seems to produce appreciable quantities of ethyl or propyl alcohol.[45] A similar process, however, is used in the American petroleum industry, where the gases from the cracking process which are rich in unsaturated compounds are treated with concentrated sulphuric acid. More recent researches [46] with coke-oven gas have shown that the absorption of ethylene may be considerably accelerated, not only by heating the sulphuric acid (95 per cent.) to 70°, but also by means of catalysts.

Damiens showed that sulphuric acid, on addition of 5 per cent. Cu_2O and some mercury absorbs ethylene very quickly with formation of ethyl hydrogen sulphate and diethylsulphate. From these products alcohol is recovered by hydrolysis with water.

If these catalysts are added to sulphuric acid, preheated until white fumes appear, or if $CuSO_4$ and Hg_2SO_4 are added, the acid will behave differently. It still absorbs ethylene at the ordinary temperature with extraordinary rapidity, but on standing after saturation, an oil boiling between 100° and 300° spontaneously separates. It consists of hydrocarbons approximately of the formula C_nH_{2n}, representing artificial petroleum formed by polymerisation from ethylene. Damiens does not give the yield of ethylene.

From the point of view of the production of liquid motor fuels from coal it is therefore possible, in principle at any rate, to produce from low-temperature carbonisation gas, or its unsaturated constituents, either ethyl and propyl alcohol or petroleum.

(*k*) THE LOW-TEMPERATURE BENZINE

It has been repeatedly pointed out that both brown coal and bituminous coal, on low-temperature distillation, yield, not benzol, but benzine. The possibility of obtaining benzine from bituminous coal is of particular interest. A gas flame coal from the Ruhr district (Fürst Hardenberg Colliery) [47] gives from 5 to 10 kg. of benzine per ton of coal comprising hydrocarbons boiling below 200°. 47 kg. of coal gave 130 grams of low-boiling benzine in the gas, and nearly double that quantity (270 grams) in the tar, or a total of 9 kg. per ton of coal. With coals of different origin the specific gravity of the benzine fraction boiling from 60° to 100° was about 0·72, similar to that found by Markownikoff for the benzine from Russian petroleum (Apscheron Peninsula), which for fraction 60° to 100° was $D^{15} = 0{\cdot}729$. That the gas benzine from bituminous coal is an excellent motor fuel has already been established. Tar benzine should be refined before use.

These points have been investigated by Häusser,[48] of the Gesellschaft für Kohlentechnik. His gas benzine was obtained in the rotary retort plant of the Graf Bismarck Colliery, and had been stripped by the method used for extracting benzol from brown coal gas. The specific gravity of the gas benzine was 0·794, the content of acid oils less than 0·5 per cent., and the boiling range was :—

76°	85°	90°	100°	110°	120°	130°	150°	165°
Drop	6%	11%	24%	43%	58%	72%	90%	95%

The spirit was therefore relatively high-boiling.

The benzine was tested on the bench in a 14/35 h.p. Audi motor engine, fitted with a Pallas carburettor, type SA III, and a 24 mm. air intake.

Häusser reports on the tests as follows : " The Audi engine was set for a compression ratio of 5·0, . . . the ignition 18 mm. in advance of the dead point. The air did not require much preheating; its average temperature was 82° before, and 37° after the carburettor. The slight preheating required assisted the efficiency. The temperature of the cooling water was normal. The carburettor was calibrated with

fuel nipple No. 110 (*i.e.* 1·10 mm. diameter)
adjusting nipple No. 120 (,, 1·20 ,, ,,)
by-pass nipple No. 110 (,, 1·10 ,, ,,)

. . . The position of the brake blocks was not altered during the test. The results of the tests are summarised in Table XI.

" The behaviour of the fuel in the engine was satisfactory. It was easily started from cold and accommodated itself readily to quick changes in the load. There was no condensation in the suction manifold. The exhaust was perfectly clear at all loads and showed a slight colouring only on going to a heavier load. The sparking plugs remained white, and the valves were dry and free from deposit at the end of the trial. The results of the exhaust analyses are noteworthy. At all loads more carbonic acid and less carbon monoxide was found than had previously been observed with motor benzol III. The low-temperature carbonisation benzine is therefore readily and completely combustible as a motor spirit, as was confirmed by trials on the road."

