

XVI.—*On the Influence of the Temperature of Distillation on the Composition of Coal-gas.*

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THE quantity of gas yielded by a certain weight of coal varies according to the applied temperature: with an increase of temperature the quantity of gas is increased and the illuminating power decreased.

The composition of the gas resulting from the application of various degrees of heat has not been very specially investigated, and this is perhaps the first systematic study of the variations in the composition of coal-gas produced by various temperatures of distillation.

In the following experiments no means were taken for the purpose of pyrometrically determining the temperatures employed; because, from the nature of the experiments, any degrees of temperature so arrived at, would, it is believed, have been illusory.

The variations of temperature in the first series are indicated by the variations in the volume of gas resulting from the distillation of equal weights of coal.

1st Series.

Some Newcastle coal was broken up and carefully mixed to ensure evenness of quality throughout the sample, from which different portions were to be taken for trial.

The coal was distilled in a small iron retort of the pattern usually employed for gas-coal testing. This retort was connected with a condenser, lime purifiers, and gasholder, and consequently the whole apparatus represented a gaswork in miniature. The charge of coal for which this apparatus is designed is $\frac{1}{1000}$ part of a ton, or 2·24 lbs., which quantity of coal can be thoroughly carbonised in periods varying from 25 to 45 minutes, according to the temperature employed and the description of coal.

It was arranged that four portions of 2.24 lbs. each of the broken and thoroughly mixed Newcastle coal should be distilled at various temperatures, ranging from a dull red heat to the highest heat attainable with an iron retort.

The manner in which these various temperatures were arrived at may be briefly described. The retort was heated to a dull red, and the first charge of coal carbonised; the fire was then increased, and the retort made perceptibly hotter, and the second charge of coal was carbonised; again the fire was increased, and the third charge of coal carbonised; and finally, when the fire had been so increased that the retort was at a bright orange heat, the last charge was carbonised.

The gas from each charge was of course separately collected and measured; the illuminating power was observed, and samples were drawn off for gas analysis.

The volumes obtained were reduced to 30-inch barometer and 60° F., saturated with water-vapour. The illuminating power is also corrected to a standard consumption of 5 cubic feet and 120 grains per hour.

The "candles per ton" in the following table are obtained by multiplying the yield of gas per ton of coals by the equivalent of 1 cubic foot in candles, or what is the same thing, multiplying the cubic feet per ton by the illuminating power, and dividing the result by 5.

	Gas per ton of coals.	Illuminating power.	Candles per ton.	
(1.)	8,250 cub. ft.	20.5 candles	33,950	1st charge.
(2.)	9,693 "	17.8 "	34,510	2nd "
(3.)	10,821 "	16.75 "	36,140	3rd "
(4.)	12,006 "	15.6 "	37,460	4th "

The four samples of coal-gas from the same coal distilled at various temperatures were analysed in a gas-analysis apparatus, somewhat approaching the Thomas type (*Chem. Soc. J.*, **35**, 231), and the following numbers were obtained:—

	(1.)	(2.)	(3.)	(4.)
H ₂	38.09	43.77	—	48.02
CO	8.72	12.50	—	13.96
CH ₄	42.72	34.50	—	30.70
C _n H _m	7.55	5.83	—	4.51
N ₂	2.92	3.40	—	2.81
Carbon-density of C H _m	2.73	2.91	—	2.62

The analysis of the third sample for CO, CH₄, N₂, was lost, and un-

fortunately no further portion of this gas had been saved when this loss was discovered, but from the figures yielded by the combustion of the gas containing the absorbable hydrocarbons, it is evident that this sample occupied an intermediate place between 2 and 4.

Oxygen was always absent in the samples of gas collected, for precautions had been taken against any introduction of air during the process of distillation. A slight pressure, equal to about $\frac{1}{10}$ of an inch of water in the gasholder, was maintained during the experiments, and thus all parts of the apparatus were under a slight pressure.

It will be seen that, with increased temperature and consequently increased volume of gas produced from the same weight of coal, there is an increase in hydrogen and a decreased quantity of methane and other hydrocarbons. The carbon-density of these latter appears to increase, and then decrease with increased temperatures.

