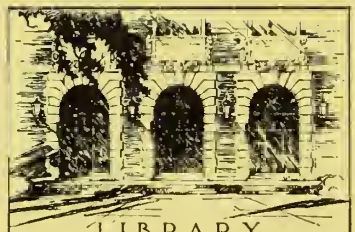

A STUDY OF CERTAIN ILLINOIS OIL SHALES

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY TERRENCE ONAS WESTHAFER

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy

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ACKNOWLEDGMENT

This investigation was carried on in the Chemical Laboratory of the University of Illinois in the years 1916-1917 and 1917-1918. It was undertaken at the suggestion of Professor S.W. Parr and carried out under his direction.

I take this opportunity to express my sincere thanks and appreciation to Professor Parr for the help and direction he has given with the present investigation.

I wish also to thank Dr. F.W. DeWolf, Mr. F.A. Holbrook, and Mr. G.H. Cady, for their cooperation in furnishing the shales used in this investigation.

I INTRODUCTION

1. Prefatory Note.- The rapidly increasing demand for petroleum products emphasizes the desirability of investigating other oil and gas producing materials. The present zoning and redistribution of coal likewise increases the desirability of using materials for gas manufacture which have been disregarded hitherto in this country. The investigation, the report of which follows, has consisted of a study of certain bituminous deposits of this state with reference to the character, amount, and modification of the products of their distillation.

2. The Ingredient Materials of Oil Shales and Analogous Deposits.- It has apparently become the tendency lately to include under the general term oil-shale all shale-like sedimentary deposits containing organic detritus from which crude oil, or more properly tar, can be obtained by destructive distillation. Such a conception has the advantage of simplicity, and furnishes a ready distinction from oil bearing deposits from which petroleum is obtained by well known methods; but its scientific usefulness is somewhat impaired for the reason that its very comprehensiveness demands explanation. It is a matter of some importance, from the standpoint of preparation for a discussion of the utilization and nature of oil rock products, to consider briefly the great variety and intergradation of bituminous deposits and the causes contributing to their differentiation.

The nature and origin of the organic remains in the deposits have very naturally constituted one basis of classification, and microscopic studies of all types of coals, cannels and shales have been worked out elaborately by various investigators. For the present purpose it is necessary only to note briefly the general type

and character of some of the contributing agencies and the resultant organic detritus. According to David White[1] the woody matter which forms the large part of peats and their alteration products, the coals, and which appears to a lesser extent in other bituminous deposits, is composed largely of carbohydrates relatively high in oxygen. Ordinary coals are therefore high in oxygen and humic acid compounds. These have their origin mainly from organic debris of vascular plants. More resistant types of organic matter of resinic nature have arisen from the decay of great amounts of resin-bearing wood; and under certain conditions of deposition there were laid down quantities of spores and pollen grains, seed envelopes, and other resinic highly resistant parts of plants. With these mingled remains of algae, small crustacea, insect eggs, larvae, and other plankton, and even fish. In contrast to the high oxygen content of the woody matter, lies the high hydrogen and low oxygen content of the organic debris derived from such resinic and fatty animal and plant remains. It is to be expected therefore that the state of the ingredient matter of any deposit at the present time is determined by the nature and proportions of the admixture of organic contributions from these sources, and the character and extent of the agencies active during the deposition and afterward.

The same authority recognizes two stages in the formation of the deposits. The biochemical stage of decomposition of the original matter includes the action of temperature, moisture, access of air, toxic biochemical products, bacterial agents, and such other agents as might concievably have been active during the deposition. With the burial of the sediment such agencies ceased acting, and then began the dynamo-chemical stage wherein various alterations have

occurred because of regional and local earth movements. Great pressures developed because of folding and the weight of overlying sediments. Locally igneous intrusions have contributed to the metamorphosis of deposits. It is quite probable that the effect of pressure is the more important and extensive, with temperature playing a secondary role, except in some cases locally where its action has been more marked. Thus occurred the gradual induration and further modification of the purer deposits like peat through lignites and coals to graphite; while the organic muds became oil shales, cannels, carbonaceous shales and graphitic shales.

The reason then is obvious why complete intergradation should exist between coals of the originary type and cannel coals, and between cannels and oil shales. With the increasing predominance of debris of fatty or resinous nature, the deposit ranges from torbanite to cannels and boghead coals, and with further increase in amount of mineral matter the deposit becomes known as an oil shale or bituminous shale; while shales containing very little organic matter are carbonaceous.

Deposits of decaying spore and pollen material, with other animal and plant debris, which have been originally laid down as organic slimes, muds and oozes, were designated by Potonie as sapropel.[2] Every bituminous shale or other deposit arising from the induration of such muds, slimes and oozes has been found to contain remains of a sapropelic nature. Potonie found that the organic material in the torbanites and cannels of Australia was of vegetable origin and consisted of algae, being in reality a fuccidal coal. Petrie[3] confirmed this finding, and reported further the presence of humic material, spores, pollen grains, etc., but the entire absence

of animal detritus. Conacher[4] found two types of vegetable remains present in the shales from the Lothians, Scotland. There were (1) macrated and carbonized plant materials similar to that of which coal is composed, and (2) certain yellow bodies made up of spores, algae, etc. Other investigators[5] have reported imprints of marine animals in Scottish shales, and concluded therefrom the possible contribution of animal substance to the organic material in the deposit. In the oil shales of the Green River formation in this country C. A. Davis[6] found the same low plant forms, like algae, present in great abundance. Along with these are pollen grains from conifer trees, insects and larvae, as well as fish scales and skeletons; but in most specimens little evidence of other than plant life occurred. Instances might be multiplied, but it is significant that, so far as microscopical studies are available, animal life seems to have played a very subordinate part in the origin of most oil shale and allied deposits. The chief interest, however, lies in the fact that deposits in which this sapropelic material is abundant have formed the raw materials for the shale distillation industry, and that with the increasing predominance of this material in the deposit the distillates are increasingly greater in quantity and in nature more and more like petroleum itself.

Whatever the chemical or physical state of the organic material in deposits may be now, the fact that more or less rearrangement of elements occurs during distillation of the raw material is well known. The elements carbon and hydrogen apparently always predominate in the distillates, with nitrogen and sulphur in much smaller but varying amounts. Other elements enter to the extent of traces into the composition of the volatile products. The extent of present

knowledge concerning the effect of contributing agencies, whether animal, vegetable, or mineral, upon the character of the deposit and upon distribution of the elements among the products of distillation, and finally their utilization, will become evident in the discussion immediately following.

3. Historical Resume of Scientific and Technical Investigations. - A critical discussion of the investigations, which have been carried out from the beginning and which have scientific and economical interest, develops with some difficulty because of the widely varying purposes of the different investigators, Only those of interest to a fuller understanding of the development of the industry as it at present exists, and its further possibilities, and those which apparently have added new facts of more than local interest, will be discussed.

The investigation of the properties of paraffin by Von Reichenbach[7] in 1830, and his observation that "a wick pregnated with it burns like a fine wax candle, and without smell" was of primary importance in the early development of interest in the distillation of bituminous deposits. He isolated paraffin with a melting point of 43.75° C. from wood tar. Stimulated by his work Laurent[8] in the same year distilled a brownish-black, very fissile French shale, containing pyrites, and reported the following composition:

Oil	20	percent
Combustible gas	14	"
Residue		
Carbon	19	"
Ash	39	"
Water	8	"

He observed that the water contained ammonium sulfide and carbonate, and that the oil, like that from coal, contained acid soluble

substances as well as compounds of the nature and odor of wood tar creosote. From the higher fraction of the oil he succeeded in freezing out and refining solid crystalline paraffin, with a melting point of 33°C, very soluble in ether, and containing 85.745 percent carbon and 14.2 percent hydrogen, a result requiring the formula C_nH_{2n}.

He further noted that the shale tar did not contain naphthalene; and was in many other respects similar to distillates from wood. From 500 grams of the shale, he recovered traces of organic matter soluble in ether, but because of the small amount recovered, he was unable to distil it for paraffin, and his question as to the probable existence of paraffin as such in the shale was unanswered.

Later, the same investigator[9] reported that the properties of the various fractions of shale tar varied with the temperature. In this connection the 80-85° fraction, refined with sulphuric acid and distilled over potassium, gave an analysis corresponding to the formula C_nH_{2n}. The 115-125° fraction, after several distillations and treatments with nitric acid gave a portion boiling at 120-121°C., and having a specific gravity of 0.755 at 12°C. This he found to be unattacked by concentrated acids, but gave solid crystalline products on chlorination in the sunlight. Ultimate analysis gave 86.2 percent carbon and 13.6 percent hydrogen. The fraction 167-170°C. similarly treated, gave 85.6 percent carbon and 13.6 percent hydrogen. By treating the fraction 80-150°C. with strong nitric acid, Laurent isolated, besides picris acid, a substance he termed ampelic acid, isomeric with salicylic acid; and from the 200-280°C. fraction he obtained a creosote oil he called ampelin, which gave oxalic acid upon oxidation with nitric acid. Laurent again pointed out that solid paraffin could be obtained in quantity from the shale tar, and

suggested the exploitation of the deposit for the manufacture of illuminating gas as well as products of distillation.

Very soon in 1839, Selligue[10], acting on Laurent's suggestion took out patents, and began to manufacture paraffin and other products on a commercial basis. This fact perhaps entitles Selligue to the credit of having first placed the distillation of shale on a commercial basis.

Scotch shale tar has perhaps received the most detailed investigation of any. C.G. Williams[11] in 1854 investigated the bases in this tar. He reported the discovery of a series of bases, identical to those procured by distillation of coal and bones, namely, the series $C_nH_{n-5}N$. He isolated pyridine, picoline, and lutidine, but found no aniline[12]. G.C. Robertson[13] obtained bases of the quinoline series from scotch shale tar. Recently, however, Garrett and Smythe[14] have identified in "green naptha", the lower boiling fraction of Scotch shale tar, the following members of the pyridine series: pyridine, 2-methylpyridine, 2:6-dimethylpyridine, 2:4-dimethylpyridine, 2:5-dimethylpyridine, and 2:4:6-trimethylpyridine. From the green oil, or higher boiling fraction, the same investigators[15] succeeded in isolating and identifying only two members of the same series; namely, 2:4:6-trimethylpyridine and 2:3-dimethylpyridine, but reported the presence of higher boiling nitrogen bases difficultly separable in the pure state and decomposing more or less at their boiling points.

A highly important investigation was carried out by Beilby[16] on the distribution of nitrogen and nitrogeneous products in the products of distillation of Scotch shale. He found that ordinary dry distillation produced a distribution of nitrogen as follows:

As ammonia in the watery distillate	17.0	Percent
As alkaloidal tars in the oil	20.4	"
In the residue	62.6	"

A further redistribution takes place in the distillation of the crude tar, giving some ammonia, and oil containing less nitrogen, and a coke of marked nitrogen content, the amount of nitrogen increasing in the order named. At about this time the Scotch manufacturers were in need of a method by which the high nitrogen content of their residue could be used to more advantage in the production of salable products, because the competition of imported petroleum products with the products they were then manufacturing was growing keener. **Beilby** passed steam through the hot residue from the dry distillation process and succeeded in improving the distribution of nitrogen to a very marked extent. His results are as follows:

As ammonia in the watery distillate	74.3	Percent
In the oil as alkaloidal tars	20.4	"
In the residue	4.9	"

He was instrumental in the development of the modern form of shale distilling retort in use in Scotland, which is also in extensive use wherever the industry has developed. The fundamental principle of the retort merits mention here. It consists of an upright cylinder, whose upper part is made of iron and whose lower part is of firebrick or other refractory material. The shale is fed in at the top and progresses downward through zones of successively rising temperature. Steam is introduced in the lower portion, and acts upon the hot residue, the resulting gases passing up through the charge, and carrying with them the vapors distilled from the shale in the upper and cooler regions. With many mechanical variations the various types of retorts now in use conform to this general principle quite

closely.

The acidic substances in the green naptha of Scotch shale tar received the attention of T. Gray[17]. From 3,200 gallons of the naptha he recovered approximately 1.5 gallons soluble in dilute sodium hydroxide. By systematic fractional distillation and conversion into nitrophenols, Gray identified the members of the phenol series and reported their approximate quantity in percentage of total creosote as follows:

Phenol	5-6	Percent
Orthocresol	12-15	"
Metacresol and 1:2:4 and 1:3:5-xylenols	30-35	"
Above 230°C.	16	"

No paracresol or creosol were found present; but guiacol was isolated in small quantity.

It was early recognized that commercial products derived from the distillation of shale and refining of the shale tar differed from parallel petroleum products with respect to their reaction with strong nitric and sulphuric acids. A.H. Allen[18] compared the extent of unsaturation of the napthas, burning oils, and lubricating oils derived from the two sources with regard to their bromide absorption. The bromide absorption was greater in the case of the shale oils, and the difference was most marked in the case of the napthas, the absorption in the case of gasolene being thirteen times as great in the shale gasolene as in the gasolene from petroleum. His results are of interest.