TABLE XI

Primary Gas Benzine " Graf Bismarck "

Revs. per min.	Torque mkg.	Eff. H.P.	Fuel consumption g./H.P./hr.	Per cent. by vol. in dry exhaust gases.		
				CO_2.	O_2.	CO.
1610	12·14	27·3	325	14·2	0·8	1·0
1500	10·79	22·6	342	13·9	0·9	1·2
1415	9·72	19·2	348	14·0	0·7	1·6
1310	8·30	15·2	364	13·7	0·8	1·4
1200	6·95	11·65	398	14·4	0·8	0·7
1110	5·87	9·1	446	14·2	1·6	0·6

Häusser concludes that the gas benzine made it possible to start the engine with ease from cold and enabled it to pick up quickly. The good pull of the engine, a feature not realised with motor benzol and certainly not with tetralin-benzol, was particularly striking. The inclination of petrol to pre-ignition and knocking is, according to Häusser, not observed in gas benzine from coal. This is shown by the fact that the compression ratio used for benzol could be maintained. Häusser ascribed the good performance of gas benzine in the engine to the greater hydrogen percentage and the more even boiling curve. He states :—

" Whilst of motor benzol and benzol mixtures from 55 per cent. to 75 per cent. or more boil below 100°, the corresponding fraction of low-temperature gas benzine amounts only to about 25 per cent. If the boiling point of a constituent is taken as an approximate measure of its combustibility in the engine, it is found that low-temperature gas benzine contains an almost uniform series of constituents of ascending boiling points, each of which ignites the next higher one. This property is within limits more important than the boiling range, which does not differ much from that of motor benzol. The more even boiling curves account also for the good pull of the engine. The low-temperature gas benzines burn more quietly and yet with sufficient rapidity to ensure a satisfactory rate of combustion. On the other hand, the bulk of motor benzol burns fairly quickly so that the higher boiling and less combustible constituents get little chance for simultaneous combustion, and hence gives a poor pull."

Benzines from bituminous and brown coal are, by contrast with the benzol products from coke ovens, very stable in the cold. The various fractions of coal benzine do not freeze, or give solid deposits at temperatures down to − 50°.

In the purification of the low-temperature gas benzines the most important point is the separation of the phenols and other acid constituents by means of caustic soda. This purification appears only to be necessary where the distillation has not been conducted with care, and the final boiling point lies above 200°. A further refining for the removal of unsaturated resinifying compounds is hardly required. The calorific value of the different fractions of a coal benzine (after purification) is approximately 11,000 calories.

Trutnovsky [49] reports on the gas benzines of brown coal. Brown coal from Styria was slowly distilled in the rotating drum, the gas obtained was passed through tubes charged with activated carbon, and the adsorbed benzine was subsequently liberated by the aid of steam. The benzine obtained had specific gravity $D^{15} = 0{\cdot}742$, and gave the following fractions : 23° to 46°, 33 per cent. ; 46° to 80°, 41 per cent. ; 80° to 100°, 12 per cent. ; residue above 100°, 8 per cent. ; loss about 6 per cent. The yield of benzine referred to the low-temperature gas was 62 grams per cb.m., or 0·46 per cent. referred to dry coal.

The gas benzine from brown coal had an unpleasant smell and consisted essentially of unsaturated compounds, olefines and *cyclo*-olefines, and only to a small extent of paraffins and naphthenes. Trutnovsky considers, therefore, that the usual methods of refining and working-up should be discontinued in the case of these benzines, and that new methods will have to be worked out which will remove only the undesirable constituents.

(*l*) THE POSITION OF PRIMARY TAR BETWEEN COKE-OVEN TAR AND PETROLEUM

As repeatedly stated, the hydrocarbons of primary tar are more closely related to petroleum than to coke-oven tar, and particularly to oils which are mainly naphthenic in character.

The mixture of hydrocarbons in primary tar is optically active, as Fischer has established in collaboration with Gluud.[50] Optical activity has so far been found only in petroleum but not in coal tar.

The high hydrogen content of the light oils and benzine from primary tar is shown by their density, which, for products from many coals [51] and according to Broche [47] for unrefined benzines, agrees with that of Russian benzine.

The paraffin wax of the high-boiling fractions of primary tar, of which Gluud [26] determined individual constituents, is found in petroleum, but not in ordinary coal tar, which contains anthracene instead.

