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REPORT
of
Committee on Thesis

The undersigned, acting as a Committee of
the Graduate School, have read the accompanying
thesis submitted by Walter McClellan Lauer
for the degree of Master of Science

They approve it as a thesis meeting the require-
ments 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.

Geoff Frankforter
Chairman

Samuel L. Hoyt
Edwin Christian

June 2nd 1917

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REPORT
of
COMMITTEE ON EXAMINATION

This is to certify that we the undersigned, as a Committee of the Graduate School, have given Walter McClellan Lauer final oral examination for the degree of Master of Science..... We recommend that the degree of Master of Science... be conferred upon the candidate.

Minneapolis, Minnesota

June 2nd 1917

Geo B. Frankforter
Chairman

Fred Christensen

Samuel L. Hoys

13 Dec 17 W. R. S.

AN INVESTIGATION OF WOOD OIL

A THESIS

Submitted to the
Faculty of the Graduate School
of the
University of Minnesota

by

WALTER M. LAUER

In partial fulfillment of the requirements
for the degree
of
MASTER OF SCIENCE

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The chemical nature of wood may be said to consist principally of cellulose, lignin, water, and of ash forming materials. If wood is destructively distilled the cellulose and lignin molecules are broken up and charcoal and pyroligneous acid are among the products formed. P. Klason, Heidenstam, and Norlin (Ark. Kemi Min. u. Geol., 1908, Bd. 3, 9) represent this destructive distillation by the following equation:-



Total amount of products, contained in the pyroligneous acid, in the tar and in the gases.

They further state that the destructive distillation of Cellulose forms charcoal, acetic acid, and tar; whilst lignin forms principally charcoal, acetic acid, wood alcohol and tar.

The term "Wood Oil", according to E. Looft, is used to designate the low boiling portions of Wood Tar and also the less volatile portions and residues of crude Wood Spirits. (Emilius Looft, *Annalen der Chemie und Pharm.* 1893, 275 p.366)

Fraps states that Wood Vinegar contains the whole series of saturated fatty acids up to and including caproic acid, namely, formic, acetic, propionic, butyric, valeric, and caproic acids. According to him it also contains some valerolactone, pyrocatechol, and three unsaturated acids, namely, alpha crotonic, beta crotonic, and angelic acids. He further states that wood creosote is a mixture of phenols and their acid ethers; phenol, the three cresols, xylenols (1, 3, 4 and 1, 3, 5), ortho ethyl phenol, guaiacol, methyl guaiacol, ethyl guaiacol, propyl guaiacol and finally the dimethyl ethers of pyrogalllic acid, methyl pyrogalllic acid and propyl pyrogalllic acid.

Mabery (*American Chemical Journal* 1883-4 p.256) reports acetaldehyde, methyl formate, methyl acetate, methyl alcohol, dimethyl acetal, acetone, and allyl alcohol as products of dry distillation of wood at low temperatures. The high boiling oils when fractionated were pale yellow, but turned dark brown on standing. He further states that a constant boiling point could not be obtained between 75° and 200°.

Hentzschel (*Annalen der Chemie und Pharm.* 1893, 275 p.318) succeeded in isolating adipic ketone from wood oils. He started with oil which had been distilled twice. After redistillation (8 to 10 times) the fraction 120-140° was treated with syrupy sodium bisulfite solution. The crystals were then washed with alcohol and ether, dried in vacuum and then put into a warm saturated soda solution. An oil was then ob-