	Sp. g.	Gms. Br. per 100 gms. sample
Gasolene from shale	.665	67.1
Gasolene from petroleum	.652	5.1
Naptha from shale	.718	94.9
Naptha from petroleum	.690	10.0

Burning oil from shale	.801	38.7 Percent
Burning oil from petrol.	.806	17.2 "
Lubricating oil from shale	.889	56.4 "
Lubricating oil from petroleum	.862	21.6 "

He was, of course, unable to derive any conclusions as to the exact volumes of olefines, since the bromine absorption number is not a measure of volume relationships in the case of such complex products.

G. Kraemer and W. Bötcher[19] were the first to contend that the hydrocarbons in petroleum, shale tar and coal tar differs not in character so much as in relative proportions of two classes of hydrocarbons: those unattacked and those attacked by concentrated sulphuric acid . With the first group they classed paraffine and napthenes, and with the second, benzene and napthene derivatives, and olefins. After the presence in shale tar oils of unsaturated hydrocarbons had been demonstrated, A.K. Miller and T. Baker[20] examined the fractions of shale naptha boiling from 75-85° C., 120-125° C., and 140-145° C. They found each fraction to consist of about 50 percent paraffine (and napthenes), the remainder being partly olefins and partly less saturated hydrocarbons, and they demonstrated the presence of the normal olefins up to nonylene. They commented upon the fact that in the manufacture of oil gas the paraffins are almost totally destroyed, and no olefin higher than hepthylene[21] is obtained, while light shale tar oil is rich in paraffins and olefins, evidently produced by decomposition at lower temperatures than those used in the manufacture of oil gas.

Basil Steuart[22] demonstrated the presence in the lower fractions of shale tar of pentane, hexane, heptane, and certain isomers, and found that they were quite probably associated with certain

cyclic compounds; namely, methyltetramethylene, pentamethylene, methylpentamethylene, hexamethylene, and methylhexamethylene. He likewise proved the presence of benzene and toluene, and reported the approximate percentage of benzene in the fraction originally boiling from 55 to 75°C as 2.6 percent, and the percentage of toluene in the fraction 80 to 90°C. as 2.5 percent. The same investigator[23] determined the relative amounts of paraffins and naphthenes, and olefins and other unsaturated compounds in certain lower fractions of shale oil carefully and laboriously fractionated. His results follow:

Fraction	Percent Paraffins	Percent Olefins
26-37°C	30	70
37-45°C	36	64
45-58°C	46	54
58-65°C	45	55
65-67°C	47	53
67-69°C	50	50
69-72°C	49	51

It is significant that the relative percentages of the first class of compounds increase, while the values of the other decrease with increase of temperature.

Heusler[24] made a careful comparative study of the amounts of the different types of hydrocarbons in Scottish shale tar and Saxon lignite tar oils. He found in the fraction boiling up to 110°C. in each case the following quantities:

	Percent in lignite oils	Percent in shale oils
Paraffins	16	42
Napthenes	14	10
Aromatic hydrocarbons	45	7.3
Olefins	31	39

He ascribed the difference in aromatic content to the fundamental

difference in the chemical nature of the organic detritus in the raw materials. This question had been raised previously, it will be remembered, as early as Laurent; but Heusler was the first to offer a definite hypothesis. He concluded in this particular case that the difference in question was due to the fact that the Scotch shales contained animal residues, while the lignite contained plant residues only. He also disputed Berthelot's well known theory[25] that the presence of aromatic constituents in the products of distillation of organic materials arose through the formation first of acetylene and its subsequent polymerization under the influence of high temperature to benzene and other aromatic compounds.

Heusler reported the following paraffin content in carefully fractionated oil from which had been taken the acid and basic compounds:

Fraction	Sp. G. 15°C	Percent Paraffins
105-120°C	.7290	40
120-130°C	.7405	40
130-140°C	.7470	40.8
140-150°C	.7555	42
150-160°C	.7605	42.8
160-170°C	.7650	44

Here it is to be noted, that the percentage of paraffins increases with the temperature, but is lower than that reported by Steuart. Heusler established the presence of paraffins of the formula C_8H_{18}, C_9H_{18}, $C_{10}H_{20}$, and the corresponding naphthenes. He likewise reported the presence of benzene, toluene, metaxylene and cumol, but no naphthalene; and found that the lower boiling fractions contain nitriles of fatty acids in small quantity. In this particular oil he found the percentage of sulphur in the fractions 130°-140°C. and 170°-180°C. to be about .25 percent.

The comparison which Heusler made between shale tar oils and lignite tar oils is of some importance in the consideration of the effect of the nature of the organic detritus in the raw material upon the type of distillate obtained. Of course, it is to be remembered that any comparison of this sort is valuable only in so far as the conditions attending distillation of the raw material have been the same. But it is also happily the fact that very similar methods are used in the distillation of shale and of lignite.

While investigation in connection with the probable relationship of all organic deposits is progressing, the extent to which the nature of the organic residue of any deposit determined the yield and character of the products on distillation, and the extent of the effect of temperature, pressure, and the mineral constituents of the raw material have not yet been established. It is interesting to note the results of Jones and Wheeler[26], who examined the products of vacuum distillation of bituminous coals. The oils boiling below 300° C. contained the following substances.

(a) Unsaturated hydrocarbons, for the most part richer in carbon than the mono-olefins, C_nH_{2n}. These formed between 40 percent and 45 percent.

(b) Naphthenes (C_nH_{2n}) and liquid paraffins, the former greatly predominating, forming together about 40 percent.

(c) Phenols, chiefly cresols and xylenols, between 12 percent and 15 percent.

(d) Aromatic compounds, apparently homologues of naphthalene, although naphthalene itself was not present, about 7 percent.

(e) A solid paraffin in small quantity of molecular weight, 373.7.

(f) Pyridins bases in small quantity.

Benzene, anthracene and carbon disulphide were absent; naphthalene and its homologues appeared to be present in minute quantity if at all.

A comparison with the results of Heusler on shale tar will reveal remarkable resemblance, and point toward the common organic source of the types of compounds present. It is also interesting to note that Heusler postulated the probability of the derivation of aromatic substances immediately from the organic detritus in the lignite and shale, and that in the same connection Jones and Wheeler explain the presence of the napthenes, paraffins, and olefins, as well as the aromatic substances by the assumption that the compounds themselves exist in the bituminous substance linked to more complex groupings which are the degradation and polymerization products of wavy and resinic substances. The original unsaturated compounds may have , under the influence of dynamic pressure, become polymerized or converted into compounds containing the naphthene grouping.

In connection with the solubility of the organic material present in shale and analogous deposits there exist remarkable points of difference. Whereas the bitumen present in lignite is quite readily extractable with benzol and like solvents, that in most bituminous shales is soluble in these solvents with great difficulty. Many investigators assume the presence of a combination of some sort between the organic material and the mineral substance of the shale, and give the name kerogen to the hypothetical compound[27]. Indeed, the Scotch shales are quite frequently referred to as kerogen shales. On the other hand the organic matter in Australian torbanite and cannel coal is soluble to quite an appreciable extent, and these shales are called kerosene shales. Conacher[4] ascribes the failure

to obtain appreciable amounts of extract by solvents to the fact that the solubility of resins rapidly decreases with age.

Recent investigations of particular interest in connection with the present report have been carried out under the direction of the United States Geological Survey and concern the extent and characteristics of oil shale deposits in the United States. These have included a study of the yields and character of distillation products of shales varying in age from Devonian to Eocene. According to Winchester[6] the shales of the Green River formation (Eocene) of Colorado, Utah and Nevada, are the richest so far examined, and compare favorably with the oil shales which have been worked for considerable time in Scotland and France. Shales of Cretaceous age in the Rocky Mountain States have so far not proven of great value. Black Triassic shales of North Carolina will yield oil on distillation, and the diatomaceous Tertiary shales in the California oil fields may eventually become the source of commercial quantities of oil and other products. Shales of Carboniferous age of the type of so-called "roof-slate" from coal mines in Kentucky and Illinois yield as much as 16 gallons of oil per ton of shale, and cannel like shale in western Pennsylvania yields as high as 45 gallons per ton.

The Devonian shales of the middle and eastern states were the first to attract attention, and, according to Baskerville[28], fifty-five companies of more or less importance had been organized and were distilling shale and like substances in the United States before the exploitation and rapid development of the petroleum fields.

The salient features of the investigation of Winchester[29] of 132 samples of shale from the area in and adjacent to

northwestern Colorado are worthy of note. The samples showed a variation in yield of oil from 0.31 to 90.0 gallons per ton of shale. The yield of ammonium sulphate from 110 samples, distilled without steam, ranged from 0.4 to 18.3 pounds to the ton. The yield of inflammable gas ranged from 500 to more than 4500 cubic feet per ton in 26 samples. All samples were taken near the outcrop, and it is quite probable that some of the more volatile constituents may have been lost by evaporation or weathering. The oils obtained from the distillation of the shale were reddish brown and at ordinary temperatures range from liquid to semi-solid vaseline like products, with specific gravity from .8449 to 0.9496, with that of a large majority below 0.90. Steam distillation in many cases improved the yield of oil which was increased from 10 to 50 percent. The oil resulting from steam distillation was uniformly of greater specific gravity than that obtained from the same shale by dry distillation. Fractional analysis of the oils indicated possible yields of gasoline from 6 percent to 12 percent, kerosene from 28.5 percent to 49 percent, paraffin 1.63 percent to 7.70 percent, and sulphur contents from 0.42 percent to 1.42 percent. The investigation also disclosed the fact that under dry distillation conditions 11.1 percent of the possible maximum yield of ammonium sulphate was recovered, while the use of steam increased this average recovery by the factor 2.5.

Two samples of shale oil were subjected to the Pittman[30] process of refinement, using 150 pounds pressure and temperatures from 525°C. to 600°C. in the furnace. The samples used gave 22.6 percent and 19.0 percent distilling below 175°C. Treatment of the residuum above that temperature resulted in a recovered oil giving additional fractions below 175°C. The quantitative recovery is not

stated.

The shale oils in general are characterized by a large proportion of unsaturated hydrocarbons, involving a considerable loss in refining by the usual methods. D. T. Day[31] reported the results of experiments in hydrogenation of the oils under pressure and in the presence of catalysers. Samples were distilled under a pressure of 70 to 80 pounds in an atmosphere of hydrogen. The still contained a coil of tubes filled with a catalyser consisting of finely divided nickel with a small proportion of palladium, namely, ten ounces to the ton. The vapor of the oil and the hydrogen passed together through the catalyser before leaving the still. The shale oils which, under ordinary distillation, yielded oils ranging from 17° to 24° Baume, gave by this method oils from 24.4° to 39.7° Baumé. On redistillation of the lower seven cuts with steam there was obtained a large yield of naphtha suitable for all purposes for which gasoline is used.

Of particular interest are the reports of two investigators concerning oil shales found in Illinois. G.H. Ashley[32] has recently tested a sample of roof shale over No.5 coal from East Capitol mine, Springfield, Illinois. The calculated yield of oil per ton of shale was 11.9 gallons, with 9.6 gallons water and .61 pounds of ammonia. The yield of gas was 2.922 cubic feet. A sample from the roof shales of the same coal in Gallatin county yielded 16 gallons of oil, 7.5 gallons of water, and 3.44 pounds of ammonia. The investigation did not extend further.

The occurrence of a deposit of oil shale in the northwestern part of Illinois and adjacent areas in Wisconsin and Iowa is reported by G.H. Cox[33]. Analysis of a sample taken from this deposit taken

from the neighborhood of Platteville, Wisconsin, showed the following results:

Natural oil by extraction with benzol	0.36	percent
Oil by destructive distillation	2.86	"
Loss and gas	1.91	"
Water	8.71	"
Mineral residue	6.16	"

The oil obtained closely resembled creosotic oils obtained from wood, and it was suggested that the shale would serve better as a gas producing material. No appreciable increase in yield was obtained by vacuum distillation, showing that but a small quantity was present in the shale as oil.

4. *Scope of the Present Investigation.* - The present investigation has consisted of the preliminary examination of samples of shales outcropping in different localities of the state. Following the preliminary tests, an experimental plant was built with adequate capacity to care for the products of the distillation of twenty pound lots of the shales. A series of comparative runs with six different samples were made, and the type and yield of the gases and tars from them were investigated. A shorter series of runs under different conditions of distillation furnished the basis for a study of the modification of the yield and character of the products from the shale yielding the greatest amount of tar. This shale was also tested with regard to its gas producing qualities by the use of the water gas reaction. A further and more complete study was made on the tar from this shale.

The term tar used in this report is synonymous with the more usual term oil. The reason for its use lies in the belief that in the classification of natural and artificial bitumens, tar should include products of an oily nature which are won by artificial means

from the medium containing them. When tar is mentioned, it is understood that reference is made to the crude product of shale distillation. All products made by subsequent distillation of the tar are called tar oils, or simply oils.

SHALE DISTILLING PLANT

II EXPERIMENTAL WORK

1. Shale Distilling Plant. - The primary consideration in the design of the experimental plant used in this investigation was the distillation of shale in large enough lots to furnish distillates in suitable quantities for fairly thorough testing. The apparatus was built from standard materials and fittings on hand. Although the idea of convenience and economy of labor and time was kept in mind, there was no intention to evolve any unique mechanical features; hence, no claim is made for any possible commercial application of it. A photograph of the plant is found on page 20 and a diagrammatic drawing on page 25.