The proportion of benzene in primary tar benzine is quite insignificant, as Broche has once more confirmed by recent researches. It amounts to only a few per cent. in the fraction 60° to 100°. This is confirmed by the work of Frank and Arnold [52, 53] on commercial low-temperature carbonisation benzine, which also contains only minimal percentages of benzene.

A certain amount of benzene in petrol is, moreover, nothing uncommon. Engler's "Erdöl" gives several pages dealing with aromatic compounds occurring in petroleum.

Markownikoff [54] found almost 4 per cent. of benzene in the light oil fraction boiling below 105° of Russian petroleum from Grosny. This by no means puts this Russian benzine in a class with coal tar benzol. On the contrary, the resemblance of primary tar benzine to natural petroleum benzines is all the more emphasised. Reference to Engler's "Erdöl" will show the existence of very different kinds of petroleum of paraffinoid, hydroaromatic (naphthenic), and largely unsaturated or aromatic nature.*

With respect to the definition of a primary tar given by Gluud and myself

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* The presence of large quantities of unsaturated aliphatic hydrocarbons cannot be advanced against the likeness to petroleum. From Wietze crude oil 65 per cent. are dissolved out by conc. H_2SO_4 (Engler, "Erdöl," 1, 274). For the unsaturated hydrocarbons in petroleum and their conversion into naphthenes see Höfer, "Das Erdöl," 4th ed. 312–313.

a few years ago, it should be understood that the naphthalene test must be carried out as described. The disclosure by more refined methods of the presence of minimal quantities of naphthalene, as we have ourselves first shown in our Institute,[27] does not disprove the petroleum character of the primary tar hydrocarbons. For naphthalene occurs in many kinds of petroleum, for example, according to Engler's "Erdöl," [55] fraction 108° to 210° of Borneo petroleum contains 7 per cent. of it. In any event, as regards the significance of the naphthalene test, the statement on p. 32 must hold good.

The presence of true aromatic compounds in natural petroleum is an argument for the similarity between the hydrocarbons of primary tar and petroleum. Their quantitative estimation would alone be of value.

The physical properties, in particular the density of the hydrocarbon fractions, will always afford a ready guide for the distinction between mixtures of petroleum-like hydrocarbons rich in hydrogen, and coal-tar-like products, which are poor in hydrogen.

These considerations prove therefore that the hydrocarbons of primary tar are more closely related to those of petroleum than to those of coke-oven tar, which latter are predominantly aromatic in nature (benzene, naphthalene, anthracene and their homologues).

In contrast to coke-oven tar, carbolic acid, the phenol of lowest boiling point, is present in very small quantity in properly prepared primary tar. In addition to cresols and xylenols (see p. 27), mostly high-boiling phenol homologues are found, similarly to those which occur in certain petroleums (Engler, "Erdöl," **1**, 434).

(*m*) SEMI-COKE

Bituminous coal, brown coal and peat leave on distillation a semi-coke, a kind of smokeless fuel containing from 10 to 15 per cent. of volatile matter. To the proper utilisation of this semi-coke much thought has been given, as it is mostly very porous and friable, and occasionally (especially in the case of brown coal) liable to spontaneous ignition even at low temperature.

The application of semi-coke as smokeless fuel, which was first tried in England, meets with considerable difficulties, for its friability and high porosity become very troublesome on handling and during transport. One might expect that on making the coal denser by compression, while still in the retort and in a plastic condition, a coke of better physical qualities should be obtained. With this end in view Parr and Olin [56] fitted a screw-actuated piston into a horizontal stationary retort, by means of which the coal rammed into the retort was compressed during carbonisation.

