "
		4760.3 "
	Residue (Pitch)	252.0 "
	Water	10.8 "

Table III.

Fraction	Range of Temperature	Weight of Tar Oil	Specific Gravity
1	60°- 130°	172.5 grams	0.8779
2	130°- 135°	74.2 "	0.9030
3	135°- 145°	69.5 "	0.9090
4	145°- 150°	54.5 "	0.9140
5	150°- 160°	92.0 "	0.9180
6	160°- 170°	108.0 "	0.9309
7	170°- 180°	201.0 "	0.9477
8	180°- 189°	266.5 "	0.9686
9	189°- 191.5°	98.2 "	0.9795
10	191.5°- 194°	149.0 "	0.9846
11	194°- 199°	212.0 "	0.9898
12	199°- 201°	98.5 "	0.9930
13	201°- 204°	178.0 "	0.9955
14	204°- 206°	256.3 "	0.9965
15	206°- 208°	173.5 "	0.9989
16	208°- 210°	222.5 "	0.9989
17	210°- 213°	96.5 "	0.9980
18	213°- 216°	101.5 "	0.9970
19	216°-220°	224.5 "	0.9953
20	220°- 225°	122.0 "	0.9933
21	225°- 230°	266.0 "	0.9923
22	230°- 235°	174.0 "	0.9977
23	235°- 240°	94.5 "	1.0016
24	240°- 245°	178.5 "	1.0036
25	245°- 250°	133.0 "	1.0066

Table III (Continued)

Fraction	Range of Temperature	Weight of Tar Oil	Specific Gravity
26	250°- 255°	93.0 grams	1.0097
27	255°- 260°	116.0 "	1.0125
28	260°- 270°	117.0 "	1.0177
29	270°- 275°	82.0 "	1.0212
30	275°- 285°	144.5 "	1.0238
31	285°- 290°	61.0 "	1.0263
32	290°- 292°	94.5 "	1.0202
33	292°- 295°	<u>20.0</u> "	1.1620
Total		4544.7 "	
Residue (Pitch)		204.8 "	

It is of interest to note that the specific gravity of fractions 17-22 of boiling range 210°- 235° are lower than those preceding or following. This may indicate a break down of some constituent at this temperature. It should be noted that it was impossible to get a fraction of a definite boiling point, and that the specific gravity increased generally with the temperature.

Analysis of Pyroligneous Acid

The pyroligneous acid which was separated from the tar oils was then analyzed according to the scheme shown diagrammatically.

Pyroligneous Acid

Add CaCO_3
Distill at 85°C .

Remaining solution:
Calcium salts of acids,
phenols and light oils.

Distillate containing
acetone, methyl alcohol
and pyridine.

Extract with ether

Add H_2SO_4 and
distill

Water solution
containing calcium
salts

Ether fraction
containing phenols
and light oils

Residual solution:
pyridine sulphate

Distillate
containing acetone
and methyl alcohol

Concentrate
add H_2SO_4 and
distill

Add NaOH and
distill

Determine acetone
and methyl alcohol
according to the
memorandum from
R.C. Palmer of the
Forest Products
Laboratory.

Light
oils

Sodium phenolates
in solution

Carboxylic
acids

Treat with H_2SO_4

Titrate

Phenols in
ether

Total acids

Distill off
ether

Determine acetic acid

Phenols titrated
with iodine

Formic acid by
difference

A sample of 1000 grams was taken, to which was added an excess of finely pulverized, chemically pure calcium carbonate, which reacts with the carboxylic acids but not with the phenols. After shaking thoroughly for complete reaction, the excess calcium carbonate was removed by filtration or a Büchner funnel. The excess calcium carbonate was washed several times with distilled water to make sure it had ^{been} freed from any soluble calcium salts. The filtrate was then distilled at a temperature of 95°- 100°C., using a three bulb return fractionating ^{column} until the volume in the distilling flask was reduced to a volume of about 200 cc. The distillate contained the acetone, methyl alcohol, possible traces of phenols and pyridine which was retained for further examination.