The retort is a fiftyfour inch length of four inch iron pipe, having at either end a companion flange nine inches in external diameter. It is supported within the furnace by two iron bars under the top flange. The bars lie upon the surface of a square of thick asbestos board which forms the top of the furnace and lies immediately upon the upper tier of fire bricks. The board fits snugly around the retort two inches below the flange, together with asbestos cement immediately under the flange, and serves to protect the cast iron flange from the direct heat of the furnace. The companion flange closing the bottom of the retort is fitted with an inch by two inch nipple, an inch by inch by three-eighths inch tee, and an inch by three-eighths inch bushing, through which projects upward a thermocouple well, made of a twenty inch length of three-eighths inch pipe, capped at the top. Through the three-eighths inch opening in the tee, connection is made with the steam preheater. The thermocouple well projects upward ten inches into the heated zone of the retort.

The head of the retort consists of a companion flange fitted with a four inch close nipple, a four by four by two inch tee, and a four by two inch bushing. To the bushing is connected a short two inch nipple carrying at its top a brass stop cock of two inches internal diameter, through which the shale is introduced. To the two inch opening in the tee is attached a two inch close nipple, a two by two by one inch tee, and a bushing through which there projects backward and downward into the retort the top thermocouple well, made of a capped three-eighths inch pipe which extends downward into the heated zone of the retort about four inches. The vapors escape into a one inch main suitably connected to the inch opening in the last mentioned tee. The complete head up to the lower part of the brass stopcock is covered with a thick coating of asbestos cement, and bricks are placed around the flanges and head in the manner shown in the photograph to prevent excessive radiation and cooling. The heated zone of the retort is four feet in length.

The furnace is built of firebrick set in fireclay and silica in the ordinary manner. Its dimensions are approximately 28 by 28 by 48 inches outside. The heating zone is approximately 10 by 10 by 48 inches. Vents were left in the walls at regular intervals for observation, and in the top layer of bricks for the escape of gaseous products of combustion. The furnace is supported upon a brick floor, in turn supported by six tee irons laid across the tops of fireclay building blocks in the manner shown best in the photograph. The bottom of the furnace is sixteen inches above the floor.

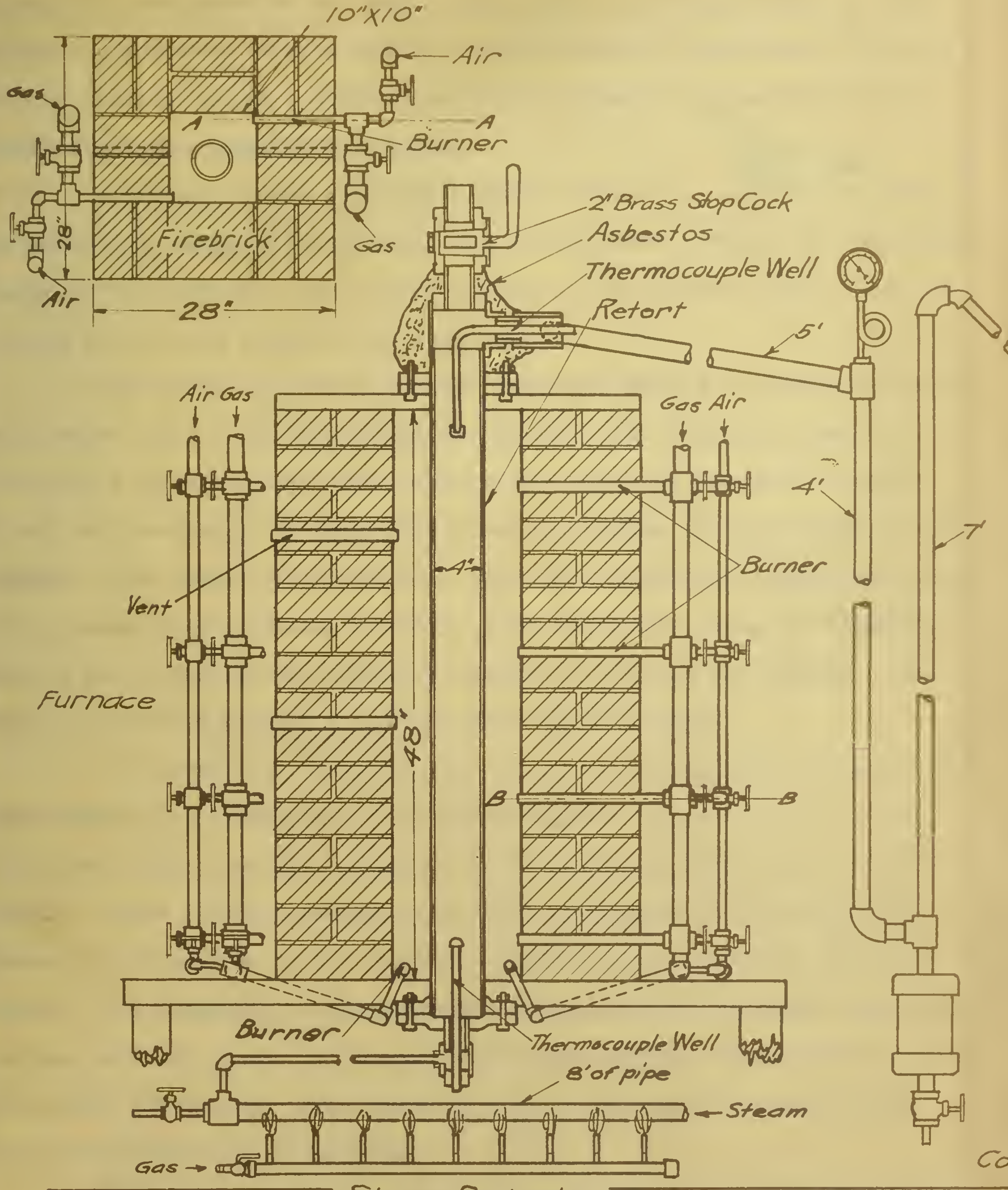
The heating elements of the furnace consist of twelve burners, four on each side and four around the bottom. Gas and air connections are made to the burners in the manner indicated in the

drawing. Each burner is a separate unit which may receive air or gas, or both, as desired and in the proper quantity. The side burners enter the furnace at opposite corners of the heating zone, and their flame does not impinge directly upon the retort pipe. With the proper velocity of air and gas the flame received a whirling motion, and the equal distribution of heat is very readily accomplished. The system admits of great latitude in the manner and rate of heating, and is fairly readily kept in proper adjustment. Each burner unit is made from standard size pipe on the ordinary blast burner principle.

The condensing system consists of two parts: (1) seventeen feet of one inch iron pipe, connected as in the drawing with due regard to efficient and complete drainage and mechanical accessibility, and (2) forty feet of half inch pipe coiled and mounted in a barrel, which has proper water and drainage connections not shown in the diagram. The air condensers drain into a trap made from a four by six inch iron nipple capped at either end. The top cap connects the trap to the condenser by means of a machine bored and tapped one inch opening, while the outlet on the bottom cap is made of half inch fittings. A pressure gauge completes the equipment of this part of the system. Connection is made to the coil as indicated in the diagram. The coil drains through a half-inch gate valve into a two liter separatory funnel fitted on the iron pipe nipple by a rubber stopper. The funnel is not shown in the illustrations.

The uncondensable gases are led through half inch pipe connections to the gas tanks. These are made of twenty-two pound galvanized iron sheeting, riveted and soldered, gas and water tight. Each consists of two parts: a bell three feet in diameter and four feet

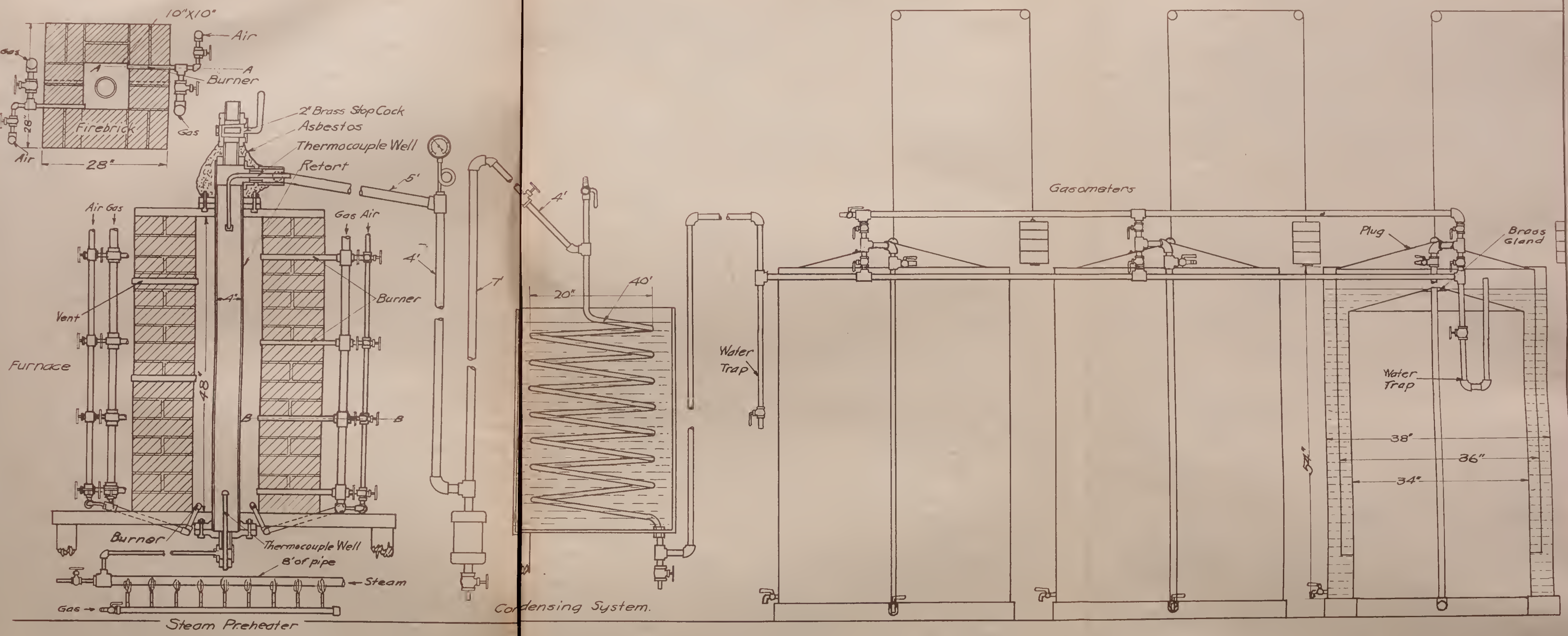
from bottom to shoulder, and a water container, the inner cylinder of which is 34 inches in diameter, and the outer one 38 inches in diameter. The height of the inner cylinder is one-half inch less than that of the bell, while the height of the outer cylinder is fifty-four inches. Each tank is properly braced and supported on a circular wooden platform, itself properly braced and mounted on heavy casters. This feature allows the tank to be moved readily even when full of water. Pipe connections are made with the sheet iron by means of brass glands riveted and soldered to the sheet iron. Each tank is provided with a valve for drainage at the bottom, and receives the gas through the half inch fittings shown in the drawing. A half inch valve at the bottom of the gas line at the point at which it runs under the tank provides a means to drain the pipe should it fill with water accidentally. Other valves and cocks are attached as indicated and serve for gas outlets or the attachment of a water manometer if desired. The tanks are connected together in such a manner that it is possible to manipulate them separately or together as desired during the filling or emptying of the gases stored in them. The bells are supported by weights hung over two inch pulleys, and the weights are regulated in such a manner that the pressure on all tanks is nearly identical. With very little care two or all the tanks could be filled simultaneously with the advantage of avoiding the necessity of taking more than one gas sample from a run giving more gas than the capacity of one tank alone. Each tank has a capacity of 28 cubic feet. The water traps shown in the drawing serve the purpose of catching any oil that may have condensed in the line, and the one at the end of the gas tank system serves also to protect the tanks from any suddenly developed pressure in the system.



Furnace

Steam Preheater

Co



SHALE DISTILLATION PLANT

After the shoulders of the bells rise above the water level in the tanks the pressure on the system is approximately equivalent to that of one inch of water. About five inches pressure is sufficient to start the bells upward when empty.

A running crane arrangement with block and tackle lift mounted above the furnace facilitates the lifting and removal of the heavy parts of the retort. The retort itself is so mounted that it can be lifted out of the furnace for repairs.

The steam preheating system consists merely of one inch iron pipe eight feet long, connected at one end with suitable traps to the high pressure steam line, and at the other by means of a short piece of three-eighths inch pipe through a union to the bottom of the retort. The burner consists of a four foot length of half-inch pipe with sixteenth inch holes bored at inch intervals along its length, and is connected in the ordinary manner to air and gas supply. The whole is mounted within a loosely laid brick furnace.

The remaining fixed feature of the plant is shown only in the photograph, and consists of two gas washers. They are made of two-inch iron pipe five feet long, with fittings as shown in the photograph. Three tightly rolled eight-inch cylinders of wire netting, placed at intervals of six inches beginning at the bottom of each washer, are intended to disperse the gases passing through into finer bubbles and by reason of the greater surface thus offered cause more efficient absorption. The washers may be connected in the system during distillation if desired.

