

XLIII.—*The effects of Pressure and Cold upon the Gaseous Products of the Distillation of Carbonaceous Shales.*

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THE distillation of carbonaceous shales at a low red heat, as practised on the large scale for the production of hydrocarbon illuminating oils, is well known to be accompanied by the simultaneous production of gas.

The quantity of shale distilled in the United Kingdom is very large, producing several millions of cubic feet of gas daily (when the whole of the works are in operation), and its illuminating power averages from 24 to 26 candles. The gas is employed for illuminating towns in the vicinity of the works, but the quantity utilised in this way bears a very

small proportion to the production, on account of the great distance of works from large centres of population.

At ordinary atmospheric temperatures and pressures, the gas has some resemblance to ordinary coal gas, especially in the property of having condensable vapours abstracted by contact with cold dense liquid hydrocarbons, the efficiency of the absorption being, however, dependent upon the temperature of the gas and the mass and temperature of the absorbent liquid. The process is in use on the large scale for the removal of light naphthas from shale-works gas, but is difficult to control in warm weather, or even at ordinary temperatures.

The experiments which I have now the honour to submit to the Society were made with gas taken, by permission of Young's Paraffin Light Company, from the gas-main (at a point immediately before its junction with the lime purifiers), which supplies the town of West Calder, N.B., with gas from their works. The gas was, consequently, in a crude state, and its temperature did not exceed  $10^{\circ}$  during the whole course of the experiments, which were made in severe winter weather.

The experimental apparatus used in the inquiry was constructed as follows:—A force-pump, having a piston 33 millimeters in diameter, was attached to a four-meter length of iron tube of about 15 millimeters internal diameter. This tube was placed at a slight inclination, and at its opposite extremity a loaded valve was fixed, which allowed the gas to blow off at any required pressure up to 10 atmospheres.

At a point 3 meters distant from the pump, a brass reservoir of about 500 c.c. capacity was screwed by means of a T-joint to the horizontal main, so as to hang vertically.

At a short distance farther from the pump the horizontal main was closed by a brass diaphragm, the gas being made to descend about 60 millimeters by 2 copper tubes of about 7 millimeters internal diameter into a second brass reservoir of similar capacity to the first, from which it ascended to the main on the further side of the diaphragm by two more tubes. The object of this arrangement was to afford the means of cooling the gas considerably below zero, after it had been deprived of all liquids condensable at atmospheric temperatures. This was effected by surrounding the copper tubes with ice and salt, protected by a non-conducting casing of dry sawdust.

Before the commencement of each experiment, the efficiency of the pump for *air* for a given number of strokes was determined by measuring the volume passed through the loaded valve at the pressure intended to be used in the experiment with gas. These figures afforded the data for calculating the volume passed for a given number of pump-strokes when gas was substituted for air, observations being taken upon speed and pressure at regular intervals.

The pressure, however, was maintained very constant, being registered by a Bourdon gauge at about 140 lbs. per square inch during the whole course of the experiments, and the pump worked remarkably steady at the rate of about 130 strokes per minute, the power to drive it being obtained by a belt attached to the shafting of a mechanic's shop.

*Experiment I.*—538 litres of gas passed through the apparatus in one hour and three-quarters. At the conclusion of the experiment the load on the valve being too suddenly removed, it was suspected that the contents of the first receiver were partially transferred to the second. On this account the liquids were mixed together. They amounted in volume to 84 c.c. The specific gravity of the mixed liquid was .684 at 16°.

*Experiment II.*—467 litres of gas passed through the apparatus in one hour and a-half, the liquids produced were as follows:—

Condensed at + 5°, 54 c.c. of sp. gr. .690 at 16°.  
 „ - 18°, 23 c.c. of sp. gr. .650 at 16°.

The average sp. gr. of the mixed liquids would, therefore, be .678. This and the preceding experiment were made the same day.

*Experiment III* was made 10 days after the date of the first two. The efficiency of the pump was carefully determined by two hours' observations with air, as the piston cup leather had been in use some time. The pump was then set to work with gas for five hours, and the quantity passed through the apparatus was determined as 1,274 litres; the liquids obtained were—

Condensed at + 16°, the main  
 being surrounded with water as } 114 c.c. of sp. gr. .691 at 16°.  
 that temperature.

Condensed at - 18° ..... 81 c.c. of sp. gr. .658 at 16°.

These figures show that the average sp. gr. of the mixed products would be .677. Calculating the production of liquids per litre of gas, the first experiment yielded .156 c.c., the second .165 c.c., and the third .153 c.c.

Expressed in English imperial measure, the results show a condensation of liquids of sp. gr. .680, equivalent to about one gallon per 1,000 feet of gas.

The experiments having been made in the months of January and February, it is probable that larger quantities of condensable liquids could be obtained in summer months, their sp. gr. being correspondingly increased.