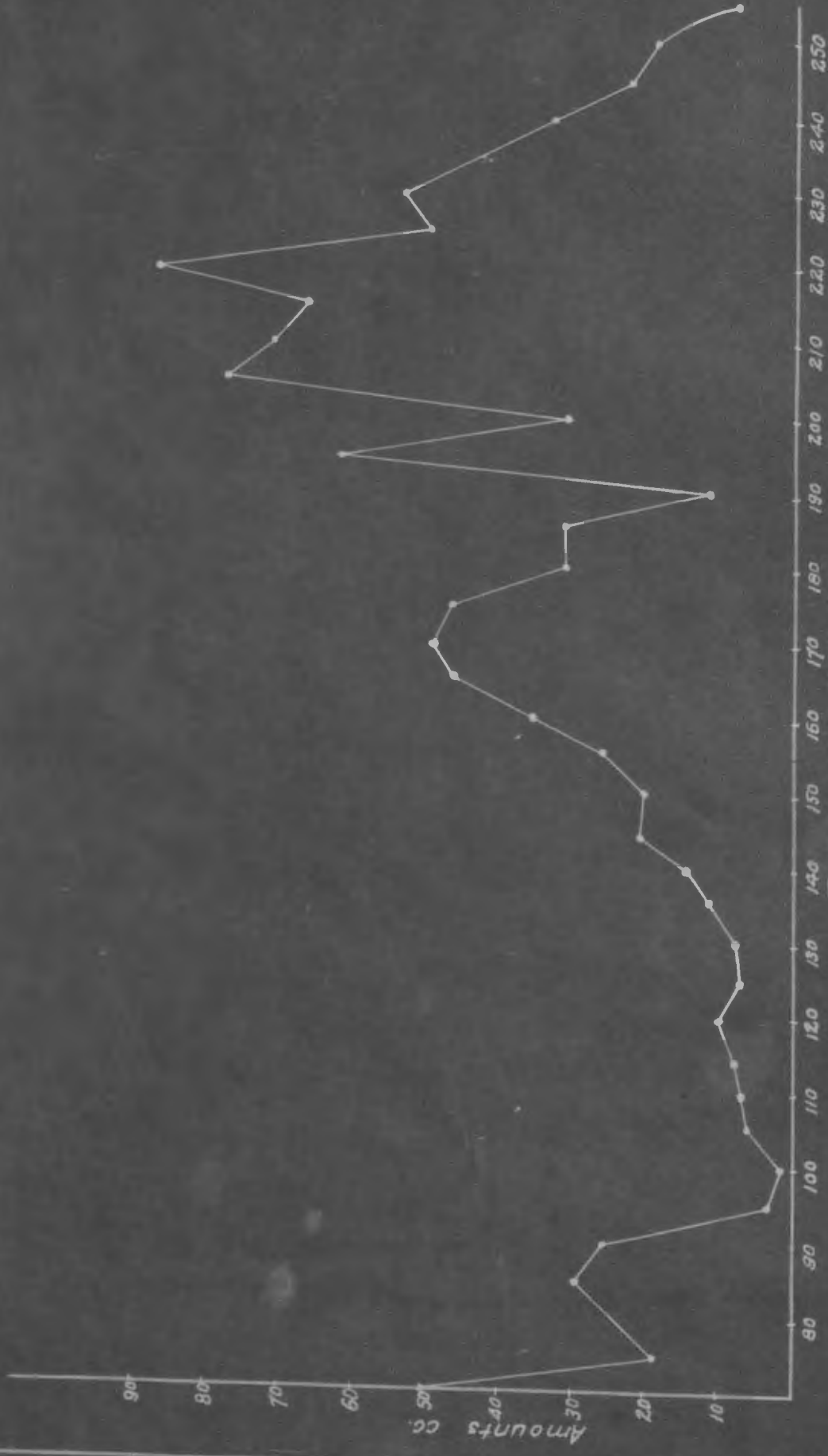
tained which after drying with CaCl_2 distilled entirely between 130 and 130.5° . He states that the usual yield of adipic ketone is from 3 to 4% but reports having obtained a 7 $\frac{1}{2}$ % yield in one case.

Cahours (Liebig's Annalen 76 p.286) treated raw wood spirits with conc. sulfuric acid. A clear oil separated out which after washing with water, was distilled fractionally over phosphoric acid. The fraction boiling between 108 and 112° was toluene, while that boiling between 128 and 130° was xylene and the portion distilling at 148° was identified as cumene.

It can readily be seen from the variety of substances found in wood oil that the material is of a rather complex nature. The purpose of this investigation was to find if possible any probable use to which the crude wood oil may be put, or to determine whether or not any substance or mixture of substances of industrial application could be isolated from the crude wood oil under investigation.

EXPERIMENTAL

Distillation. Ordinary fractional distillation using a Hempel tube was first tried. Fifteen hundred cc. of the material was taken and fractions collected every fifteen degrees. The first fraction (less than 90°) separated into two layers. The top layer was then redistilled but no constant boiling point was obtained. A larger sample was then taken and everything collected up to 100° . The top layer was again taken and redistilled repeatedly, but as before no pure substance or constant boiling mixture was obtained. However, the substance procured in this manner was colorless and boiled between 54 and 56° . The material was highly unsaturated, but upon attempting to make a saturated compound



Distillation Curve

by treatment with bromine or iodine a black tarry substance resulted. The amount obtained was so small that it was thought inadvisable to spend any more time trying to identify the substance since separation on an industrial scale would be accompanied by great difficulty and expense. The remaining fractions (90 to 260°) were then redistilled and fractions at five degree intervals were collected. The curve shows the amounts of material obtained in the different fractions.

An attempt was made to effect better separation by passing a stream of air through the distilling flask thus preventing superheating. The distillation was then carried on very slowly, but no appreciable change in results was found. Distillation under diminished pressure produced corresponding results.

Steam Distillation was also resorted to, but without avail. The distillate separated into two layers and the top layer was redistilled, but again no substance with definite boiling point could be isolated. The material that distilled over was highly unsaturated as would be expected, but here again, upon treatment with iodine or bromine, a tarry material resulted.

TREATMENT WITH SODIUM BISULFITE.