The whole distilling system, exclusive of the tanks, is capable of withstanding thirty pounds steam pressure without leakage. Only pressures near atmospheric were used in the investigation. Some

trouble developed due to leakage around the gaskets used between the flanges, but it was overcome finally by the use of copper covered asbestos gaskets, six and three-fourths inches in diameter, heavily plastered just within the ring with a thick paste of oil and graphite. This method of gasketing proved to be easier to manipulate and superior in other respects to the use of high temperature garlock or other patent gasket materials.

The temperature measuring elements consists of thermocouples of Nickel-chromium No.16 resistance wire and advance resistance wire of the same size, welded at the hot junction with the oxy-acetylene flame, and connected from the cold junctions by means of copper leads to a millivoltmeter of 200 millivolt capacity. The elements were four feet long, and are insulated by means of closely wound asbestos string. After several heats such elements need to be recalibrated. With careful manipulation they are quite lasting. They were calibrated against a standard thermocouple unit of platinum and platinum-rhodium. The advantage of the use of such elements lies in the ease and cheapness of replacing those worn out.

2. Description of Testing and Analytical Apparatus.- Electric resistance furnaces were used for the analytical distillation of smaller samples of distillates. These furnaces were of one type and differed only in dimensions and length and capacity of the heating unit. For distilling kilogram samples of shale from an iron retort and similar quantities of shale tar a furnace was developed whose advantage lay in the ease and rapidity of its assembling. Sixty-five feet of No.16 Hoskins nickel-chromium resistance wire were wound on a three-sixteenth inch mandrel in a lathe. The resultant coil was stretched to the proper length and mounted spirally on a

core consisting of a seven-inch length of seven-inch stove piping, covered with three layers of thin asbestos paper held in place by sodium silicate. The spiral and core were then covered with a three-eighths inch thick coat of alundum cement paste, and the whole dried quickly by means of a lighted Bunsen burner placed within the pipe. The dried heating element was mounted within a sheet iron can of suitable dimensions and loosely packed with ground asbestos. A lid of the proper dimensions completed the furnace, and through the lid copper leads connected the ends of the resistance element with binding posts mounted on the lid. Such an element consumed approximately seven amperes at 110 v. without external resistance, and was of sufficient capacity for the purpose in hand. The rate of heating was regulated with ease by the use of external coiled resistance. After one or two runs to fairly high temperature the dried alundum core became quite rigid and strong, and after the sheet iron piping had fallen away a thin coat of alundum cement was placed on the inner surface of the old core.

A furnace of similar type and smaller size was used for the distillation of smaller samples of shale tar. The heating element of this furnace consisted of forty feet of No. 18 nickel-chromium resistance wire, and possessed a current carrying capacity of six and one-half amperes without external resistance. The core of the furnace was approximately six inches long by five in internal diameter. Since the furnace was used for analytical distillation of samples of different shale tars, the necessary feature was the adjustment of external resistance to guarantee the same rate of heating on each sample. This was accomplished by means of a combined carbon and lamp resistance with an ammeter in the circuit.

For the distillation of five kilogram quantities of shale tar a four gallon hot water boiler was fitted up with an iron condenser four feet long, and mounted within loosely laid brick walls. A covering of asbestos board prevented excessive cooling and decomposition of the refluxing tar at high temperatures. The distilling head was fitted in the usual manner with a thermometer well. The burner consisted of two lengths of half-inch pipe with one-sixteenth inch holes bored at inch intervals throughout their length and connected properly to air and gas supply. In this still the tar was distilled to coke, the maximum temperature at the distilling head attaining slightly over 500° C.

The gas analysis apparatus was a modified Orsat apparatus developed in this laboratory by F. E. Rowland. It consisted of the usual water jacketed buret, a system of absorption pipets filled with short pieces of glass tubing and the usual absorbent solutions, and an explosion pipet for methane and ethane. A unique feature consisted of an upright electrically heated pyrex tube filled with copper oxide sticks for the combustion of hydrogen and carbon monoxide. The apparatus is fully described by the maker.[46]

Other apparatus used in the investigation is conveniently mentioned under later captions.

3. Manipulation of the Distilling Plant. - Before beginning a run a small weighed amount of residue from previously distilled shale, sufficient to fill the retort to the bottom of the heated zone, was introduced through the brass stopcock at the top. The proper charge of the ground and sampled shale was then introduced through a funnel in the same manner. The weight of the shale used varied with the specific gravity of the shale itself, and was always

just enough to fill completely the heated zone of the retort. Charges varied with different shales tested from 20 to 25 pounds. With all valves properly adjusted, the burners were then lighted, and the proportion of gas and air adjusted so that the distillation proceeded slowly and the rise in temperature indicated by the thermocouples was gradual, with the temperature at the top slightly above that of the bottom to prevent cooling and condensation of vapors in the upper part of the shale charge. The distillation proceeded gradually, most of the condensate collecting in the first trap. Varying amounts of lighter oils were always collected in the second trap, the amount increasing with the rate of distillation of the shale. After being washed free of ammonium in the strippers the gases were collected in the tanks.

Certain runs were made with the introduction of preheated steam early in the course of the distillation or after the completion of the dry distillation. The rate of input and the pressure of the steam were carefully regulated by means of the bottom valve, the operator observing closely the indications of the pressure gauge.

The run was continued until a temperature of about 700° C was attained at both top and bottom, although so far as the condensible distillates were concerned, the distillation was usually complete before 550° C. In the testing of samples from different deposits, every care was taken to make the conditions of distillation similar. An ordinary dry distillation consumed about three hours time.

After completion of the run, the furnace and retort were allowed to cool for several hours. The steam pipe was disconnected if it had been used, the bottom of the retort removed, and the residue collected in a large pan. The retort was then closed again, steam

MAP OF ILLINOIS SHOWING LOCATION OF SHALES

connections made, and the apparatus flushed out with steam, after the removal from the traps of the distillates. Any tar flushed over with the steam in either trap was added to the distillate. Very rarely were more than traces recovered in this way. The subsequent treatment of the products will be described under following captions.

4. The Raw Materials. - The raw materials used in this investigation were collected from outcropping deposits from several localities in the state of Illinois. The map on the preceding page 31 shows the approximate localities from which the samples were taken.

Sample No. 1. Shale from Schuyler County, S. W. 1/4. Sec. 12, R. 1 W., T. 1 N., 4th P. M. The sample consists of three feet of paper shale directly over Coal No. 2. The shale has large concretions, often one and one-half by three feet in diameter, and is fine grained and tough at the top and fissile at the bottom.

Sample No. 2. Shale from Schuyler County, S. W. 1/4, Sec. 23, T. 2 N., R. 1 W. The outcrop is two feet thick and probably lies above coal No. 5. It is a black, somewhat decomposed carbonaceous shale containing fossils and concretions.

Sample No. 3. Concretions from the shale described above. They are hard and tough, and have uneven fracture.

Sample No. 4. Shale from Schuyler County, N. W. 1/4, Sec/31, T. 1 N., R. 1 E., 4th P. M. Four feet of blue shale just above coal No. 2.

Sample No. 5. Shale from the same locality as No. 4. Above No. 4 are fifteen feet of blue clay shale, and above this six feet black fissile carbonaceous shale, from which this sample was taken.

Sample No. 6. Cannel shale from Johnson County, N. W. 1/4, Sec. 35, T. 11 S., R. 4 E. The outcrop is 42 inches thick. The shale is

black, and has conchoidal fracture. It is hard, tough, ignites easily and burns readily with a smoky flame.

Sample No. 7. Same shale as Sample No. 6, excepting that the sample was taken by sampling a twenty-ton pile of cannel mined and dumped beside the outcrop. Somewhat mixed with leaner material.

Sample No. 8. Chocolate colored shale above deposit from which No. 6 was taken. The outcrop is fifty inches thick.

Sample No. 9. Sample from Union County, three miles south of Jonesboro, S.E. 1/4, Sec. 1, T. 13 S., R. 2 W. This sample is a section of two bands of chocolate colored shale about sixteen to eighteen inches thick and eighteen feet apart; both lying in an exposed bank of many feet of tough, fissile, gray and green shale. The shale has uneven fracture, and is hard and flinty.

Sample No. 10. Shale from Union County, three miles northwest of Jonesboro on Caney Creek. S.W. 1/4, Sec. 11, T. 12 S., R. 2 W., 3d P.M. This sample was taken from the lower ten feet of at least thirty-five feet of chocolate colored and black fissile shale.

Sample No. 11. Sample from upper twenty-five feet of the bed described above.

Sample No. 12. Shale from Union County, two miles north of Anna, S.W. 1/4, Sec/9, T. 12 S., R. 1 W., 3d P.M. Fossiliferous brown shale from bed fifteen feet thick.

Sample No. 13. Mailed to E. A. Holbrook. Exact location not known. Sample of brown soapy shale.

Sample No. 14. Sample of so-called roof-slate, from Lovington Coal Company mine, Moultrie County. Bed two to three feet thick, lying above coal No. 6. The shale is black, hard and heavy, possesses uneven fracture, and contains pyrites.

Sample No. 15. Sample of cannel from same locality as No. 6. This sample consisted of a 1500 pound shipment of freshly mined shale from a shaft sunk about one-fourth mile from the outcrop from which samples No. 6 and No. 7 were taken. The material is slightly heavier and less weathered than No. 6.

These samples were furnished by the Illinois State Geological Survey, Dr. F. W. DeWolf, Director. Samples No. 1 to No. 13 inclusive were collected by Mr. F. A. Holbrook, and sample No. 14 by Mr. G. H. Cady of the Survey. Sample No. 15 was received from Dr. J. F. Blanchard, Ozark, Illinois. Samples No. 1 to No. 5 were received at this laboratory November 21, 1916; samples No. 6 to No. 13, January 20, 1917; sample No. 14 and sample No. 15, December 5, 1917.

The deposits from which samples No. 10 and No. 11 were taken are Devonian. The remaining samples are from Pennsylvanian deposits, except perhaps Sample No. 12, the horizon of which has not been definitely determined.

5. Preliminary Examination of Raw Materials.- On the arrival of the lots of raw materials at the laboratory they were crushed, ground to one-quarter inch mesh, and sampled by the usual method. A 200 gram portion ground to pass a 60 mesh sieve was stored in an air-tight bottle. From this portion samples were taken for the preliminary tests.

Lots No. 1 to No. 13 were first examined chiefly for the purpose of determining those of greatest promise for subsequent distillation in large quantities. In each case were made a proximate analysis, a determination of total nitrogen, and an extraction with benzene. Then followed a distillation of a kilogram portion in an electrically heated iron retort. Soon after they were received, lots No. 14 and

No. 15 were treated in the above manner for comparative purposes.

The proximate analysis consisted of determinations of moisture, volatile matter, and ash. The methods used were adapted from the Report of Committee E-4 on Methods of Sampling and Analysis of Coal (34), and were carried out as follows:

Determination of Moisture.- Two glass weighing capsules with ground caps were heated in a Freas' Electric Oven at 110°C. for one hour, cooled in a desiccator over concentrated sulphuric acid for thirty minutes, and weighed. A portion of material slightly in excess of one gram was transferred with a spatula from the container to each of the capsules, and brought exactly to 1-gram weight (± 5 mg.) by quickly removing the excess weight with the spatula. The open vessels were then placed in the oven preheated to 110°C., and a current of air dried by sulphuric acid passed through. The samples were heated in the closed oven for one hour, the oven opened, the capsules covered, and placed in a desiccator over concentrated sulphuric acid to cool. They were then weighed.

Determination of Volatile Matter.- A one-gram sample of the material was weighed rapidly into a counterpoised aluminum scoop. From this the sample was transferred carefully to a platinum crucible of approximately 20 c.c. capacity which, with its tight fitting cover, had been previously heated for ten minutes in the flame of a Meker burner, then cooled in a desiccator, and weighed. The cover was fitted on the crucible, and the sample subjected to a preliminary heating of about five minutes, during which time the heating was so regulated that the volatile matter was discharged at a rate not sufficient to cause sparking. After this preliminary heating the crucible was placed in the flame of the Meker burner (No. 4) about 1 cm.

above the top of the burner, and the heating continued for seven minutes. The temperature lay between 900°C. and 950°C. After the more rapid discharge of the volatile matter ceased, the cover was tapped into place. With the completion of heating, the crucible was allowed to cool in the usual manner and weighed.

Determination of Ash.- One gram of material was ignited in a shallow porcelain crucible. The heating was carried out slowly at first, until the volatile matter had been driven off. The flame of the burner was then so adjusted that the head increased to low redness (700°C. to 750°C.). The material was stirred frequently with a platinum wire, and the heating was continued until it was ascertained by the usual methods that constant weight had been reached.

Determination of Fixed Carbon.- The percentage of fixed carbon is ascertained by subtracting from 100 the sums of the percentages of moisture, volatile matter and ash.

Determination of Total Nitrogen.- This determination was carried out by a modification of the Kjeldahl method. A one-gram sample was boiled with 30 c.c. concentrated sulphuric acid (H_2SO_4), .5 g. copper sulphate ($CuSO_4$), and 10 g. potassium sulphate (K_2SO_4) in an 800 c.c. Kjeldahl flask until all the particles were oxidized and the solution became clear. The heating was continued for approximately two hours after this state had been reached. After the solution had cooled sufficiently a few crystals of potassium permanganate were added to insure complete oxidation.

