[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. IV.]

OIL-GAS.[1]

BY W. A. NOYES, W. M. BLINKS AND A. V. H. MORY.[2]

SOME years ago Armstrong and Miller[3] made a study of the gas made from petroleum by subjecting it to a high temperature, and of the oil deposited on condensing the gas. The following study of the gas made from petroleum by a somewhat different process and which gives in some respects different results may be of interest.

In the Pintsch system[4] as described by Armstrong and Miller two **D** shaped retorts of cast iron are set one above the other, the largest size in use being six feet four inches long, ten inches' wide and nine and three-fourths inches deep. The retorts are heated to a bright cherry-red and the oil may be run into the upper retort at the rate of about twelve and one-half gallons per hour. About eighty feet of gas per gallon of oil is considered a good yield.

By the Citizens Fuel and Gas Company of Terre Haute, gas is made from petroleum in large generators, one having a capacity of about 450 cubic feet of gas per minute, and two smaller ones with a capacity of 250 feet per minute, during the generation of the gas. The larger generator consists of an outer cylindrical shell of three-eighths-inch boiler steel, twenty feet high by eight feet in diameter, lined with fire-brick to a thickness of sixteen inches. The interior is composed of alternate chambers and checker-work compartments of fire-brick. Starting at the bottom there is an open chamber to the height of two and one-half feet, then, resting upon six twelve-inch arches, the checker-work of brick is built up, rows of brick, touching end to end and two and one-half inches apart, extending from wall to wall, composing the first tier, then upon these other rows are laid at

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[1] Read at the Brooklyn meeting, August 15, 1894.

[2] The work described in this paper formed the basis of a thesis presented to the Faculty of the Rose Polytechnic Institute by Mr. W. M. Blinks and Mr. A. V. H. Mory for the degree of Bachelor of Science.

[3] *J. Chem. Soc.*, (London) 49, 74, (1886).

[4] *J. Soc. Chem. Ind.*, *1884*, 463. We are indebted to Mr. W. B. Laudon of Lafayette College for this statement, as the Journal is not accessible to us.

right angles to the first, then the next tier so as to be directly over the open squares formed by the first two rows, and so on, making the checkerwork to the height of five and one-half feet. The bricks are laid in, one upon another, without mortar or fire-clay

Above this checkerwork is a chamber three feet high, then arches and more checkerwork for five and one-half feet and then another chamber extending to the top. A heavy iron door fourteen inches in diameter is provided at the top. By opening and shutting this it is made to act as a regulator for equalizing pressures when reversing operations. For heating the generator, oil is injected into the top and middle chambers by means of a steam-jet, air being admitted at the same points through five-inch valves. For generating gas, oil is injected into the top chamber through three jets. The gas which is formed leaves the chamber at the bottom through a sixteen-inch pipe lined with fire-brick and leading into the water-seal. The gas as it leaves the generator is too rich for burning in ordinary burners, hence in the seal-box it is diluted with ordinary air injected by steam through a four-inch pipe into the top of the seal. In the process as formerly used this air was injected into the generator with the oil and the oxygen which it contained appeared as carbon dioxide and carbon monoxide in the gas produced. This form of the process is still in use elsewhere.

The seal-box is three and one-half feet in height by four feet in diameter and the pipe leading from the generator dips eight inches below the water surface. A stream of cold water runs continuously into the seal-box, condensing the tar which is carried with the overflow water into the tar well. From the seal the gas passes through a tower scrubber twenty feet in height where it is washed with cold water, then through a tubular condenser, from this through a second scrubber and then through two purifying boxes, 14 × 14 × 3 feet with a twenty-four inch seal. From the purifiers the gas passes through the station meter and thence to the holder. The purifying material used is technically known as Laming's Mass, and is prepared by treating wood shavings with copperas and lime, four barrels of copperas and about the same amount of lime being used to 300 bushels of shavings.

TEMPERATURE.

The destructive distillation of the oil in the process of gas-making is an endothermic operation, large quantities of heat being taken up from the hot brickwork, and the operation can only be carried on for from seven to ten minutes at a time, when the heating must be recommenced and continued for approximately the same length of time.

The temperatures in the generator were measured by noting the melting-points of salts. The salt was wrapped in platinum foil; this was placed in a sheet iron tube attached to an iron rod and the insertion was made through a hole in the side of the generator.

Measurements of the lowest temperature were made by introducing the salts immediately after the gas-making ceased and withdrawing them at the end of two minutes. Sodium chloride was unaltered in all trials at the first temperature, potassium chloride fused in about three minutes, while potassium bromide melted in less than two minutes. The lower temperature is, therefore, between the melting-points of potassium bromide and potassium chloride.