The remaining portion was then extracted with ether to remove any tar acids and any oils that might be present. This ether extraction was retained for the determination of tar acids.

The salts of the carboxylic acids in solution were then liberated by adding 20% sulphuric acid precipitating calcium sulphate which was removed by filtration. The filtrate was then distilled, and the distillate titrated for total carboxylic acids direct with 0.5082 normal sodium hydroxide. It was found that 25 cc. sample required 23.9 cc. of a 0.5082 normal hydroxide to neutralize the carboxylic acids.

Calculation for total acids.

25 cc. of fraction used.

23.9 cc. of 0.5882 normal sodium hydroxide used.

$$\frac{60 \times 0.5082}{1000} = 0.0305 \text{ grams of acetic acid per cc.}$$

$$\frac{23.9 \times 0.0305}{25} \times 1000 = 29.08 \text{ grams of total acid.}$$

Determination of Acetic Acid

According to the method used by R. C. Palmer of the Forest Products Laboratory, acetic and formic acids were determined. An excess of 25 grams of finely powdered mercuric oxide was added to 25 cc. of the distillate obtained from the total acid determination. This mixture is then made up to 100 cc. After shaking thoroughly for complete reaction it was placed on a steam bath. At the end of two hours, enough more mercuric oxide was added so that the mercuric oxide was precipitated in the bottom, giving an excess of about 15 grams. The mixture was allowed to remain on the steam bath for one hour longer. The total mixture was then transferred to a 500 cc. distilling flask, and an excess (50 cc.) of syrupy phosphoric acid was added to decompose any mercuric acetate that may have been formed. The mixture was then distilled, and the residue washed with 100 cc. of water dropped in from a dropping funnel to make sure all the acetic acid had been distilled over. The distillate was then titrated with 0.5082 normal sodium hydroxide, using phenolphthalein as indicator. It was found that it required 17.8 cc. of 0.5082 normal sodium hydroxide to neutralize 25 cc. of acid solution. From preceding determinations of total acids, it was found that 1 cc. = 0.02908 grams of total acid.

Calculations

$$\frac{60 \times 0.5082}{1000} = 0.0305 \text{ grams of acetic acid per cc.}$$

$$\frac{17.8 \times 0.0305}{25} = 0.02164 \text{ grams of acetic acid in 1 cc.}$$

$$0.02908 - 0.02164 = 0.00744 \text{ grams formic acid in 1 cc.}$$

$$0.00744 \times 1000 = 7.44 \text{ grams formic acid in 1000 cc.}$$

$$0.02164 \times 1000 = 21.64 \text{ grams acetic in 1000 cc.}$$

Determination of Acetone, Methyl Alcohol and Pyridine.

The acetone, methyl alcohol, and pyridine distillate was made basic with 10% sodium hydroxide to fix the phenols that might have been carried over in the distillation. This mixture was then distilled almost to dryness, the residue being retained for the tar acid determination. The distillate containing the methyl alcohol, acetone and pyridine was then neutralized with 20% sulphuric acid to fix the pyridine. The mixture was then distilled almost to dryness, the residue being kept for the pyridine determination.

Determination of Acetone

According to R. C. Palmer of the Forest Products Laboratory, acetone was determined by taking 25 cc. of the acetone alcohol fraction and treating with 10 cc. of a twice normal sodium carbonate solution. 50 cc. of one tenth normal iodine were added, counting three minutes by a stop watch and beginning to count when the pipette was one half empty. At the end of three minutes, 10 cc. of three normal sulphuric acid was

added. The mixture was then titrated with one tenth normal sodium thiosulphate, using starch as indicator. The difference between fifty and the number of cc. of the sodium thiosulphate used equals the cc. of iodine absorbed.