When the crude material was treated with a saturated solution of NaHSO₃ and allowed to stand no crystals separated out. Four hundred cubic centimetres of the oil were taken and shaken vigorously with a strong solution of NaHSO₃ and allowed to stand, but the addition product did not appear. A small amount of acetone was then added and the

crystalline compound $\begin{array}{c} \text{CH}_3 \quad \text{OH} \\ \quad \quad \diagdown \quad / \\ \quad \quad \text{C} \\ \quad \quad / \quad \diagdown \\ \text{CH}_3 \quad \text{SO}_3\text{Na} \end{array}$ separated out in a short time. The wood oil was then treated with NaOH and SO₂ was passed into the mixture

until saturated, thus forming the NaHSO_3 while in intimate contact with the wood oil. Here again the two layers were formed, but the crystalline addition compound did not separate out. Fraps treated certain fractions after having been distilled repeatedly, with syrupy NaHSO_3 and was able to isolate valeric aldehyde, acetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone and adipic ketone in small quantities. From the experimental evidence above cited it is obvious that Fraps either worked with an oil that had been obtained very differently from the one in our possession or that it is absolutely necessary to fractionate before the addition compound could be obtained. Here again it became very evident that commercial separation of the aldehydes and ketones by means of the bisulfite method would not be possible with the present facilities since the aldehydes and ketones could not be separated directly from the crude oil. Distillation, in order to obtain fractions corresponding to those studied by Fraps, would also be out of the question on account of the expense involved.