Parr and Olin succeeded in this way in raising the specific gravity of the outer portion of their semi-coke (which uncompressed had a specific gravity of 0·65) to 0·73, an increase of 12 per cent. The core remained more porous. On the other hand it was to be expected that carbonisation with the application of external pressure would render the withdrawal of the tar and gases more difficult. I have succeeded in devising an astonishingly simple contrivance [57] which meets all requirements. When the rotating drum is used for intermittent distillation of the coal, a massive iron roll of about 10 cm. diameter, and somewhat shorter than the drum, is placed within the charge of disintegrated coal. Upon heating and revolving the drum, the coal, as it becomes plastic, cakes and forms a lining on the wall of the drum. The roll lying loose in the drum compresses the coal, the density increasing with the plasticity. When degasification is completed, the coke lining adhering to the wall of the drum begins to crumble and fall in. As the noise attracts attention, the rotation of the drum can be stopped at the right time. On opening, it is seen that almost the whole drum is lined with a uniformly dense layer of semi-coke. In a small-scale experiment I obtained, from 15 kg. of gas flame coal, 11·3 kg. of compressed semi-coke and 1·5 kg. of tar oil, or about 75 per cent. of semi-coke and 10 per cent. of oil. The semi-coke produced had an average density of 0·68, whilst without use of the heavy roll the density was 0·45. The increase in density would therefore amount to about 50 per cent. The determination was made by grinding pieces of coke to cubes exactly 1 c.c. in volume, and weighing them. The yield of crude oil was not influenced by the use of the heavy roll. The calorific value of the crude oil was about 8800 calories.

This semi-coke provides a dense smokeless coal quite fit for transport. Its properties are of vital importance for the economics of the process. The rolling-down of the semi-coke within the retort and during the detarring and degasification, which is characteristic of this process, is not directly applicable to continuous rotary retorts in which the coal is fed in at one end and the coke is taken out at the other end.

It was to be expected that the production of a compressed semi-coke would not be directly possible with all coals. The condition is that the coal softens while being heated, and this property does not exactly depend upon the amount of bitumen in the coal. It is known, of course, that brown coal, whether rich or poor in bitumen, will not cake. Yet it was conceivable that a compressed semi-coke might be obtained by blending non-caking and caking coals, or by adding certain substances in definite proportions yet to be determined.

Various experiments were made in this direction,[58] the results of which are summarised in Table XII. The coals were finely ground in a ball mill and were distilled without the aid of steam. Charges of about 10 kg. of coal, or coal mixture, were used. Distillation was stopped either when the noise of the dropping coke pieces was heard, or when the temperature in the centre of the drum (measured in the usual way) had risen to 525°, when, according to our previous experience, the formation of primary tar was completed. In the experiments in which a compressed semi-coke was produced the maximum temperature was only about 450°, owing to the bad thermal conductivity of the coke lining formed.

TABLE XII.

Raw Material.	Moisture in coal. %.	Coal used.	Tar.	Coke.	Gas.	Coke quality.
Gas flame coal (Lohberg Colliery) Dinslaken.	1·2	10 kg.	8·4	76·92	not determ.	firm
Fat coal (Rheinpreussen Colliery).	0·6	10 kg.	2·5	87·52	564	,,
Union briquette (Rhenish).	13·2	10 kg.	6·86	58·18	754	fine powder
Gas flame coal + Union briquette.	—	5 kg. + 5 kg.	6·04	67·88	866	,, ,,
Gas flame coal + Union briquette.	—	7½ kg. + 2½ kg.	8·82	72·54	846	,, ,,
Gas flame coal + Carbonising brown coal (Riebeck's Montan Works.	—	7½ kg. + 2½ kg.	11·91	68·09	776	,, ,,
Carbonising brown coal (Riebeck).	11·9	10 kg.	19·49	54·48	1037	,, ,,
Brown coal semi-coke + Brown coal tar.	—	4800 g. + 4800 g.	not determ.		365	,, ,,
Brown coal semi-coke + Brown coal tar oxidised under pressure.	—	3390 g. + 3390 g.	,,	,,	434	,, ,,

A gas flame coal (Lohberg Colliery, Dinslaken) and a fat coal (Rheinpreussen, Röttgersbank) both yielded a compressed, firm semi-coke which formed a crust on the walls of the drum and could be easily broken into pieces. The previous experiments were thus confirmed. With Central German brown coal rich in bitumen, and with Rhenish lignite (Union briquettes), not the slightest tendency of the semi-coke to caking could be observed. The coal was discharged in the same fine powdery condition in which it had been fed into the apparatus.