The cooled solution was diluted with approximately 150 c.c. water, an excess of 33 percent sodium hydroxide (NaOH) solution was added, followed by a few pieces of granular zinc to prevent bumping and a small portion of paraffin, which tended to prevent frothing.

The solution was then distilled through a Hopkins head, and the ammonia caught in 30 c.c. (or known volume) of standardized hydrochloric acid solution to which had been added three drops of methyl orange. The excess acid was then titrated against a standardized sodium hydroxide solution. The manipulations were accompanied by the usual precautions, and a blank run resulted in a correction factor of small value which was applied in computation of the values given.

Some of the samples proved very difficult to oxidize, and the heating occupied in some cases from 8 to 12 hours.

Determination of the Bitumen Content.- This determination was essentially an extraction with benzene. Ten grams of the finely ground sample were weighed into an extraction capsule free from fat, and extracted in the Soxhlet reflux apparatus in the usual manner for ten hours with 100 grams of pure benzene from a supply previously distilled so as to be free from residue on evaporation. On completion of the extraction, the solution was transferred to a tared 120 c.c. beaker, the benzene carefully evaporated on an electric hot plate. The last traces of the solvent were driven off by raising the temperature of the plate slightly above 100°C. for a short time. The beaker was then allowed to cool in the dessicator and weighed.

Determination of Yield of Tar.- One kilogram portions of one-fourth inch mesh material were distilled in an iron retort heated in the electric furnace previously described. The distillations were approximately of six hours duration, and were carried to the point at which no further condensation was observed. The tar and water forming the condensed distillate were received in a flask, and the gases allowed to escape through a pipe into the atmosphere outside. The final temperature attained approximated 600°C.

The tar and water were separated after standing for a few hours in water slightly warmed. The volume of the tar at 25°C. was then recorded. The number of cubic centimeters of tar multiplied by the factor .24 gives the yield in gallons per ton.

The results of the preliminary examination are embodied in Table I.

Table I.

Results of Preliminary Tests on Raw Materials.

Sample No.	Moisture	Volatile	Ash	Fixed Carbon
1	1.75	21.15	63.80	13.30
2	3.95	21.00	74.95	-----
3	0.72	39.13	51.60	8.55
4	0.53	7.02	93.40	-----
5	1.67	9.33	88.11	0.90
6	1.77	33.73	38.50	26.00
7	1.96	31.69	42.85	23.50
8	1.80	8.75	88.35	1.60
9	1.30	10.50	92.55	-----
10	1.01	10.29	87.40	1.30
11	1.25	11.60	85.51	1.64
12	3.25	9.82	89.20	-----
13	1.05	8.25	88.65	2.05
14	1.42	17.97	58.65	21.96
15	1.65	36.80	38.45	23.10

Table I (continued)

Results of Preliminary Tests on Raw Materials.

Sample No.	Yield of Tar from 1 kilogram (cc)	Yield of Tar in gallons per ton	Per cent Bitumen extracted by Benzene	Per cent Total Nitrogen
1	61.1	14.7	0.67	0.97
2	22	0.5	0.19	0.39
3	3.1	0.7	0.19	0.37
4	none	----	----	0.18
5	Trace	----	----	0.36
6	160.2	38.4	1.09	0.89
7	150.0	36.0	0.98	0.82
8	Trace	----	----	0.35
9	Trace	----	----	0.13
10	18.7	4.5	0.15	0.41
11	17.5	4.2	0.20	0.51
12	None	----	----	0.04
13	Trace	----	----	0.26
14	68.2	16.4	0.60	0.83
15	203.5	48.8	1.16	0.92

A consideration of the data in the preceding table will aid in determining the general character and promise of the samples examined. With the exception of samples No. 4 and No. 12, all of the samples give a black residue after the total volatile matter has been driven off; they contain organic debris in traces at least. The values of ash are uniformly high. All the materials are of the type of indurated muds, slimes, or oozes. The values obtained in the proximate analysis are affected to some extent by certain disturbing factors. Discrepancies are particularly evident in samples No. 2, No. 4. No. 9, and No. 12, whose fixed carbon values are not given. Here the sum of the percentages are greater than 100 percent without the fixed carbon. No fixed carbon value is to be expected in samples No. 2 and No. 12. The same factors without doubt affect all the determinations; but their effect is much less marked in the samples having greater values of fixed carbon. The whole difficulty is quite probably due to the fact that the true amount of volatile matter was increased over its true value by the expulsion from the ash of such constituents as water of hydration, carbon dioxide, and possibly other less important volatile matter; while all of these products were not completely driven off in the ash determination. As evidence of this the four samples above mentioned contain considerable amounts of calcium carbonate; they effervesce readily with dilute hydrochloric acid. All of the samples contain water of hydration, which appears as condensable distillate in the lower layer as ammonia water when the shale is subjected to distillation. In spite of these difficulties, however, it may be stated that the higher the volatile matter and fixed carbon values, the greater the yield of tar on distillation. The values obtained in the proximate analysis are of

sufficient accuracy for the purpose in hand.

A cursory examination of the data will show the possibilities of the different materials in point of yield of tar. The first thirteen samples were collected and examined chiefly in the hope of locating a deposit yielding sufficient amounts of tar to make it possible later distillation in quantity and a study of its products. The yields of the thirteen samples vary from zero to 38.4 gallons per ton. Sample No. 15 represents a shipment of freshly mined material from the deposit showing the highest yield. One contributory cause to the fact that sample No. 15 shows a considerably higher value than sample No. 6 is perhaps the fact that the latter sample, obtained near the outcrop, may have suffered weathering to some extent, while the former was certainly subjected to no such conditions. However, other causes than weathering may have been active; it is well known that yields may vary considerably throughout any particular deposit. Finally, it is to be noticed that only four deposits are represented which give yields of more than traces of tar, and of these four, only three exhibit values of possible commercial interest. It must be remembered also in this connection that the values obtained by laboratory distillation are maximum values, and in actual practice the output will be lower. The nature of the tarry distillates is the subject of subsequent discussion.

The extraction data are of some interest. With the exception of the cannel deposit, represented by samples No. 6, No. 7, and No. 15, none of the materials gave one percent extract to solvent benzene. The yield of extract from the cannel deposit was barely more than that value. The oily or asphaltic matter as such evidently exists in the materials in very small amounts if at all. Hence, the only method

which can be employed on a large scale to obtain the tar from them is that of distillation. In contrast, the shales in the Northwest were reported by D. T. Day (31) to yield as much as six percent of their weight to benzene, and 6.2 percent to ether; and according to Petrie (3) the New South Wales torbanite, a kindred material to the cannel used in this investigation, contains marked amounts of soluble bitumen. In this regard will be remembered the contention of Conacher (4) that the solubility of resins decreases with age; for the shales of the Northwest are of a much later ~~earlier~~ geological period, the Eocene, than the Pennsylvanian and Devonian shales used in this investigation.

The benzene solution containing the extracted material varies in color from a light yellow to a deep reddish-brown cast with a beautiful green fluorescence, and the benzene free extract contains both nitrogen and sulphur. The amounts obtained were too small to make a further examination.

The nitrogen content in all of the shales is less than one percent, and varies considerably. The richer the shales in organic residue, the greater is the percent of nitrogen. While the equivalent of the total nitrogen can never be expected to be recovered as ammonia, its value is one factor of importance in the valuation of the shale; in a measure it determines the maximum possible yield of ammonium sulphate. The question of the relation of nitrogen to the origin of the deposit itself is to be discussed hereinafter. The nitrogen values in the samples yielding more than traces of tar compare favorably with those of the shales previously examined in this country and those at present supplying raw materials for already established industries.

In consideration of all the facts presented, a simple classification may now be made with respect to type. Deposits from which samples No. 4 and No. 12 were taken do not contain appreciable quantities of organic detritus. Samples No. 2, No. 3, No. 5, No. 8, No. 9, and No. 13, represent deposits of a more or less carbonaceous nature. The oil-shales, or bituminous shales, however, include the deposits from which were taken samples No. 1, No. 6, No. 7, No. 10, No. 11, No. 14, and No. 15. The term oil-shales will be applied hereinafter in discussing these particular samples.

6. Products of Distillation of Oil Shale.- A series of runs were made with different oil shales using the distillation plant which has been previously described. The method of making the distillation has also been recorded. The duration of each run occupied about three hours time, the heat being turned off when the maximum temperature at the bottom reached 650° C. The end of the distillation so far as condensible distillate was concerned, became evident by the cooling of the air condenser, but it was observed that fairly rich gas was given off up to the maximum temperature attained during the run.

After the completion of the run, some time was allowed for the complete drainage of the distillates into the traps. The combined distillates were then drawn off into a tared separatory funnel of suitable size, weighed, and allowed to stand in warm water until thorough separation had taken place. The proper weight was recorded as weight of total distillate. Standing in warm water failed to cause some of the distillates to separate completely. In such refractory cases the careful addition of 25 or 50 c.c.s dilute sulphuric acid (H_2SO_4) with gentle rotation broke the emulsion. The water was

stored for future examination, and the funnel and tar were again weighed for the determination of amount of tar.

The ammonia water was combined with the water used to strip the gas of ammonia, and the volatile nitrogen compounds determined as ammonia by distillation of a properly sized sample with an excess of 30 percent sodium hydroxide (NaOH) solution. The yield of ammonia calculated to pounds of ammonium sulphate ($(NH_4)_2SO_4$) per ton of shale appears in Table II.

TABLE II

Yields of Products on Experimental Distillation of Oil Shales.

Run No.	15	16	17	18	19	20
Sample No.	1	10	11	14	6	15
Weight of Charge (gms.)	9080	10896	9080	10896	8172	9080
Weight of Charge (lbs.)	20	24	20	24	18	20
Weight of Total Distillate(gms.)	859	655	705	1047	1548	2082
Weight of Tar (gms.)	411	85	67	572	1118	1536
Per cent of Tar	4.5	0.8	0.7	5.2	13.5	17.1
Specific Gravity of Tar at 25°C.	.926	.936	.931	.920	.897	.901
Volume of Tar (cc)	444	91	72	622	1247	1705
Yield of Tar per ton of Shale (gallons)	11.7	2.0	1.9	13.7	36.6	45.1
Weight of Water (gms.)	448	570	638	475	430	546
Per cent of Water	4.9	5.2	7.0	4.3	5.2	6.0
Volume of Gas at N.t.p. (cu.ft.)	31.0	14.5	22.0	39.4	57.5	58.6
Volume Gas per ton	3100	1208	2200	3285	6389	5860
B.t.u. of gas	690	600	510	640	690	760
Total yield $(NH_4)_2SO_4$ per Ton (lbs.)	9.06	1.67	1.75	6.26	8.62	9.15
Theoretical Yield $(NH_4)_2SO_4$ (lbs.)	91.49	38.67	48.11	79.29	84.32	86.78
Per cent of Recovery of $(NH_4)_2SO_4$	9.9	4.3	3.2	7.9	10.2	10.5

The yields of tar reported above are uniformly lower than the yields from the same shale distilled in smaller quantities in the iron retort (Table I). The reasons are of course obvious. Indeed, in the case of the lignite industry, sixty percent of the yield of tar on laboratory distillation is taken as the probable commercial yield. Scottish practice is somewhat similar. It is quite probable that the yields here stated would be approximated in commercial distillation.

It is to be noticed that the watery distillate forms in some cases the greater part of the total condensible distillate, and varies in value from nearly 5 to 7 percent of the original charge of shale.

The gas yields vary with those of the tars, the smallest recorded being 0.6 cubic feet to the pound of shale and the highest 3.2 cubic feet.

The ammonium sulphate yields are rather unpromising. It must be remembered, however, that the temperatures used in this type of destructive distillation are conducive to the recovery of rather small percentages of the total nitrogen present. Winchester (29) reports the average recovery from the gas of 11.1 percent of the theoretical amount. The average recovery shown in the above table is 7.7 percent.

7. Examination of the Shale Tars. - In order to determine the chemical character of the tars obtained from the shales in the experimental distillations, they were fractionated and analyzed.

A 200 gram portion of the thoroughly mixed tar was weighed into a tared 500 c.c. Pyrex distilling flask. In two cases, in which the amount of tar did not permit taking a sample of this amount,

50 grams were used. The flask was fitted to an eighteen-inch condenser, the tip of which had been pointed to facilitate the dropping of the distillate. The neck of the flask was well covered with shredded asbestos resting on top of the furnace, and the 400°C. thermometer was likewise protected from air currents by means of a piece of glass tubing throughout its length. The smaller electric furnace, previously described, was the heating unit employed. At the beginning of distillation the outside resistance was so regulated that the heat input was extremely slow until almost all the water had been driven over. Difficulty in frothing was not encountered. After this point the heat input was increased until the distillate dropped from the end of the condenser at the rate of one drop per second. The same rate of heating was carefully employed in the fractionation of all the samples.

Cuts were made at 150°C., 225°C., 300°C., and finally at the point at which the appearance of a red viscous substance was observed. This red product, consisting of chrysene, picene, and the decomposition products of the heavier oils, was caught separately, and the distillation continued until the residue had coked. The thermometer was elevated when the temperature approached 400°C. Decomposition of the tar was reduced to a minimum by precautions in the distillation, and rarely began before 350°C.