The following table gives the amount of each constituent in cubic feet per ton of coal yielded at the three different temperatures; and it will be observed that as the temperature of distillation is increased, more and more of the carbon and hydrogen in the coal is brought into the shape of permanent gas:—

Number of experiment.	Composition of gas.					Composition of hydrocarbons absorbed by SO ₃ .
	H ₂ .	CO.	CH ₄ .	C _n H _m .	N ₂ .	
1.....	38·09	8·72	42·72	7·55	2·92	C 2·73 H 3·84
2.....	43·77	12·50	34·50	5·83	3·40	C 2·91 H 4·12
3.....	—	—	—	—	—	—
4.....	48·02	13·96	30·70	4·51	2·81	C 2·62 H 5·76

Number of experiment.	Cubic feet of each constituent yielded by 1 ton of coal.					Carbon vapour per 100 vols. of gas.	Ratio carbon vapour.
	H ₂ .	CO.	CH ₄ .	C _n H _m .	N ₂ .		Illuminating power.
1.....	3142·4	719·4	3524·4	622·9	240·9	72·08	3·51
2.....	4242·6	1211·6	3344·1	565·1	329·6	63·93	3·59
3.....	—	—	—	—	—	60·66	3·62
4.....	5765·3	1676·0	3685·8	541·5	337·4	56·49	3·62

There is much that is inexplicable in the connection between the percentage volume of the C_nH_m hydrocarbons and the photogenic power of coal-gas; and it was known long ago that there is no direct pro-

portionality between the two. Some years ago a method of determining the photogenic power of coal-gas by analysis was worked out in a manner (first perhaps conceived by the illustrious Dr. Henry) somewhat as follows:—The percentage volume of hydrocarbons absorbable by chlorine or bromine was determined, also the specific gravity of the gas before and after the absorption of the hydrocarbons (other than methane). By these means the specific gravity of the absorbable hydrocarbons was arrived at, and it was found that by multiplying the percentage volume of the C_nH_m into their specific gravity in a state of vapour as they existed in the gas, a number was obtained agreeing very closely with the photogenic power as determined by candles with the photometer. Of course for so empirical a method to have yielded such results is more of an accident than anything else.

The influence of such neutral gases as carbonic anhydride and nitrogen is better understood. These gases have a deleterious influence proportional to their specific heats, as I pointed out in 1876 (*Journal of Gas Lighting*, vol. 30), and as was demonstrated by Rossetti (*Gazzetta chimica italiana*, 7, 422; *Chem. Soc. J.*, 1878, Abstr., 467). The influence of such gases as methane, carbonic oxide, and hydrogen, in spite of the researches of Frankland and Thorne, is not quite clear. It is evident that methane is a more useful constituent than hydrogen or carbonic oxide. Frankland and Thorne found that benzene-vapour yielded 5·3 per cent. more light when diluted with carbonic oxide than with hydrogen; but the method of photometry employed in that research does not make it quite clear whether the result can be accepted as approximating very closely to the truth.

Gases of different illuminating power, consumed at different rates in a fish-tail burner, can hardly be expected to yield results having much relation to a common standard. For instance, their benzolised hydrogen was burned at the rate of 4·95 cubic feet, and had an illuminating power corrected to the 5-foot standard of 28·58 candles. It is fair to assume that with any other rate of consumption the illuminating power corrected to 5 feet would have been different.

The benzolised carbonic oxide was consumed at the rate of 4·22 cubic feet per hour, and when corrected to the 5 cubic feet standard, the illuminating power was 23·48 candles. Had the benzolised carbonic oxide been consumed at 4·95 cubic feet per hour, as was the benzolised hydrogen, the illuminating power corrected to 5 feet would have been different.

Some experiments I made a few years ago would indicate that carbonic oxide is a greater diluent of luminosity than hydrogen. Trials were made for the purpose of ascertaining how many volumes of carbonic anhydride, nitrogen, air, carbonic oxide, and hydrogen

respectively, would completely disilluminate 100 vols. of coal-gas (17 candles) by previous admixture. By disillumination is meant the disappearance of any white luminosity in the flame, which was burned from a jet, and was therefore symmetrical in shape.

The results obtained are tabulated below.

100 Volumes Coal-gas required for Disillumination.

Luminosity recoverable by previous heating	{	196 parts air.
of mixture		196 „ N ₂ .
		100 „ CO ₂ .
Luminosity not so recoverable.....	{	627 „ CO.
		1233 „ H ₂ .

It does not necessarily follow from these results that the illuminating power of a luminous gas would be effected equally by admixture with carbonic oxide or hydrogen (in quantities considerably short of what is required for total disillumination) in the proportion of 627 to 1233 respectively.

These experiments of mine are somewhat confirmed by those recently made by Dr. Percy Frankland (p. 30 of this volume), an abstract of which has appeared in some of the papers. From this I gather that he found ethylene to yield more luminosity in hydrogen than in carbonic oxide. It must not be forgotten that illuminating power is an arbitrary and variable standard. By using different burners and rates of consumption, widely different results can be obtained, and in experiments of this kind it is highly desirable that the conditions of experiment should be as fair for one gas as for another.

From the researches of Landolt, Hilgard, Blochmann and others, it would appear that hydrogen and methane disappear on combustion more rapidly than carbonic oxide. It seems difficult, with our present knowledge of the subject, to come to any precise conclusions as to the relative value of carbonic oxide and hydrogen in coal-gas, though it would be easy to mix coal-gas of known candle power with small quantities of CO and H₂, and observe the loss of candle power.