Calculations according to R. C. Palmer
of the Forest Products Laboratory

31.8 cc. of $\text{Na}_2\text{S}_2\text{O}_3$ added.

$$1. \frac{\text{cc. of } \frac{N}{25} \text{ iodine} \times 0.09677}{25} = \text{grams of acetone in 100 cc}$$

$$2. \frac{\text{Weight of distillate}}{\text{Specific gravity}} = \text{cc. of distillate}$$

$$3. \frac{2 \times \text{cc. distillate} \times \text{grams acetone per cc.}}{100} = \text{grams of acetone per liter.}$$

$$1. \frac{(50 - 31.8) \times 0.09677}{25} = 0.0705 \text{ grams acetone per 100 cc}$$

$$2. \frac{1.091 \text{ Kg}}{0.9976} = 1094 \text{ cc. of distillate}$$

$$3. \frac{2 \times 1094 \times 0.000705}{100} = 1.542 \text{ grams of acetone per liter}$$

Determination of Methyl Alcohol

According to the method recommended by R. C. Palmer of the Forest Products Laboratory, a portion of the acetone, methyl alcohol fraction was used to determine the specific gravity by means of the Westphal balance at 25°C. The per cent of alcohol corresponding to a given specific gravity can be obtained from the tables of Ditmar and Fawcett. (See Van Nostrand's Chemical Annual or Smithsonian Physical Tables.) The specific gravity was 0.0076. The per cent corresponding to this value is 1.31% by weight.

Determination of Phenols

Phenols were determined according to the method given by W. M. Gardner and H. H. Hadgson, J. Chem. Soc. 95-1819 (1909)

The ether extract containing phenols, pyridine and light oils, obtained by washing the solution of the calcium salts of the carboxylic acids, was evaporated, leaving a residue of phenols and light oils. This residue was made alkaline with 10% sodium hydroxide and distilled to drive off the pyridine. The distillate was retained for the pyridine determination. The residue, together with the residue obtained from the acetone, methyl alcohol and pyridine portion, when distilled with 10% sodium hydroxide, was made acid to liberate the phenols. The phenols were recovered by steam distillation. 25 cc. of this phenol portion was then diluted to 200 cc. and an excess of one tenth normal iodine was added using starch as an indicator. A few drops of 20% sodium hydroxide were added until the color of the iodine disappeared. Dilute hydrochloric acid was then added in excess to separate the unabsorbed iodine, which was titrated with one tenth normal sodium thiosulphate. In the case of iodine, one molecule of iodine is absorbed by one molecule of phenol.

Calculations

25 cc. of phenol solution required 49.71 cc. of iodine

N of iodine = 0.0846

$\frac{126.9 \times 0.0846}{1000} = .001074$ grams iodine per cc.

94:253.8 = x:0.01074

$x = 0.0039$ grams equivalent per cc. of phenol.

$49.71 \times 0.0039 \times 40 = 7.75$ grams of phenol in sample.

Determination of Pyridine

The pyridine distillate resulting from the ether extract containing the phenols, pyridine and light oils after the phenols had been fixed with 10% sodium hydroxide, was made acid with 5% sulphuric acid and distilled almost to dryness. This residue was added to the pyridine obtained from the acetone, methyl alcohol fraction. The whole amount was distilled with steam until a volume of 500 cc. was obtained. This distillate was then titrated with one tenth normal hydrochloric acid.

Calculations

$\frac{N}{10}$ HCl = 0.00365 grams per cc.

24 cc. of $\frac{N}{10}$ HCl required to neutralize 25 cc. of pyridine sample

1 cc. of pyridine 0.0079 grams of pyridine.

$\frac{24 \times 0.0079 \times 1000}{25} = 7.58$ grams of pyridine in 1000 cc. sample

Determination of Aldehydes

No positive quantitative tests could be obtained for the presence of aldehydes. The following tests were tried without definite results.

1. Resinification with dilute alkali solutions.
2. Reduction of an ammoniacal silver solution.
3. No color was restored to a solution of magenta decolorized by sulphurous acid - Schiff's reagent.
4. No precipitation with aniline forming a condensation product.

Summary of the Pyroligneous Acid Analysis.