The fractions were received in tared Erlenmeyer flasks of proper capacity, and the weight of the fraction ascertained. The amount of water rarely exceeded two percent of the portion taken for distillation, and most of it appeared in the first fraction. Rarely the second fraction was somewhat clouded because of traces of water, but standing a short time allowed this to settle out. The water was

carefully removed with a pipet and weighed. The weight of coke was ascertained by weighing the flask after cooling.

The specific gravity of the crude tar as well as the tar oils was determined by the Westphal balance where quantities allowed. The ordinary plummet requires at least 15 c. c. of material for submergence. For quantities less than 15 c. c. and greater than 7 c. c. a special plummet was used. This was made from a glass bulb filled with mercury, and its factor was ascertained readily by comparison of readings with an ordinary plummet using distilled water. The specific gravity of very small quantities of oil was determined by weighing in small pycnometers with capillary tips. Two such pycnometers were employed, having a capacity of about .2 c. c. and 1 c. c. respectively. Their accurate volume was ascertained in the usual way.

In the case of the crude tar, the specific gravity was determined at 25°C., a temperature at which all the tars were liquid; but with the tar oils, specific gravities were obtained at the prevailing room temperature and corrected to the value at 25°C. by use of the factor .00081, the coefficient of expansion. This value had been previously ascertained as the average value for oils of the type under consideration, and was determined by the method set forth in Holde's Examination of Hydrocarbon Oils (34).

The chemical examination of the tar oils consisted of determinations of their content of unsaturated, paraffin, and aromatic hydrocarbons. The content of acidic compounds was determined in the fractions boiling from 150°C. to 225°C. and from 225°C. to 300°C.; while the basic content was ascertained in the first three fractions.

For the determination of acids and bases present in the fractions long 100 c. c. ground glass stoppered burets were found convenient.

Such a portion as the fraction would allow, 10 c. c. to 25 c. c., was pipetted into the buret, and well shaken with an equal portion of 10 percent sodium hydroxide solution (sp. g. 1.19). The mixture soon separated, except in the case of the higher boiling fractions, which rather readily formed emulsions. Such emulsions were, however, fairly easily broken up by allowing the buret to stand in warm water for a time. After complete separation in any case the reading was not taken until the buret and its contents had attained the initial temperature. The decrease in volume of the oil was ascertained and the percentage of acidic constituents calculated.

The soda tar layer was then run off, the oil washed once with water, and shaken with an equal amount of sulphuric acid solution (1:2). The decrease in volume here ascertained represented the volume of basic compounds dissolved by the acid.

The acidic and basic compounds were removed in the order mentioned because of the observation of Hatcher and Skerrow (36) that there is evidence of compounds of phenols and cresols with the pyridine bases, which are not readily dissociated by the application of acid first.

Following the above determinations the oil free of acids and bases was washed again with water and dried over anhydrous calcium chloride. Portions of it were then used for the subsequent determination of unsaturated and paraffin hydrocarbon contents.

It had been ascertained previously in this laboratory by a series of experiments with the action of sulphuric acid of different strengths upon known mixtures of aromatic and unsaturated hydrocarbons that the absorption of the olefins would be quite quantitative at temperatures near 0°C. when the mixture was shaken with 89 percent

sulphuric acid. This strength was accordingly used in the determination of the volume of the unsaturated hydrocarbons. Difficulty was experienced with the heavier oils, however, in attempting to use the gravity method of separation. Consequently the determinations were carried out in Babcock milk testing bottles of 25 c.c. capacity in the following manner:

Two cubic centimeters of the oil were pipetted into the Babcock bottle, and the bottle placed in chipped ice. Ten cubic centimeters cooled 89 percent sulphuric acid were added, and the mixture shaken vigorously for about three minutes. After standing for fifteen minutes, sufficient acid of the same strength was added to bring the unabsorbed oily layer well within the graduated portion of the neck of the bottle. The bottle and contents were then centrifuged for a period of three minutes. Readings were taken, and the centrifuging repeated for two minutes. In all cases there was no need of repetition to obtain complete separation. After allowing the bottles and contents to stand for some time to attain room temperature, the readings were taken and the volume absorbed noted. The volume of the graduated neck of this type of Babcock bottle has a capacity of 2 c.c., and is calibrated in fifty divisions. The readings could therefore be made directly as percentage unabsorbed, and with an accuracy of one percent. The unabsorbed oil consisted of paraffins, and aromatic hydrocarbons, and perhaps naphthenes, while the amount absorbed represented the content of the unsaturated compounds of the aliphatic series, represented in the tables as olefins.

The absorption of unsaturated compounds by this method is perhaps not quite accurate. It is, however, the best known simple method at present for the determination of the volume of olefins and

other unsaturated hydrocarbons present in an oil mixture. Recently Dean (36) has confirmed the observation made in this laboratory that acid approximating the percent used does not in the cold cause polymerization of olefins to any extent and does not absorb aromatic hydrocarbons to any appreciable extent.

The method of centrifuging was also applied to the determination of the paraffins. In this case use was made of a mixture of 1000 grams sulphuric acid, sp.g. 1.84, and 28.6 grams 20 percent fuming sulphuric acid. An amount of oil consistent with the size of the fraction under examination, but usually of 2 c.c. volume, was transferred to the bottle. Four times its volume of the acid mixture was then added to the oil, in four equal portions, the mixture being shaken well between the additions of acid. The mixture was then kept in a boiling water bath for one hour, but shaken about every ten minutes. Low boiling oils were heated for a longer time, 2 hours, at a temperature well below the boiling range of the oil. After the completion of the heating, the bottles were removed from the bath, allowed to cool, and ordinary concentrated sulphuric acid added to raise the unabsorbed oil to the neck of the bottle. The sample was then centrifuged, and readings were taken in the same manner as in the case of the olefin determination. The whirling cooled the sample with the result that higher boiling oils examined became solid. In such cases determinations were repeated, the sample having first been dissolved in an equal portion of kerosene, previously freed from unsaturated and aromatic compounds.

The volume percentage of aromatic compounds is equal to 100 minus the sum of the percentages of paraffins and olefins. In cases in which the determinations were carried out on oils previously freed

from acids and bases, the proper calculations were made to obtain the true percentage based on the original oil fraction.

A record of the results of the fractional distillations appears in Table III, and the results of the chemical analysis of the tar pils are shown in the tables immediately following Table III.

TABLE III

Results of the Fractionation of the Shale Tars

Tar Sample No.	1		10		11	
First Drop at	43° C.		52° C.		48° C.	
Amount Used (gms.)	200		50		50	
	Grams	Percent	Grams	Percent	Grams	Percent
To 150°C	22.1	11.05	2.8	5.6	3.2	6.4
150° C.-225° C.	38.5	19.25	7.4	14.8	8.2	16.4
225° C.-300° C.	68.9	34.45	14.2	28.4	14.3	28.6
Over 300° C.	55.8	27.9	18.7	37.4	16.2	32.4
Red Product and Loss	5.2	2.6	2.4	4.8	3.5	7.0
Coke	7.4	3.7	3.2	6.4	3.4	6.8
Water	2.1	1.05	1.3	2.6	1.2	2.4

Tar Sample No.	14		6		15	
First Drop at	41° C.		55° C.		52° C.	
Amount Used (gms.)	200		200		200	
	Grams	Percent	Grams	Percent	Grams	Percent
To 150° C.	12.3	6.15	11.4	5.7	12.4	6.2
150° C.-225° C.	36.8	18.4	27.9	13.95	27.0	13.5
225° C.-300° C.	64.1	32.05	43.0	21.5	45.0	22.5
Over 300° C.	51.9	25.95	94.0	47.0	83.0	41.7
Red Product and Loss	23.1	11.55	13.9	6.95	21.0	10.5
Coke	6.8	3.4	5.8	2.9	8.0	4.0
Water	5.0	2.5	4.0	2.0	3.2	1.6

TABLE IV

Results of Analysis of Shale Tar Oils

Cut	Sp.Gr.at 25°C.	Per Cent Paraffins	Per Cent Unsaturated Hydrocarbons	Per Cent Aromatic Hydrocarbons	Acids	Bases
		Tar from Sample No. 1				
To 150°C.	.797	50	40	9		1
150-225°	.857	41	44	4	7	4
225-300°	.932	33	54	4	4	5
Over 300°	.953		55			
Crude Tar	.923		64			
		Tar from Sample No. 10				
To 150°C.	.810	48	41	11		
150-225°	.833	39	45	7	6	3
225-300°	.897	32	56	6	4	2
Over 300°	.975		57			
Crude Tar	.936		59			
		Tar from Sample No. 11				
To 150°C.	.802	48	42	10		
150-225°	.827	37	48	6	5	4
225-300°	.908	31	55	7	3	4
Over 300°	.945		59			
Crude Tar	.931		64			
		Tar from Sample No. 14				
To 150°C.	.780	39	51	7		3
150-225°	.842	34	44	9	8	5
225-300°	.914	28	54	8	6	4
Over 300°	.932		57			
Crude Tar	.920		62			
		Tar from Sample No. 6				
To 150°C.	.770	54	34	10		2
150-225°	.823	44	37	6	8	5
225-300°	.865	42	38	11	5	4
Over 300°	.926		46			
Crude Tar	.897		55			
		Tar from Sample No. 15				
To 150°C.	.776	59	27	12		2
150-225°	.828	48	31	9	6	6
225-300°	.871	35	50	8	4	3
Over 300°	.930		65			
Crude Tar	.901		72			

The tars from this series of runs are of the same general typ their specific gravity varies from 0.897 to 0.896 at 25°C., and they contain very small percentages of water, 2.5 being the highest percentage recorded. Light oils range from 5.6 to 11.05 percent; medium oils, boiling from 150°C. to 225°C., yield from 13.5 to 18.4 percent, and heavy oils, boiling from 225°C. to 300°C., yield from 21.5 to 34.45 percent of the crude tar. About fifty percent of the crude tar is distilled over under 300°C. The fractions of boiling points over 300°C. are frozen to vaseline-like products readily, and yield solid paraffin in more or less abundance. This product differs from petroleum paraffin in that it contains olefins and unsaturated compounds in greater amount.

The low amount of still coke obtained in all cases, 2.9 to 6.8 percent, is a marked point of difference between shale tars and high temperature coal tars. Free carbon is present only in traces in the tars examined.

The lighter oils distilling over are light yellow in color; but the color deepens as the temperature rises. The heavier fractions are brownish green in color. The color of all the fractions changes on standing, however; that of the light oils becomes quite red. Sunlight accelerates the change, but it seems to be one of oxidation chiefly. Polymerization products also form, and in some cases collect in the bottom of the flask in small amount but in a separate layer.

All the tars contain sulphur compounds to some extent. Their presence is indicated by the odor of the vapors. The tars from samples No. 6 and No. 15 were the least offensive in this respect, and that from No. 14 the most offensive. This is to be expected, for the

sulphur contents of the shales from which they were distilled were 1.18 percent and 6.62 percent, respectively.

No naphthalene could be separated by freezing from the 150°C.-225°C. fractions of any of the tars. Anthracene was found present in the fraction boiling over 300°C. from the tar from Sample No. 15.

After about 90 percent of the tar was distilled over, a red sticky product began to come over. This product includes the decomposition products of the heavier tar oils, and is probably not a constituent of the original tar. It consists in part of picene.

The crude tar contains a considerable amount of dissolved gases. At the beginning of distillation hydrogen sulphide and methane are in evidence. Not a little of the loss on distillation is due to these gases, and to the gases resulting from the decomposition of the heavier boiling compounds. Decomposition began in most cases at about 330°C.; its occurrence was marked by the presence of yellow fumes.

The chemical analysis further establishes the fact that the tars from the series of distillation under consideration are remarkably similar in type. Aromatic compounds are present in greater amount than in Scottish commercial shale tar products. But the amount is still small in comparison with that of either the unsaturated aliphatic compounds or the paraffins. The paraffins listed in the table quite likely include naphthenes. This has been found the case at least in a later study of tars from shale sample No. 15.

Small percentages of acids and bases occur in all the tars. These certainly are of the same types that appear in coal tar, and that have already been detected in shale tar, namely, phenols and naphthenols as acids, and pyridine and quinoline bases. Since the

lower members of the pyridine series are quite soluble in water, the percentages represented in the table cannot be taken as a measure of the total amount of these bases in the distillation products of the shales.

It is worthy of note that as the boiling limits of the fractions rise their content of unsaturated compounds of the aliphatic and polymerised type rises, while their paraffin and naphthene content diminishes. The high percentage of unsaturated compounds in the crude tars is quite possibly due to the fact that the tar contains a small percentage of water.

It is further of interest to note the close similarity of the tars from samples No. 10 and No. 11, which are from the upper and lower parts of the same deposit. This similarity is not evident in the tars from samples No. 6 and No. 15, which represent the weathered and unweathered shale of the same deposit. The tar from the latter sample has uniformly more paraffins and less unsaturated compounds than has the tar from sample No. 6. Their respective specific gravities, however, differ little.