I hope soon to have an opportunity of making some experiments in this direction.

On looking over the numbers obtained by the analysis of the four samples of gas, I found a simple relation between the illuminating power and the carbon, which is expressed in the table under the ratio

$$\frac{\text{Carbon vapour}}{\text{Illuminating power}}$$

2nd Series.

Many years ago Dr. Henry studied the composition of the gas coming off the coal at various stages of the distillation. I do not know where his original memoir may be found, but the following table is taken from *Chemical Technology*, 2nd ed., vol. 1, part ii, page 581: Ronald and Richardson, 1855.

Time of collection.	Specific gravity.	Absorbed by chlorine	Light carburetted hydrogen	Carbonic oxide	Hydrogen	Nitrogen
		Out of 100 parts of gas from Wigan cannel coal.				
1st hour	0·6·0	13	82·5	3·2	0	1·3
	0·620	12	72	1·9	8·8	5·3
	0·630	12	58	12·3	16	1·7
5—10 hours after commencement	0·500	7	56	11	21·3	4·7
	0·345	0	20	10	60	10

The following experiments are in the same direction as those of Dr. Henry. The samples were taken off clay retorts distilling Newcastle coal in the ordinary process of gas-making; but precautions were observed to prevent access of air into the retort or gas collected, by ensuring that the gas was being distilled and the samples collected under a slight pressure. Under these circumstances I have always failed to find any trace of oxygen in the gas. The samples were taken from the ascension pipe connected with the retort, and therefore contained the usual impurities of crude coal-gas. Before passing the portions of the samples for analysis into the measuring tube, the trace of ammonia was always removed by dilute sulphuric acid.

In the practice of gas making, a red-hot retort, on being first charged with coal, suffers a considerable reduction of temperature, owing to the mass of cold coal suddenly thrown in, and the early portions of gas distilled off are therefore not submitted to the action of a very high temperature; but as the coal becomes more and more carbonised, and the retort has less work to do, the heat gains on the coal, the portion near to the sides of the retort being perhaps red-hot, and consequently the latter portions of gas have to suffer the disintegrating action of a much higher temperature than the early portions. Thus, the gas collected at various stages of the distillation might be expected to exhibit variations in composition somewhat similar to those yielded by the same coal distilled at various temperatures.

I have tabulated the results obtained from three different retorts

working under slightly different conditions as regards temperature and weight of coal.

1st Case.

Samples collected from a clay retort which was charged with a quantity of coal requiring six hours for complete distillation.

	Time after commencement of distillation.		
	40 minutes.	3 hours.	5 hours 45 minutes.
H ₂ S.....	0·40	0·78	0·38
CO ₂	2·08	1·34	0·59
H ₂	25·36	48·36	71·94
CO	4·52	6·73	7·52
CH ₄	56·46	37·46	14·61
C _n H _m	8·81	3·13*	2·78
N ₂	2·37	2·20	2·18
	100·00	100·00	100·00

* Carbon density of C_nH_m..... 3·2

2nd Case.

The retort in this case was charged with a quantity of coal expected to be completely distilled in four hours. The retort was, however, under charged, as the sample drawn off 2 hours 45 minutes after commencement suggests, and was considerably hotter than in the first case.

	Time after commencement of distillation.	
	30 minutes.	2 hours 45 minutes.
H ₂ S	1·31	1·38
CO ₂	1·52	
H ₂	41·68	68·51
CO	4·33	8·49
CH ₄	43·65	19·45
C _n H _m	6·01	0·84
N ₂	1·50	1·33

3rd Case.

Retort charged with a quantity of coal requiring six hours for distillation :—

	Time after commencement of distillation.			
	10 minutes.	1 hour 30 minutes.	3 hours 25 minutes.	5 hours 35 minutes.
H ₂ S	1·30	1·42	0·49	0·11
CO ₂	2·21	2·09	1·49	1·50
H ₂	20·10	38·33	52·68	67·12
CO	6·19	5·68	6·21	6·12
CH ₄	57·38	44·03	33·54	22·58
C _n H _m	10·62	5·98	3·04	1·79
N ₂	2·20	2·47	2·55	0·78
	100·00	100·00	100·00	100·00
Carbon density of C _n H _m	2·86	3·1	3·38	2·29

The second series yields results generally in accord with those obtained by Dr. Henry, and with some published by Prechtel in 1835. As the distillation proceeds, the hydrogen rapidly increases, whilst the methane decreases. In the third case the carbonic oxide is very regular in amount; though in the first and second cases the carbonic oxide increases towards the end of the distillation, the decrease in hydrocarbons absorbable by SO₃ is very marked, and from the numbers obtained in the third case it would appear that their carbon density rises and then falls as the distillation proceeds.