At the highest temperature sodium carbonate fused but calcium fluoride was unaltered. Experiments with sodium sulphate were rejected because the salt was apparently reduced by the gases to which it was subjected.

In assigning a temperature in degrees some difficulty is experienced, as authorities differ as regards the melting-points of these salts. The following values are given by Carnelly,[1] and quoted in the work of Mills and Rowan on fuels, page 341, and by Victor Meyer, and Riddle.[2] The values of the latter, however, are stated as being preliminary only and the melting-point of sodium carbonate especially, is stated, in a later paper, to be too high.

	Carnelly.	Meyer and Riddle.
Potassium bromide	......	715° C.
Potassium chloride	734° C.	766° C.
Sodium chloride	772° C.	851° C.
Sodium carbonate	814° C.	1098° C.
Calcium fluoride	902° C.	......

The lower temperature may be stated with some degree of certainty as being about 750° C., while the higher temperature is probably 900° to 1,000° C.

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[1] *J. Chem. Soc.*, [London] *1878* and *1880*.

[2] *Ber. d. chem. Ges.*, 26, 2443.

COMPOSITION OF THE GAS.

The following determinations of the technical composition of the gas were made with Orsat's apparatus, the determinations of methane and hydrogen being made by explosion with an excess of air and the addition of oxyhydrogen gas, the large amount of methane rendering an explosion with air alone almost impossible. The illuminants were determined by absorption in fuming sulphuric acid. The first two determinations were duplicated with Hempel's apparatus with almost identical results. The "total carbon" in the gas was determined by exploding a known volume of the gas with an excess of air and determining the volume of carbon dioxide formed. The ethylene and propylene are calculated on the assumption that the illuminants consist exclusively of these two gases. It is well known, of course, and will be further shown below, that this is not the case, but for the purpose of calculating the heat of combustion of the gas the error introduced is slight and is certainly less than on the assumption, usually made, that the illuminants consist entirely of ethylene.

The heat of combustion is calculated on the basis of one cubic foot of the gas at 0° C., burned to carbon dioxide and vapor of water. The following values are used, deduced from the values given in Winkler's "Technische Gasanalyse."

One cubic foot of ethylene	gives 1573.3	English heat units.
" " " propylene	" 2324.8	" " "
" " " carbon monoxide	" 342.4	" " "
" " " methane	" 964.3	" " "
" " " hydrogen	" 289.8	" " "

	Feb. 20. Undiluted gas. Per cent.	Feb. 20. Diluted gas. Per cent.	May 22. Diluted gas. Per cent.	June 5. Diluted gas. Per cent.
Carbon dioxide	2.3	2.1	0.7	0.8
Illuminants	28.1	19.9	19.3	15.9
Oxygen	0.2	5.9	7.0	7.7
Carbon monoxide	0.6	1.8	0.0	0.0
Methane	44.8	32.3	33.2	36.0
Hydrogen	20.5	14.2	6.9	6.1
Nitrogen	3.5	23.9	32.9	33.5
	100.0	100.0	100.0	100.0
Total carbon—carbon dioxide	115.7	85.6	85.5	77.0
Illuminants { Ethylene	16.2	10.3	6.3	7.5
Illuminants { Propylene	11.9	9.6	13.0	8.4
English heat units per cubic foot	1025.0	744.0	741.0	678.0

The small amount of carbon dioxide and carbon monoxide present in the gas is worthy of especial remark. Steam is used to inject the oil into the generator, but the analyses show that the steam must pass out at the end almost entirely unchanged. It follows from this that in an atmosphere of reducing gases and at a temperature of 700° to 900° C. it is impossible to burn carbon to carbon monoxide or dioxide by means of steam. This is still more apparent in those forms of the process in which air is introduced into the generator. One of us has made many analyses of gases produced in that way and in every case the oxygen of the carbon dioxide and carbon monoxide combined was less than that of the air introduced. These facts have a very important practical bearing as regards the use of steam with petroleum in the manufacture of gas.

The gas directly from the producer contained 1.83 grains of sulphur per cubic foot. The purified gas contained 0.025 grain per cubic foot.

EFFICIENCY.

The amount of oil required for 1,000 cubic feet of gas varies somewhat with the condition of the generators. The following determinations were made:

I. Feb. 20. One run of the large generator when it was about to be shut down for repairs.

Oil per 1,000 cubic feet of diluted gas, for heating···	2.3	gallons.
" " " " " " generating	10.7	"
Total··········· ·········	13.0	"

II. June 5. Average of five runs of the large generator just fitted with new brickwork.

Oil per 1,000 cubic feet of diluted gas, for heating···	1.4	gallons.
" " " " " " generating	9.7	"
Total······················	11.1	"

On comparing the analyses, it will be seen that the gas of June 5 was diluted somewhat more than that of Feb. 22, so that the real difference in efficiency is only about six per cent. As the oil used was different and that of June 5 was, apparently, of better quality, no reliance can be placed on the difference.