The fact that the aromatic content is higher than has been hitherto reported for shale tars, may be due to some extent to the nature of the organic residue in the shales, but is more probably due to decomposition occurring during the distillation of the shale. A study of the gases will reveal the fact that such decomposition has taken place.

8. Analysis of the gases.- The gases obtained in the series of experimental distillations of shale now under consideration were submitted to a technical analysis. Carbon dioxide, hydrogen sulphide and other acidic constituents were removed first by potassium

hydroxide solution. Oxygen was absorbed in alkaline pyrogallol, and acetylene in an ammoniacal solution of cuprous chloride. Unsaturated compounds of higher molecular weight than ethylene were removed by means of a 95 percent sulphuric acid solution. Bromine water removed the ethylene. The aromatic constituents were taken out by means of fuming sulphuric acid of approximately 12 percent strength. Hydrogen and carbon monoxide were removed by passing the gas over copper oxide at 300°C., and the methane and ethane were determined by explosion with an excess of air. The heat values of the gases were determined in the Parr gas calorimeter.

A summary of results follows:

TABLE V

Results of Technical Analysis of Gases
Percent by Volume

Shale Sample No.	1	10	11	14	6	15
Carbon dioxide	4.8	16.6	17.2	12.1	6.7	5.0
Oxygen	0.5	0.4	0.1	0.3	0.3	0.3
Acetylene	0.2	0.1	0.1	0.2	0.0	0.1
Unsaturated Hydrocarbons	3.4	0.5	0.4	2.2	4.4	6.0
Ethylene	0.9	1.9	1.2	0.8	1.2	1.3
Aromatic Hydrocarbons	0.5	0.5	0.6	0.4	1.0	1.3
Hydrogen	43.0	46.7	45.2	47.4	34.9	29.4
Carbon monoxide	5.0	4.6	3.8	6.8	2.3	3.0
Methane	23.1	12.4	12.7	14.5	23.1	25.1
Ethane	32.2	14.1	7.2	14.3	21.9	24.5
Nitrogen and Residue	3.0	2.2	1.5	1.0	2.2	3.0
B.T.U.	690	600	510	640	690	760

Like the tars and tar oils, the gases from the shales studied are not markedly different. Their total hydrocarbon contents vary with the yield of tar from the shale. One feature of particular interest is the fact that acetylene is present in exceedingly small traces, if at all. Aromatic hydrocarbons are present in measurable quantities, however; the percentage of total unsaturated hydrocarbons does not exceed 7.3 percent in any of the gases. Hydrogen is in all cases the predominant constituent, and has quite evidently resulted both from the original decomposition of the organic material of the shale and from secondary reactions. Another source arises in the action of steam on the carbon of the residue at the temperatures used. Thus $C+H_2O=CO+H_2$.[45] The percentage of carbon dioxide varies, but in no case exceeds 17.2. The value for this constituent, which includes as well hydrogen sulphide and sulphur dioxide, has a small factor of error due to loss in the water over which the gas was caught and stored. Precautions were taken to insure the accuracy of all the gas analyses, however, by saturating the water of the gas tanks thoroughly with shale gas before any gas values were taken, and by analysing the gases as soon as possible after the distillation of the shale.

9. Examination of Light Oils.- In shale gas, as in coal gas and natural gas, there are present hydrocarbons which yield light oils when the gas is passed through some sort of absorbent medium such as a heavy oil. Such compounds consist of low boiling members of all the aromatic hydrocarbon series whose vapor pressures cause them to be carried over with the so-called fixed gases. These light oils may be removed more or less completely by compression or cooling, or both, or by absorption.

The light oils were removed from the gases studied by aspirating

them through heavy Havoline oil previously steam distilled to 170°C. to remove any light oils present in it. The absorption train consisted of the two gas washers described in connection with the distillation plant, and of five gas wash bottles of efficient type. The total amount of heavy oil used in each case was about two and one-half liters. The gas was drawn through at the rate of ten cubic feet an hour. After the completion of the absorption, the oil was poured into a five liter pyrex flask and steam distilled, the light oil and water being received in a small separatory funnel. At the completion of distillation, the water was drawn off, and the light oil transferred to a tared flask.

The yield of light oil varied with the yield of the tar from the shale, and in cases in which the yield was too small to fractionate, the oils were analyzed without fractionation. The light oils were fractionated twice through a three-bulb distilling column.

TABLE VI

ANALYSIS OF LIGHT OILS

Sample No.	Fraction	Percent Weight	sp. g. at 25°C.	Percent Paraffin Hydrocarbons	Percent Unsaturated Hydrocarbons	Percent Aromatic Hydrocarbons
1	-	-	-	58	36	6
14	-	-	-	63	28	9
6	To 95°C.	52.2	0.719	67	27	6
	95-125°C.	35.5	0.733	64	27	9
	125-133°C.	3.5	0.738	75	22	3
15	To 95°C.	40.5	0.721	72	22	7
	95-125°C.	44.3	0.728	70	24	6
	125-133°C.	6.7	0.742	-	-	-

The light oils in general show lower percentages of unsaturated hydrocarbons and aromatic hydrocarbons respectively, than do the corresponding 150°C. cuts of the tars. The recovery of oil was sufficient for fractionation in two cases: Samples No. 6 and No. 15. Fifty grams of each were fractionated and cuts made at 95°C., 125°C., and 155°C. In the case of light oil from sample No. 6 the boiling limits were 41°C. and 133°C., and of sample No. 15, 38°C. and 153°C.

The percentages of aromatic hydrocarbons for the different cuts may be considered approximately the content of the aromatic hydrocarbons whose boiling points lie within the boiling limits of the cuts: thus 75-95°C., benzene, b.p. 80.5°C.; 95-125°C., toluene, b.p. 110.3°C.; and 125-155°C., xylenes, etc. The percentages obtained by chemical methods are in fair agreement with the values which would be expected from the specific gravities of the cuts. The following gravity relations exist between the two types of hydrocarbons:[37]

Temperature limits of fraction	Sp.g. of aromatic hydrocarbons at 15°C.	Sp.g. of non-aromatic hydrocarbons at 15°C.
To 95°C.	0.880	0.720
95-125°C.	0.871	0.730
125-155°C.	0.869	0.760

The specific gravities given for the oils above are calculated to the temperature of 25°C. For calculation of the values at 15°C. the coefficient of .00081, mentioned previously, may be used. The values for toluene, in which interest centers chiefly, are 7.8 percent for the cut from sample No. 6, and 4.5 percent from Sample No. 15. Approximately 2.5 percent toluene is present in the light oils from sample No. 6, and 2 percent in the light oils from sample No. 15.

For the purpose of showing the yields of light oils per ton

of shale the following table is given:

TABLE VII

THE YIELDS OF LIGHT OILS FROM STRIPPED GASES

Sample No.	1	10	11	14	6	15
Amount of light oil (gms.)	17.7	Trace	Trace	19.4	60.8	63.4
Sp.G. at 25°C.	.745			.743	.733	.732
Volume of gas stripped (cu.ft.)	31.0	14.5	22.0	39.4	57.5	58.6
Gallons light pil per ton of shale	0.62			0.57	2.44	2.28

The amount of light oils recovered by absorption in the above experiments was not the maximum.

10. Summary of Yields of Products.- The following table summarizes the yields obtained in the experimental distillation of shale calculated for one ton of shale:

Sample No.	1	10	11	14	6	15
Gallons of Crude Tar at 25°C.	11.7	2.0	1.9	13.7	36.6	45.1
Cubic feet of Gas (n.t.p.)	3100	1208	2200	3285	6389	5860
B.T.U. of Gas	690	600	510	640	690	760
Gallons of Light Oil from Gas	0.62	-	-	0.57	2.44	2.28

11. Modification of Products of Distillation.- The effect of varying the conditions of distillation on the yields and types of the products from oil shale is of considerable interest from a

technical as well as a scientific standpoint. The technical application concerns itself, for the present at least, chiefly with the possibility of increasing the light oil yield for motor fuel and of producing toluene and other aromatic substances of value as intermediates for various industries. The chief scientific interest has to do with the yet unanswered question: "What is the nature of the organic detritus in the shale, and what is the effect of the inorganic material of the shale on the decomposition of the primary products of distillation?"

The thermal decomposition of hydrocarbons has been the subject of many investigations.[38] Petroleum products, pure hydrocarbons and mixtures, and coal tars have received an amount of attention perhaps in the order named. It has already been established that the tars from the oil shales used in this investigation, in fact all shale tars, are intermediate in type between petroleum on the one hand and coal tar on the other. The constituents of coal have their counterparts in shale, but in different measure. The fatty organic matter of shale readily yields paraffins and naphthenes of the type which predominate in most petroleums. There seems sufficient basis therefore for the general prediction that increase of temperature in distillation will bring about more decomposition, which with pressure will more readily form aromatics, and without pressure will increase the light oil yield.

Mention has already been made of the work of Jones and Wheeler (loc. cit.) concerning the constituents of coal. They postulated that not only certain aromatic, naphthenic, and unsaturated hydrocarbons but also phenols and similar hydroxy-compounds may arise from the primary decomposition of different types of organic residue

in the coal, and that subsequently secondary decomposition gives the products ordinarily obtained in coal tar. For instance, benzene and anthracene were absent from vacuum distilled coal. These products appear in high temperature coal tar in considerable amount. The same types of fossil life that contributed to coal-building contributed to shale-building, but in different measure. How different is a matter to be determined for each particular deposit. There is no justification therefore in predicting to what extent decomposition will occur without first determining the primary products of distillation. The investigators mentioned, as well as Pictet and Bouvier[39], used the method of vacuum distillation. It seems apparent that the whole purpose of vacuum distillation is to hasten the passage of vapors out of the zone of decomposition. Steam distillation will attain the same end, since it likewise lowers the vapor pressure and pushes the vapors out of the retort.

For the purposes of the present investigation the previously described experimental plant was made use of for a short series of runs under different conditions. The plan followed, therefore, consisted of distillation of twenty-pound lots of shale from which sample No. 15 was collected. This shale proved to be the richest under investigation, and therefore best adapted to such a study. Three comparative distillations were made: one run of four hours duration, beginning with a cold furnace and ending with a maximum temperature of 650° C.; one quick run of one and one-half hours, beginning with the furnace heated to 300° C., and ending with the same maximum temperature, and one run with steam, during which the steam preheated to 250° C. was passed slowly through the retort after the distillation had proceeded to about 250° C. This last run was stopped at 650° C.,

and occupied about two hours and a half. The runs are designated respectively Nos. 21. 22. 23. An examination of the tars was made and heating values of the gases were determined in the usual manner.

The effect on the yields is shown in Table VIII.

TABLE VIII

Results of Runs Under Different Conditions

Run No.	Description	Yields per ton of shale			Sp. G. Tar at 25° C.	B.t.u of Gas
		Tar (Gals.)	Gas (cu. ft.)	Ammonium Sulphate (pounds)		
	4 hrs. to 650° C.					
21	4 hrs. to 650° C.	47.6	6340	9.8	.903	705
22	1 1/2 hrs. to "	44.4	7360	10.1	.910	720
23	Steam 2 1/2 hrs. to "	49.1	9447	15.4	.892	590

The quick run decreases the yield of tar noticeably, increases the yield of gas, and slightly increases the ammonia yield. Although there is an increase in yield of gas, there is a corresponding decrease in its heating value. The steam run increases the yield of tar slightly, the yield of gas considerably, at the same time lowering its heating value. This is no doubt due to the formation of hydrogen and carbon monoxide and dioxide by action of steam on the residue toward the end of the run and on the iron of the retort, The ammonia yield is also increased. Steam decreases the specific gravity of the crude tar.

TABLE IX

RESULTS OF FRACTIONATION OF TAR - ONE LITER SAMPLES

	Percent Volume	Percent Volume	Percent Volume
Run No.	21	22	23
To 170°C.	9.1	12.7	8.2
170-230°C.	12.2	13.2	11.8
230-300°C.	21.7	20.3	30.6

TABLE X

ANALYSIS OF TAR FRACTIONS

Run No.	21				22				23			
	Par.	Uns.	Arom.	Acids	Par.	Uns.	Arom.	Acids	Par.	Uns.	Arom.	Acids
To 170°C	56	23	5	6	47	40	8	5	70	20	3	7
170-230°C	63	26	6	5	45	43	9	3	69	22	3	6
230-300°C	59	32	9		45	49	6		73	25	2	

The yield of light oil is increased somewhat by rapid heating, and changes very little with steam. Steam preserves the paraffin (and naphthene) hydrocarbons, and tends to prevent formation of aromatic hydrocarbons. Rapid heating seems to cause some decompositions. The effect on acids is not marked enough to draw any conclusions.

It seems evident that the primary products of shale distillation consist of hydrocarbons insoluble in fuming sulphuric acids, and they are probably a mixture of paraffin and naphthenes. Likely with the source of thermal decomposition the naphthenes are in part dehydrogenerated, and the unsaturated compounds polymerized to form aromatic hydrocarbons. The paraffins, which are the most unstable of all, rapidly decompose, yielding olefins and hydrogen.

This much is evident: All the tars give qualitative test for anthracene, but on refractionation with a Hempel column of the middle oil and freezing of the 210-325°C. fraction, no naphthalene separates out. Anthracene may be formed without the interposition of naphthalene in a series of the maldecompositions.