In order to ascertain how far addition of this gas flame coal to the lignite briquettes would influence the properties of the semi-coke, equal quantities of the two coals in finely powdered condition were well mixed and distilled in the drum. The coke residue obtained was a fine powder, and did not show the slightest inclination to caking. A good mixture of three parts of finely powdered gas flame coal and one part of finely powdered lignite briquettes gave on distillation the same result. Central German brown coal, rich in bitumen, behaved likewise. Thus, even considerable excess of gas flame coal when mixed with brown coal did not lead to a caked semi-coke, such as the gas flame coal had given when distilled alone. In other words, even a relatively small addition of brown coal renders bituminous coal non-caking. Similar observations had already been made in practice and are applied in the gasification of bituminous coal in producers, where in order to prevent caking some brown coal is sometimes added, and this fact furnishes a good confirmation of the experience we gained in our roll experiments.

Two further experiments were made. Brown coal semi-coke was mixed in a kneading machine in equal proportions, in the one case with ordinary brown coal tar, and in the other with brown coal tar oxidised under pressure,* and then distilled. In neither case caking took place. This was perhaps hardly to be expected with the addition of brown coal tar, in view of the experience with brown coal itself, which, during distillation, may be regarded as a mixture of coal substance and tar, although in different proportions. Yet it appeared possible that the tar oxidised under pressure might exert a favourable influence, as its asphalt content would supply a bituminous substance of high melting point, which, on decomposition, might induce caking; for the caking of coal requires the presence of a bitumen, which by partial decomposition assumes a higher melting point and remains fluid until converted into coke. In experiments recently made in this Institute,† directed to ascertain the amount of semi-coke required to inhibit the caking of bituminous coal, Broche found that relatively small additions would suffice, ranging from 15 per cent. upwards, according to the coal dealt with.

It would undoubtedly be most expedient to grind the semi-coke, which by nature is very friable and inflammable. It is certainly an excellent material for this purpose, and as powdered fuel application becomes more common, it would give a great impetus to the production of semi-coke and low-temperature carbonisation. For one must not fail to recognise that the production of oil by low-temperature carbonisation of coal cannot prove economical, unless a really satisfactory use is found for the 70 per cent. of residue obtained.

There is a possibility of utilising the semi-coke by adding it to strongly-intumescent coking coals. In the Saar district, for instance, it is hoped to produce a better coke by these means. Its combustion as powdered fuel, however, appears more profitable, since it can be ground with particular ease.

Matters are somewhat different with the semi-coke from brown coal

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* Brown coal tar (3·6 kg.) was oxidised for 2½ hours at 200°, and 35 atm., passing 400 litres of air through it.

† Unpublished.

(German "*Grude*"). This material is much appreciated for combustion on special grates on account of its peculiar capacity for incandescence. The Grude dust, moreover, can be fired in powdered-fuel burners like the dust from brown coal itself.

Apart from the ease of kindling and its combustibility, the semi-coke from bituminous coal has the further advantage of burning without producing smoke or soot. The constituents which cause smoking and sooting, essentially the ingredients of primary tar, are no longer present in the semi-coke. Differing from ordinary coke, and having retained some volatile constituents (mainly hydrogen), the semi-coke still gives a flame. Thus semi-coke may replace raw coal where heating arrangements depend on flame formation. The composition of semi-coke is compared with that of coal in Table XIII; the figures refer to dry, ash-free products, and the corresponding values for ordinary coke have been added.[59]

TABLE XIII

	Volatile matter. %	Coke residue. %	C. %	H. %	O. %	N. %	S. %
Orig. Lohberg coal .	39·7	60·3	82·2	5·2	8·7	2·1	1·8
Semi-coke from Lohberg coal . . .	17·2–18·3	81·7–82·8	84·9	3·9	7·5	1·9	1·8
Ordinary coke . .	2·6	97·94	96·59	0·4	O + N 1·64		1·37

The volatile matter content of semi-coke of upwards of 15 per cent. shows that degasification is not complete at a maximum temperature of 550°; a point has been reached at which the liberation of tar from the coal has ceased, but the temperature at which semi-coke passes into coke with further liberation of gas lies at 700° [60] or above. Hence the volatile matter in ordinary high-temperature coke is materially lower and does not exceed 2 per cent.*

It could not be assumed that semi-coke produced at a definite temperature should have a fixed percentage of volatile matter. It was rather to be expected that on carbonising, for example, at 450°, gas would still be evolved after completion of the tar formation, as long as the semi-coke is kept at this temperature. Thus the proportion of volatile constituents left in the semi-coke would be further diminished. Anyhow, one might anticipate that the semi-coke would, after being completely freed of tar, vary in volatile matter according to the

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* At about 700° coke becomes an electric conductor, obviously by formation of carbon and gas from the still-existing carbon compounds of the semi-coke. (Fischer and Pfleiderer, *Abh. Kohle*, 1919, **4**, 399).

temperature at which carbonisation had been effected. This is confirmed by more recent experiments of Broche,[61] which are summarised in Table XIV.