So much time was taken for other parts of the work that these determinations were not repeated so many times as they should have been. Apparently, however, about ten gallons of oil are used in the large generator for generating 1,000 cubic feet of diluted gas and 1.5 to 2.0 gallons of oil are used for heating. When we consider the amount of the dilution, these results are somewhat lower than those reported by Armstrong and Miller. Unfortunately they give no analyses of the gas.

The oil used on Feb. 20 contained some water and an analysis gave

	Per cent.
Carbon	81.0
Hydrogen	12.7

The specific gravity was 0.843.

The oil used on June 5 was nearly free from water and had a specific gravity of 0.865.

We will take the run of June 5 as a basis for calculating, approximately, the efficiency of its plant. If we assume the oil to contain eighty-six per cent. carbon and fourteen per cent. hydrogen one gallon of the oil would give, when burned to vapor of water, about 140,000 English heat units, and the amount of oil required for the manufacture of one cubic foot of gas would give about 1,550 English heat units. Since the gas itself gives 678 units per cubic foot (see analysis), about forty-four per cent. of the heating power of the oil is found in the gas.

Without going into the details of calculation, it may be of interest to state that about thirty-five per cent. of the heating effect of the oil used in heating the generator, is lost by reason of the high temperature of the smoke gases, and an approximately equal amount of heat is carried away by the gas during the generation of the latter. It is probable that at least ten per cent. of the heating effect of the total oil used is lost in this way, though the calculations do not show quite that amount. The remainder of the loss appears to be due mainly to the formation of tar.

PHOTOMETRIC TESTS.[1]

On May 21 a test of the candle-power of the diluted gas, as furnished to consumers, was made, using a Lumner-Brodhun

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[1] These tests were made with instruments from the Physical Laboratory, and under the direction of Prof. C. L. Mees.

photometer with a three meter bar. The instrument was made by Hartman and Braun. The Methven slit was used as the direct standard, its value being first determined in terms of a standard amyl acetate lamp which was taken as of one candle-power. A wet meter, which, during one minute, indicated the number of cubic feet burned per hour, was used. Readings were taken on the meter and photometer each minute for five, and sometimes ten, consecutive minutes. Averages of these readings were made and the gas consumption was corrected for temperature.

The first night, tests were made using an argand, a five foot bat-wing, and a small and large Welsbach burner.

The second night, tests were made with a view to determining the relative efficiencies of different sizes of bat-wing burners, and of each size burning under different conditions. The conditions chosen were those of a smooth flame with a consumption rather under the indicated amount, and of a large, forked flame burning as high as possible without blowing. The appended table shows the results obtained,

MAY 22. METHVEN = 2.57 CANDLES.

Burner	Candle power found during the test.	Rate of gas burned per hour during the test.	Candle power corrected for five feet per hour.
Argand	29.3	5.17 cu. ft.	28.4
Five-foot bat wing	33.9	5.27 "	32.2
Small Welsbach	31.4	3.25 "	48.3
Large Welsbach	57.13	6.06 "	47.1

MAY 23. METHVEN = 2.36 CANDLES.

Nature of flame.	Burner.	As above.	As above.	As above.
Smooth	2 ft. bat wing.	14.20	3.21 cu. ft.	22.12
Forked	" "	23.32	5.54 "	21.05
Smooth	3 "	18.53	3.49 "	26.54
Forked	" "	30.02	6.32 "	23.75
Smooth	4 "	19.66	3.43 "	28.66
Forked	" "	37.45	6.74 "	27.78
Smooth	5 "	28.00	4.47 "	31.32
Forked	" "	39.88	6.43 "	31.01
Smooth	6 "	25.01	3.96 "	31.58
Forked	" "	45.01	7.06 "	31.87
Smooth	7 "	29.32	4.43 "	33.10
Forked	" "	53.18	8.27 "	32.15

It will be seen that the larger burners are most efficient and that, with one exception, the smooth flame gives better results. This is especially true of the smaller burners. A sample of the gas taken on May 22 gives for the calculated heating effect 741 English heat units. The statement of the analysis is given elsewhere.

COMPOSITION OF THE ILLUMINANTS.