The results in a measure point to the probability that the shale itself is much richer in the resinic or fatty remains of plant and animal life, than in the cellulosic organic residues.

12. <u>The Effect of Steam on the Hot Residue</u>.- The nitrogen distribution. The observations of Beilby (loc. cit.) to the effect that the passage of steam through the hot residue from the distillation of shale increases the ammonia output has been noted. It was of interest to discover if the nitrogeneous residue in the shale was of such a nature that it would yield readily to this treatment. Harger[40] contends that the nitrogen in coal combined in several essentially different ways, because he finds that whereas the nitrogen determination by the Kjeldahl method yields only traces in some coals the Dumas method shows about 2 percent. Inasmuch as no details were given as to the manner of carrying out the Dumas experiment, the observation of Haas[41] on the subject might apply. Haas found that error might creep into the experiment through the formation of methane. Nevertheless, there is no doubt that the nitrogen is combined in "different ways", and the possibility exists of the failure of steam to act with the formation of ammonia from some of the combined nitrogen.

A run was made on shale ground to one-fourth inch mesh and sieved to remove dust. The distillation was carried out in the regular manner until the temperature of the retort approximated 850°C. at

the top and bottom. Preheated steam was then introduced at the bottom of the retort and passed through slowly, the rate being governed by the dropping of water from the second trap into the separatory funnel of the water condensing system, and by the constancy of the bottom temperature. The duration of the passage of steam was about six hours. The condensing steam removed the ammonia from the gas, as well as some carbon dioxide and hydrogen sulphide, no doubt. The ammonia water was stored, the tar water added, and an ammonia determination made.

The nitrogen remaining in the spent shale totaled 45 percent of the original nitrogen content, and the ammonia yield was increased to 22.5 pounds per ton, in contrast to the ordinary recover of 9-10 pounds per ton.

The water gas reaction. During the run above described the total gas yield was obtained by proper manipulation of the gas holders. Heating values were run on every tank of gas. The total yield of gas from the beginning of the run until the stopping of it amounted to 387 cubic feet, with an average heating value of 360 b.t.u. On the basis of ton lots the yield of gas is 38,700 cubic feet. Nor was the maximum amount reached. The run was stopped because of mechanical difficulties. The fixed carbon of the spent shale in this instance is 8.5 percent calculated to the basis of the fresh shale, whereas in the residue after the ordinary run there were 26.48 percent fixed carbon. The loss by the reaction with steam is 17.98 percent. Were the maximum amount of fixed carbon used for gas making under the same conditions one might expect the yield to be bettered by approximately one-third.

In consideration of any raw material for gas making, the

sulphur content and the fusion point of the ash are of the utmost importance. Shale samples No. 1, No. 14, No. 6, and No. 15 were examined for the latter, and No. 14 and No. 15 for the sulphur content.

Method of determining the sulphur. One gram of the shale with .5 gram $KClO_3$, 10 grams Na_2O_2 and .2 gram of benzoic acid were placed in a peroxide bomb, the cover clamped on, and the contents thoroughly mixed by shaking. Fusion was started by holding the bottom of the bomb an instant over a fine pointed flame from a blast lamp. The bomb was placed in running water at the start or jerk of the fusion. Sulphur was run on the fused mixture in the usual manner by precipitation with $BaCl_2$ solution after the removal of the iron and aluminum by ammonium hydroxide.

Method of Determining the Fusing Point of the Ash. Carefully ashed samples were made up into small cones similar to Seger cones, using as binder a solution of dextrin. The cones were mounted on a base of fire clay grog, slowly dried, and heated slowly in an oil furnace in which the mixture of oil and air was of such a nature to keep a reducing atmosphere during the heating. The lowest fusion point of the ash was therefore obtained. The temperature at which the cone fell over was read by means of a Fery optical pyrometer.

The results are summarized as follows:

TABLE XI

SULPHUR CONTENT OF SHALES AND FUSING POINT OF SHALE ASHES

Shale Sample No.	1	14	6	15
Sulphur, percent	-	6.62	-	1.18
Fusing Point of Ash	1090° C.	1160° C.	1240° C.	1240° C.

The sulphur is present in all the shales as organic and pyritic sulphur. In No. 1 and No. 14 the gases are at all times foul smelling, as well as the tars, while the gas from No. 15 is remarkably sweet smelling and burns with an exceedingly luminous flame. At higher temperatures, however, the gas from No. 15 becomes decidedly sulphurous.

Haber[42] has summed up the situation regarding the water gas equilibrium. This equilibrium is readily attained between the gases CO_2, CO, H_2, and H_2O. Technical importance attaches to the equilibrium when the content of CO is high and that of CO_2 is low. The location of the equilibrium between coal, carbon dioxide, and carbon monoxide, makes it theoretically possible to attain this even below 800° C. Practically, the inertness of the coal prevents attaining satisfactory values for the ratio CO/CO_2. The small content of CO_2 predicted by theory in the case of this equilibrium above 1000° C. is always exceeded somewhat in the technical preparation of the gas. The catalysing effect on this equilibrium of inert mineral ash in high ash materials has evidently not been studied. The question merits investigation.

With the possible exception of shale No. 1, the shales tested above have ash fusing temperatures well above the requirement. The ash of No. 14 and No. 15 would not fuse and cause trouble in the producer. Sample No. 6 is from the same deposit as sample No. 15, and shows the same value.

13. <u>A Further Study of Shale Tar From Sample No. 15.</u> - The tar from shale No. 15 was the subject of a more detailed study. Shale No. 15 is from a deposit of cannel coal, or rather cannel shale, on the farm of Dr. J. E. Blanchard. It is a deposit belonging to the

Pennsylvanian period. Its chief properties have already been discussed.

During the development of the experimental plant, and the experimentation to overcome mechanical difficulties, many runs on this shale were made for the recovery of the tar and ammonia water. Some dozen lots of tar varying in specific gravity from .890 to .914 (23°C.) were stored in a metal container and allowed to stand until the water had separated as completely as possible. Quantities of this tar were distilled from a still handily made from a four gallon water heater turned on its side. The tar oils from these distillations furnished the material on which the study proceeded.

TABLE XII

RESULTS OF DISTILLATION OF A THREE-KILOGRAM QUANTITY OF SHALE TAR

(Sp. G. 901 at 25°C.)

	Water To	170°C.	170°C-230°C.	230°C-270°C.	270°C-300°C.	350°C.	Over 350°C.	Residue and loss
Grams	90.3	242.2	310.0	357.7	334.2	652.9	798.5	214.2
Sp. G. at 25°C,	.776	..823	.858	.880	.910	.934	Solid	
Percent	3.1	8.1	10.3	11.9	11.1	21.7	26.6	7.2
Weight Volume c.c.	116.2	292.0	362.0	406.0	367.9	699.0		
Volume Percent	4.0	9.8	12.0	13.5	12.2	24.3		

With the exception of the light oil, all fractions came over with darkening color, which rapidly deepened on standing. At about the temperature 300°C. solid paraffin is precipitated when a drop of the distillate is allowed to fall on ice. The distillate over 350°C.

sets at 24°C. and contains 26.45 percent solid paraffin, determined by the method of Holde.[43] The method is one depending upon the insolubility of the higher aliphatic hydrocarbons in an alcohol-ether mixture at -20°C., and it gives only approximate results in the presence of soft paraffins.

The fractions 0-170°C., 170-230°C., 230-270°C., and 270-300°C. were washed repeatedly with 10 percent sodium hydroxide solution in small portions until the solution failed to give appreciable cloudiness with acids. The oils were then washed with water to remove most of the sodium hydroxide remaining, and then shaken with portions of sulphuric acid solution (1:2) to remove the bases. A washing with sodium carbonate solution followed, the oils being finally dried over calcium chloride.

The specific gravities were lowered by the removal of the acid acids and bases. The values were .751, .790, .823, .846, respectively.

Small portions of the fractions were shaken first with 89.6 percent sulphuric acid to remove olefins, then the fuming sulphuric to remove aromatics. Fuming nitric acid reacts on the remaining oil to some extent, and a mixture of nitric acid and sulphuric acid produce a tar. This together with the high specific gravity of the fractions indicates the presence of naphthenes. In the first fraction the oil unabsorbed by the fuming sulphuric acid constituted about 55 percent of the fraction. Fifteen percent of this residual oil appeared to be dissolved by the nitric acid.

14. <u>General Observations</u>.- Shale tar is formed by the distillation of shale, and yields the following different products: tar, consisting of liquid and solid hydrocarbons; tar water,

containing ammonia and the organic compounds of the same with fatty and other acids, also pyridin and pyrrol; gas and residue.

Tars from shale are intermediate between petroleum on the one hand and coal tar on the other. They contain liquid and solid hydrocarbons of the fatty series, with small quantities of acids, bases, and aromatic substances. The tars are brown to brown-red in color, and have a dark green fluorescence. Very little free carbon is present. The melting point lies within the range of 5°C. to 30°C. The nitrogen content of the average shale tar of commerce is 1.16 to 1.45 percent.[44] The nitrogen contents of those studied in the present investigation varied from .87 to 1.43 percent.

The tar waters obtained in this investigation are of the general nature of coal tar waters. The water from shale No. 15 contains an indicator or dye, whose acid form colors its ether solution yellow. In neutral solution it is rose colored, and in basic solution, red. It is probably rosolic acid. This compound has been found in coal tar waters.

III SUMMARY

The percentage proportion of the constituents in shale tar depends on the kind of shale and the method of carrying out the distillation of it. Assuming a tar of normal type to be one which has been produced with the least possible decomposition of a secondary sort, that is, one which represents the primary products of the shale the composition of such a tar can be changed by two definite lines of procedure. The normal tar may itself be subjected to certain conditions of temperature, pressure, rate of distillation, or presence of catalysers, which will give a tar of different composition. On the other hand, the substance from which the tar is derived may be subjected in the initial process within certain limits to the same conditions and bring about similar changes.

Parr and Charleton[45] have demonstrated that a low temperature tar from coal, that is, of the type which might be called normal to coal carbonization, may be made to yield under modified conditions as to temperature and pressure a tar approaching the ordinary coal tar in composition. Moreover they have established the fact that definite changes in the conditions of distillation produce definite changes in the composition of the tar. Thus paraffin hydrocarbons will entirely disappear from such a tar when distilled at 650° C., and anthracene and its homologues may be formed in the destructive distillation of hydrocarbons without the formation of naphthalene as an intermediate product. They find that steam is a protective agent in distillation, and that charcoal actively catalyses the formation of higher boiling constituents. Parr and Rowland[46], working with petroleum products find that aliphatic hydrocarbons decompose readily when

subjected to temperatures above 450° C., and confirm the observation of Parr and Charlton that aromatic hydrocarbons are the most stable, and that unsaturated compounds are intermediate between aromatic and aliphatic compounds in their resistance to decomposition.

The tars under observation in this investigation are of intermediate composition between coal tar and petroleum. We may assume that product to be the normal type of shale tar which is produced during slow low temperature dry distillation. It contains in the light oil, 0-170° C., 56 percent paraffins, 23 percent unsaturated and five percent aromatic hydrocarbons. The percent composition in the higher fractions is similar. Now, upon rapid distillation at high temperatures, the paraffins diminish to 40 percent, and the unsaturated and aromatic compounds increase in proportion. With the injection of steam a protective influence was observed similar to that found by the above mentioned investigators. That is, the steam prevents secondary decomposition, and the paraffin percentage increases from the normal value of 56 percent to 70 percent, while the aromatics decrease to 3 percent and the unsaturated hydrocarbons to 20 percent. The fact that anthracene was found present while naphthalene was not detected agrees with the observation of Parr and Charlton that anthracene may be formed in coal tar without the interposition of naphthalene as an intermediate product.

The distillation of shale is marked by a gradual rise in temperature, during which time the distilling oils are subjected to more or less rapidly increasing temperature. It is therefore not to be expected that it would be possible to produce in the distillation such far reaching changes as were observed in the decomposition of petroleum and coal tar at constant high temperatures.

The character of these shale tars is then established: they are intermediate between petroleum and coal tar. Their modification serves to verify the related lines of investigation, indicating that olefins are the decomposition products of paraffins, and that both yield aromatics on decomposition.

IV CONCLUSIONS

1. The organic detritus in the shales is derived mainly from the resinic portions of plant residues, but its nature is such that only very small amounts of it can be extracted by benzene.

2. The shale tars obtained by low temperature distillation are intermediate between petroleum and coal tar.

(1) They are lighter than water, and contain but small amounts of free carbon and sulphur compounds.

(2) Hydrocarbons are present in great abundance, with lesser amounts of compounds of acidic and basic nature.

(3) Aromatic hydrocarbons are present in small quantity.

(4) High boiling hydrocarbons constitute the greater portion of the tar.

3. The use of steam in distillation tends to preserve the paraffins by preventing secondary decomposition, but does not increase the tar yield to any great extent. Increase in the rate of heating lowers the tar yield slightly, and increases the content of unsaturated and aromatic constituents.

4. At 850°C. steam reacts readily with the carbon in the shale residue with the formation of water gas. The nitrogen in the residue is at the same time converted almost completely into ammonia.

5. One shale under consideration has probable technical value both because of the yields and the nature of its tar oils, and because of its gas producing properties.

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