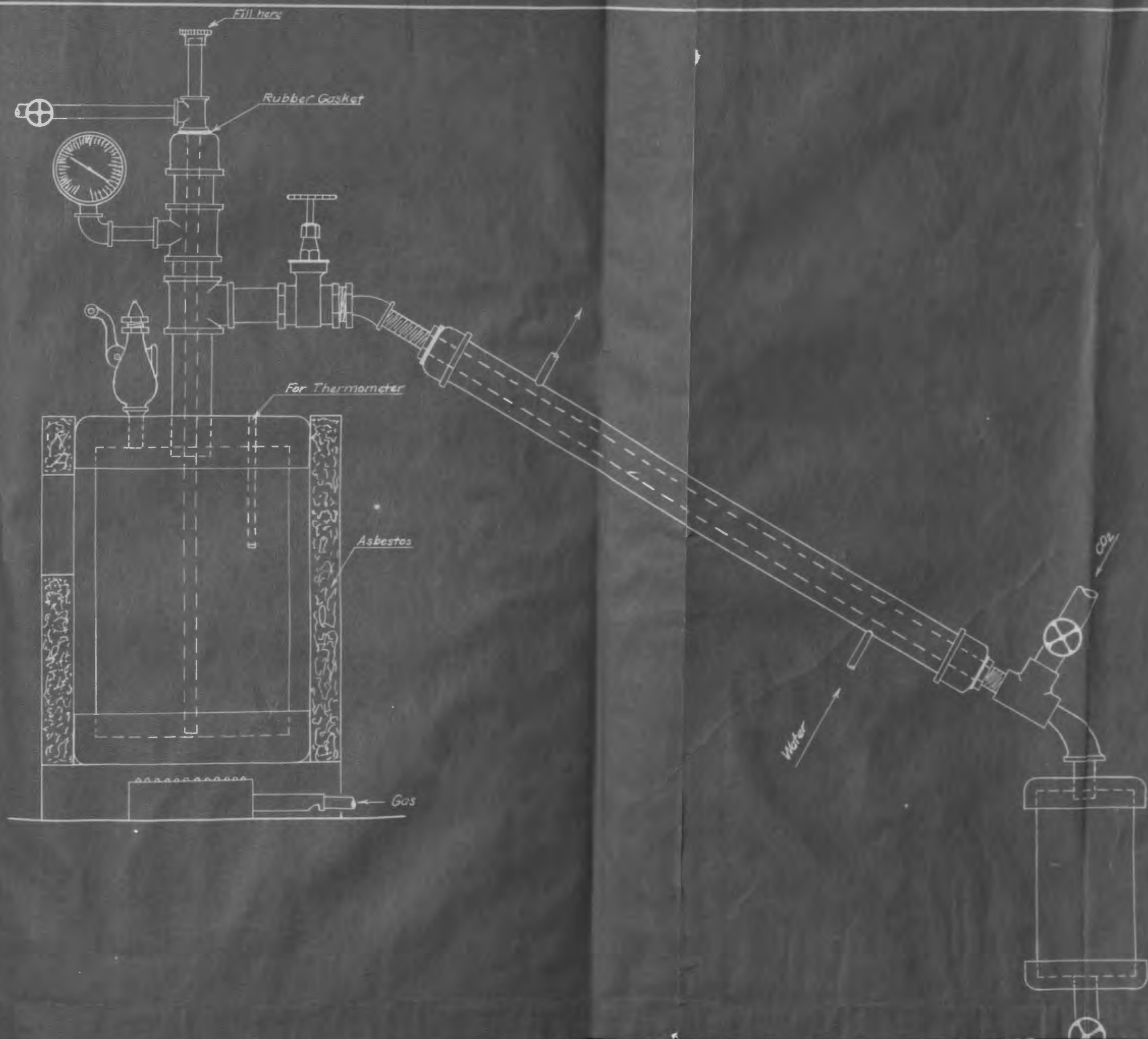
TREATMENT WITH KOH

It has been known for some time that wood creosote contains phenols and phenolic derivatives. Therefore, it was thought that we might reasonably expect to find some substances of this character in this crude wood oil. In accordance with this the oil was treated with a KOH solution in order to dissolve any phenols and any of their derivatives present. The crude oil on treatment with KOH formed two layers as expected. The part soluble was then drawn off and neutralized with HCl and a heavy black oil with a rather pleasant odor, at least pleasant compared with that of the crude oil, was thrown out.

Witt has propounded the well known theory that the coloring power of a compound depends upon two factors. The first of these is the presence of certain groups which he calls chromophores, among them being the azo group, the nitro group, the nitroso group, the double carbon linking and the quinoid group. The presence of any one of these groups accounts for a colored substance or chromogen. However, in order that a colored substance may be used as a dye, it must be able to give up its color to fabrics, therefore, the presence of a chromophore group in a compound even though it does produce a colored compound, is not sufficient. The second of these factors, according to Witt, is the presence of an auxochrome group such as the NH_2 , OH , SO_3H or, in general, any group which imparts an acidic or basic character. Since the OH group is among the auxochromes it was thought that if these precipitated phenols were coupled with a chromogen a dye would be obtained. The azo chromophore grouping was obtained by diazotizing p-nitro aniline and to this diazonium compound a solution of the crude phenols in NaOH was added. A solution which was orange colored when acid, and wine-red when alkaline, resulted. Benzene and toluene were used to extract the orange colored dye from the acid solution, but only a small amount of coloring matter was obtained, on account of the small amounts of material that were used.

DISTILLATION UNDER PRESSURE.

An apparatus was arranged as shown on the print. The flask was made of a piece of six inch wrought iron pipe with caps screwed on both ends. The top cap was tapped for an $1\frac{1}{4}$ inch pipe, a safety valve and a small pipe for the thermometer. The small pipe extends into the still and is capped. The thermometer was then placed in this pipe and the approximate temperature was thus obtained. The large pipe corresponds to



the neck of a distilling flask. The side-arm is also made of $1\frac{1}{4}$ inch pipe and is connected through a gate valve to the condenser. The condenser consists of a $\frac{3}{4}$ inch pipe through an $1\frac{1}{4}$ inch pipe. Holes were drilled in the caps at both ends of the condenser jacket so that the $\frac{3}{4}$ inch pipe passed through freely. The $\frac{3}{4}$ inch pipe was threaded at both ends and a lock nut and rubber gasket served to make a tight joint at each end of the condenser jacket. An arrangement functioning exactly like the ordinary wash bottle enables one to withdraw the residua after distillation without difficulty. The long $\frac{3}{4}$ inch pipe extends to the bottom of the still and whenever the residua is to be removed the small valve is opened and the pressure in the still does the rest. The cap screwed on the $1\frac{1}{4}$ inch pipe was threaded and a long thread was cut on the $\frac{3}{4}$ inch pipe. The $\frac{3}{4}$ inch pipe was then screwed into the $1\frac{1}{4}$ inch cap as shown. The $\frac{3}{4}$ inch tee was then turned down on to the cap and by inserting a rubber gasket a perfectly tight joint was obtained.

The crude oil was distilled in this still in an atmosphere of CO_2 under a pressure of from 50-60 pounds per square inch, but there was no noticeable difference between the products obtained by this method and those obtained by ordinary distillation.

SUMMARY

(1) Ordinary fractional distillation, as well as steam distillation, was attempted, but no definite boiling product could be isolated. Fractional distillations at pressures less than and greater than atmospheric pressure were also carried out, but as before no substance or mixture of substances with definite boiling point was obtained.

(2) Treatment of the crude wood oil with NaHSO_3 did not yield any addition compound with aldehydes and ketones as was expected.

(3) A heavy black oil soluble in KOH was isolated which, when coupled with diazotized p-nitro aniline, gave an orange colored substance in acid solution and a wine colored substance in alkaline solution. From an industrial standpoint this KOH soluble material offers more possibilities than any of the other portions of the wood oil and more extensive investigation of this part of the wood oil would undoubtedly lead to something of commercial importance.

Thanks are due Dean George B. Frankforter under whose direction this work was carried out.