The gas was found to have lost its illuminating power after being

deprived of its liquids, burning in a batwing burner with a flame not more luminous than that of a Bunsen's burner. Of the two liquids condensed, that having a sp. gr. of '650 to '660 is most interesting; it contains a small quantity of a liquid boiling below zero; after its evaporation, the liquid becomes comparatively fixed at ordinary temperatures. Both products had an offensive odour, arising from the presence of sulphur compounds, which were removable with but trifling diminution of bulk by agitation with caustic soda solution.

Upon mixing the products together and distilling them, active ebullition commenced at 30°, and two-thirds of the liquid distilled between that point and 72°, the remaining third coming over under the boiling point of water.

The action of bromine upon the liquids reveals the presence of olefines, but they will doubtless be found to consist largely of alcoholic radicles or their hydrides, as indicated by previous researches of Pelouze and Cahours, Schorlemmer, Ronalds, and Greville Williams upon light petroleum or cannel naphthas.

The *illuminating* constituents of shale-works gas being so effectually removed by cold and pressure, would appear to indicate the absence of *ethylene* in the gas, and a constitution different from that of coal-gas, and this is confirmed by experiments I have made with the apparatus described in this paper with Glasgow Corporation gas.

Dr. Wallace, the gas examiner of the city of Glasgow, informs me that Glasgow gas has a uniform illuminating power of from 24 to 26 candles, which is identical with the illuminating power of the shale-works gas used in my experiments, that it is made in the ordinary way from mixed Scotch cannel of ordinary richness, and is produced at temperatures *far higher* than those employed in distilling shale for oil.

Although I employed a pressure of 10 atmospheres, and worked the apparatus (without ice and salt or artificial cooling) fully 12 hours at about freezing temperature, there being a sharp frost during the whole of the day, I failed to get any measurable quantity of liquid. I repeated the experiment some days afterwards, with the same negative result. I expected some liquids, but it was evident that the pressure I employed would produce no results comparable with the results I obtained at a *similar pressure* with shale oil gas. The experiments with the Glasgow gas were certainly made at a point two miles from the gas-works; but, on the other hand, experience has shown that oil-works gas does not materially alter in illuminating power by travelling two miles to the towns where it is employed for illumination.

There is also an essential difference between shale-oil-works gas, and what was known as oil gas 50 years ago. The latter was obtained from resins and fats at high temperatures also. Faraday states in

his paper, communicated to the Royal Society in 1825, that the liquid from compressed oil gas had a sp. gr. of  $\cdot 821$ , and he shows it to have consisted, in the main, of benzene associated with olefines.

When larger quantities of the liquids I obtained are at command, I propose making a more complete examination of them, as well as of the gas before and after compression.

In the meantime, I may observe that the general results of the investigation, coupled with figures well known, indicate that the products obtained by the destructive distillation of carbonaceous or oil shales at low red heats, are associated as follows :—

	Per cent. by weight.
Non-luminous combustible gas .....	20·9
Volatile liquids having an average sp. gr. $\cdot 680$ dissolved in the gas as vapours .....	4·9
Commercial paraffins ranging between $\cdot 700$ and $\cdot 900$ , in sp. gr. ....	52·3
Tarry acid or basic substances .....	21·9
	<hr/> 100·0

This does not include the ammoniacal water, which is sometimes considerable.

This investigation indicates the possibility of getting a good supply of liquid hydrocarbons sufficiently volatile to be used for air-gas purposes, or what is, perhaps, of more consequence, a supply of liquids suitable for increasing the illuminating power of *poor coal-gases*. For instance, one gallon of the liquid of sp. gr.  $\cdot 650$  volatilised into 5,000 cubic feet of coal-gas, whilst increasing its illuminating power several candles, would probably not involve condensation in the gas-mains, experiment having proved to me that this liquid is absorbed by air at common temperatures to the extent of from 4 to 6 gallons per 1,000 feet. Used in reasonable proportions, the ideas of Mansfield and Lowe may be probably carried out, which have hitherto been found impracticable from the want of a cheap supply of liquids sufficiently volatile.

In order to produce the liquids on the large scale, I have proposed a method which involves—

1. The pumping of the gas by steam power into a system of tubes capable of being externally cooled, and from which condensed liquids can be drawn off by ball-cocks.

2. Employing the compressed gas (after being deprived of its liquids) for working a second engine coupled with, and parallel to, the first, thus *recovering* a portion of the force originally employed in compression.

3. Employing the expanded gas after having had its temperature reduced in the act of doing the work of pumping, as the agent for supplying the necessary cold for cooling a *portion of the condenser* to  $-18^{\circ}$ .

An arrangement which may be applicable to condensing hydrocarbon vapours from other sources, but the details of which are scarcely suitable for discussion in this communication.

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