1000 Gram Sample.

Constituents	Weight of Constituent	Per Cent by Weight
Acetic Acid	21.64 Grams	2.16%
Formic Acid	7.44 "	0.75
Acetone	1.52 "	0.15
Methyl Alcohol	13.10 "	1.31
Phenols	7.75 "	0.78
Pyridine	7.58 "	0.76
Aldehydes	trace	

Analysis of the Tar Oil

Before the analysis was begun on the tar oils, the fractions were united into four groups. Group I included all fractions distilled over between a temperature range of 60°-170° C. Group II included all fractions distilled over between a temperature range of 170° - 199° C. Group III included all fractions distilled over between a temperature range of 199° - 230° C. Group IV included all fractions distilled over between a temperature range of 230° - 295°. The specific gravity was taken of each group using a westphal balance at a temperature of 25° C. The following table gives the specific gravity of each group.

Group	Range of Temperature	Specific Gravity
I	60° - 170°	0.9068
II	170° - 199°	0.9732
III	199° - 230°	0.9971
IV	230° - 295°	1.0155

Method Used for Analysis of Each Group.

A 100-gram sample was weighed into a separatory funnel having a capacity of about 250 cc. This sample of tar oils was then treated twice with 50 cc. of a saturated solution of sodium carbonate to remove the carboxylic acids. As sodium carbonate does not react with any of the constituents except the carboxylic acids, it was possible to remove the acid by this material as a soluble salt. The tar oils form a distinct layer from the saturated solution of sodium carbonate containing the carboxylic acids, which made it possible to separate the layers. The tar oils were then washed with water to remove any traces of sodium carbonate, and dried with anhydrous sodium sulphate to remove the water. The anhydrous sodium sulphate does not react with any of the constituents. The tar oils were then separated from the sodium sulphate by filtration, and the filtrate weighed and retained for further analysis. In order to remove any oils adhering to the sodium sulphate it was thoroughly washed with ether. The ether was then evaporated, and the weight of the tar oil remaining after the ether had been expelled was added to the weight of the previous filtrate from the sodium sulphate. At this point it was considered advisable to disregard the residue from the ether washing to avoid possible error in the transference of this residue to the tar oil filtrate. The difference in weight between the 100-gram sample and the weight of the tar oil filtrate plus the weight of the residue from the ether washing represented the weight of the carboxylic acid.

The tar oil filtrate was then washed five times with 50 cc. of a 10% sodium hydroxide solution. Experiment showed that five washings of a 10% sodium hydroxide were sufficient to completely remove all the tar acids of the phenol type. Sodium hydroxide does not react with any of the remaining constituents. The sodium hydroxide containing the tar acids forms a distinct layer which made it possible to separate the tar acids from the remaining constituents. After the removal of the tar acids the remaining portion was washed with water to remove the sodium hydroxide. The oils were then dried with anhydrous sodium sulphate to remove the water. After this portion had been dried with anhydrous sodium sulphate, it was filtered from the sodium sulphate. The sodium sulphate was washed with ether until all the adhering oil had been removed. The ether evaporated, and the weight of the oil remaining after the ether had been expelled was added to the weight of the previous filtrate of the tar oil. The difference in weight of the tar oils caused by the sodium hydroxide treatment represents the tar acids.

The oils remaining were then treated twice with 50 cc. of a 20% solution of sulphuric acid to remove the nitrogen bases of the pyridine type. As sulphuric acid of this strength reacts only with the nitrogen bases, it was possible to remove this material as a soluble salt. The solution of these salts form a distinct layer, making it possible to separate this layer from the remaining oils. These were washed with water to remove all the sulphuric acid, and then dried

with anhydrous sodium sulphate. After filtration from the sodium sulphate it was weighed. Adhering oil was washed from the sodium sulphate with ether, and after evaporation of the ether its weight was added to the weight of the remaining neutral oils. The difference between the weight of the neutral oils and the oils before treating with sulphuric acid, represents the weight of the nitrogen bases.

Assuming the carboxylic acids were mainly of the aliphatic type, such as acetic acid, no further work was done at this time.

The common method of regenerating the phenols is by treatment with dilute sulphuric acid. This method was applied. The sodium salts of the tar acids were "sprung" with 20% sulphuric acid until acid. At this point the odor of phenol could be detected. This mixture was then extracted with 100 cc. of ether, two extractions being sufficient to remove all of the tar acids. The ether was then distilled off, and the residue distilled. In accordance with this reaction the tar acids came over as a light yellow liquid. No analysis was made on each individual fraction.