In order to determine the presence and the amount of benzene and similar hydrocarbons in the gas, these were determined by a modification of the method of Hempel and Dennis, (see next paper), and also by absorption in absolute alcohol and subsequent dilution with salt water. Both methods gave essentially the same result and showed that about 1.2 per cent. by volume of the gas consists of the vapor of these hydrocarbons. From the oil obtained by the second method pure metadinitrobenzene was easily obtained by nitration and crystallization.

To determine the composition of the other gases forming the illuminants, gas directly from the generator was aspirated through an absorption train consisting of two one-liter bottles packed in ice to condense the tar, then two one-half liter bottles half filled with an ammoniacal solution of cuprous chloride to absorb acetylene, next a bottle of the same size half filled with dilute sulphuric acid to absorb ammonia fumes from the cuprous chloride solution, next three Drechsel wash-bottles standing in ice-water, the first two containing one hundred grams each of bromine with about half an inch of water above, and the third containing distilled water for the collection of bromine carried over from the other two, and finally a wash-bottle half full of a solution of sodium hydroxide to absorb bromine fumes. Approximately 125 liters of gas were passed through the train to effect the saturation of the bromine.

The bromine compounds were washed twice with caustic soda, then with distilled water, were separated, dried with calcium chloride, and fractioned. More than one-half came over between 127° and 150°. The residue remaining in the distilling bulb solidified on cooling. It was crystallized from alcohol and from ligroin when it melted at 113°-113.5°. An analysis gave the following results:

0.0750 gram gave 0.1500 gram AgBr.

	Cal. for $C_4H_6Br_4$.	Found.
Br	85.56	85.11

Armstrong and Miller[1] obtained a bromide melting at 116°, which they considered to be divinyl tetrabromide (1, 2, 3, 4 tetrabrombutane). The substance described above was probably the same, but less pure, as we have worked with much smaller quantities.

The portion of the bromides boiling from 127° to 150° was redistilled and gave three fractions, the largest 129°–133°, that from 133°–139° next and that from 139°–143° least. After fractioning again, a determination of the molecular weight by the air-displacement method of Victor Meyer, was made with the portion boiling at 130° to 133°. The results agreed fairly with the molecular weight of ethylene bromide. Determinations of the molecular weight of the fraction 140°–143° were unsuccessful owing to decomposition of the bromide. There can be little doubt, however, that the bromides consisted chiefly of ethylene and propylene bromides, the former being present in much larger amount than the latter.

A considerable precipitate was obtained in the ammoniacal solution of cuprous chloride, indicating the presence of appreciable amounts of acetylene and its homologues. In this respect our results differ from those of Armstrong and Miller.

TAR.

The amount and character of the tar varies considerably with the conditions of running. Two samples of the tar were examined, one which was thick and viscous, another which was comparatively thin. No essential difference in qualitative composition was established. The lower boiling substances contained in the tar were separated by distillation with superheated steam, the higher boiling products by direct distillation. In the direct distillation much trouble was experienced from frothing and it was found necessary to heat the tar at first in small quantities in an open dish until the frothing ceased. The residue was then distilled as usual.

Without going into the details of the work the results of the study may be stated briefly as follows:

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[1] *J. Chem. Soc.*, (London) 49, 81, (1886).

Benzene and its lower boiling homologues appear to be present in the tar in only small amount. No positive evidence of their presence was obtained, although it has been shown that benzene is present in the gas.

Naphthalene is present in considerable amount and was identified by melting-point and boiling-point.

Anthracene is also present and was identified by melting-point and by conversion into anthraquinone. An approximate quantitative determination of the amount of anthracene was also made, showing the presence of about 0.35 per cent.

From the portion coming over at about 425° there was obtained, by crystallization, a solid melting at 250° and probably crysene.

From the portion boiling still higher a green crystalline solid melting at about 240° was obtained but not in sufficient amount for its identification.

Attempts to isolate phenol were unsuccessful, though it is probably present in small amount.

The results of the investigation confirm the conclusion of Armstrong and Miller that benzene and allied hydrocarbons may be formed, at high temperatures, from hydrocarbons which bear no simple relation to them.

In conclusion we wish to express to Mr. J. J. Kirkham, Superintendent of the Terre Haute Citizen's Fuel and Gas Company, our thanks for many favors shown us in the course of the work.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. V.]

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.[1]

BY W. A. NOYES AND W. N. BLINKS.

SOME time since Hempel and Dennis[2] described a method of determining benzene vapors in illuminating gas which depends on their absorption in a very small quantity of absolute alcohol. The amount of mercury required and the difficulty of applying the method as described by these authors led us to

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[1] Read at the Brooklyn meeting. August 15, 1894.

[2] *Ber. d. chem. Ges.*, 24, 1162. Also the translation of Hempel's Gas Analysis by L. M. Dennis, p. 221.