According to the common method, nitrogen bases can be regenerated by treating with alkali. The solution containing the salts of the pyridine bases was neutralized with 10% sodium hydroxide liberating the free nitrogen bases. At this point the odor of pyridine could be detected.

The neutral oils were distilled in order to get a purer oil. This oil on distillation came over practically

colorless and remained colorless for several days, after which it seemed to darken a little. It is believed that these oils contain unsaturated hydrocarbons, because of the ease with which bromine is added. No attempt was made to isolate these hydrocarbons, nor was any further analyses attempted on this fraction.

The following tables give the separate results obtained from the four separate fractions. The quantities are represented as percentages by weight.

Fraction 20° - 170° C.

Constituents Sample	I	II	III	Average
Carboxylic Acids	11.03%	9.35%	12.01%	10.46%
Tar Acids	14.10%	15.23%	12.10%	13.81%
Nitrogen Bases	00.75%	1.02%	00.93%	00.90%
Neutral Oils	73.83%	74.82%	75.12%	74.59%

Fraction 170° - 199° C.

Constituents Sample	I	II	III	Average
Carboxylic Acids	8.5%	11.4%	8.7%	9.2%
Tar Acids	27.5%	24.6%	30.9%	27.6%
Nitrogen Bases	10.9%	8.5%	8.8%	9.4%
Neutral Oils	52.5%	54.9%	51.3%	52.9%

Fraction 199° - 230° C.

Constituents Sample	I	II	III	IV	V
Carboxylic Acids	None	None	None	None	None
Tar Acids	68.40%	67.00%	65.60%	66.00%	67.00%
Nitrogen Bases	1.79%	6.72%	4.19%	3.04%	7.21%
Neutral Oils	29.83%	26.40%	38.72%	36.66%	25.77%

Fraction 199° - 230° C. (Continued)

Constituents Sample	VI	VII	VIII	IX	Average
Carboxylic Acids	None	None	None	None	None
Tar Acids	62.50%	64.00%	63.40%	63.60%	65.30%
Nitrogen Bases	3.89%	3.37%	6.19%	4.18%	4.90%
Neutral Oils	33.59%	32.61%	30.38%	32.19%	30.68%

Fraction 230° - 295° C.

Constituents Sample	I	II	III	IV	V	VI	Average
Carboxylic Acids	None	None	None	None	None	None	None
Tar Acids	58.60%	58.00%	62.40%	59.50%	59.90%	59.50%	59.48%
Nitrogen Bases	4.09%	4.51%	3.11%	2.44%	1.94%	1.25%	2.89%
Neutral Oils	37.20%	37.45%	34.41%	38.03%	39.15%	38.75%	37.51%

From the various analyses we can calculate the percentage composition by weight of the crude tar on the basis of a 100-gram sample of tar.

Constituents	Pyroligneous Acid	Tar Oil	Total
Water	25.40%	None	25.40%
Carboxylic Acid	0.79%	1.45%	2.23%
Acetone	0.04%	None	0.04%
Alcohol	0.35%	None	0.35%
Phenols (Tar Acids)	0.21%	12.15%	12.36%
Pyridine (Nitrogen Bases)	0.21%	1.16%	1.37%
Aldehydes	Trace	None	None
Neutral Oils	None	14.09%	14.09%
Pitch	None	44.20%	<u>44.20%</u>
		Total	100.04%

Conclusions

1. Though pyroligneous acid contains acetic acid, formic acid, acetone and methyl alcohol, the quantity is so small that it is not worth recovering.
2. The high content of tar acids in the tar oil could be separated by distillation and used for antiseptic purposes.
3. Neutral oils might be used for softening pitch, which could be used for making roofing paper.
4. Pitch could be used for making roofing paper, and might be used where a water proof paint is desired.

This work was done under the direction of Dr. C. A. Mann in the Chemical Laboratories of the University of Minnesota.

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