TABLE XIV

Volatile Matter in Semi-coke made at different Temperatures

Coke made at	Volatile matter.				
	After completion of tar formation.	After further carbonising during			
		1 hour.	2 hours.	3 hours.	4 hours.
° C.	%.	%.	%.	%.	%.
500	7·3	6·5	6·4	5·4	5·2
480	10·1	9·9	9·2	8·3	7·5
450	12·1	11·2	10·7	10·0	8·1
430	13·3	12·1	11·3	11·0	10·2
410	13·5	12·6	12·3	11·9	11·8

Volatile matter in semi-coke from Lohberg gas flame coal is lower with higher temperature, and *vice versa.* The volatile may be 16 per cent. and more, if the carbonising temperature is kept sufficiently low. Similar observations have been made in the brown coal industry. Thus Seidenschnur[62] succeeded in obtaining, instead of the ordinary Grude coke, a coke of much higher volatile content which he called brown coal flame coke. This product was obtained by the cautious distillation of brown coal in a current of hot combustion gases in shaft kilns. The brown coal flame coke formed—a semi-coke with a very high percentage of volatile matter—is said to be set alight with an ordinary match, and to burn with a colourless flame right down to ashes almost free of carbon.

The gasification of semi-coke to water gas or producer gas seems to be, next to its combustion as powdered fuel, the most suitable application of this product. It has been pointed out that almost the whole of the nitrogen, and most of the sulphur, in the coal remain in the semi-coke. Economically it would therefore appear useful to use the semi-coke so that the nitrogen can be recovered in the form of ammonia, and the sulphur in the form of hydrogen sulphide.* The gasification of the semi-coke is the best way of achieving this, for it is known that with an abundant use of steam, gasification will yield most of the coal nitrogen as ammonia. It has been found in practice that semi-coke, having lost all caking power and being highly reactive owing to its porosity, is an excellent producer fuel, and with it the throughput

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* This might be recovered as elementary sulphur with the aid of active carbon and air by the Bayer process.

of a producer is nearly doubled. It is, of course, advisable to charge the semi-coke hot as it comes from the rotary retort. The gasification of semi-coke will also render low-grade fuels, which are high in ash, available for low-temperature carbonisation, but the question in all cases will be whether suitable application can be found for the producer gas or water gas, either for heating or for power purposes.

At this stage, when speaking of the application of water gas, reference should be made to interesting and promising experiments on the preparation of liquid fuels from water gas. They concern the conversion, by catalytic processes under pressure, of water gas into liquid fuels, and will be described in a separate chapter (Synthol process).

(*n*) The Heat Balance of Low-temperature Carbonisation

The heat balance of low-temperature carbonisation and of the thermal decomposition of coal in general has formed the subject of several investigations.[63] According to Strache and Grau,[64] the gross heat of carbonisation is "the quantity of heat, referred to liquid water and liquid tar at 0°, which is either absorbed or liberated by the chemical process of gas-making (heat of decomposition), plus the caloric energy necessary for overcoming external work in the formation of gas. The net heat of carbonisation is that referred to water and tar, not in the liquid, but in the vapour state. This value is obtained by subtracting the heats of vaporisation of water and tar from the gross heat of carbonisation." The experiments performed with coal, brown coal, wood and cellulose indicated a certain relation between the sign of the gross value and the oxygen percentage of the material. Table XV gives the values and means for the gross heat of carbonisation. In the case of bituminous coal the figures are mostly negative (endothermic); its carbonisation requires therefore a continual supply of external heat.

Brown coal and lignite, on the other hand, show a positive heat of carbonisation (exothermic) which is largest in the case of wood, and it has long been known in charcoal burning that carbonisation, once started, progresses spontaneously with considerable liberation of heat.

Table XV

(*a*) Bituminous Coal I: − 16; − 15; − 15; + 19; − 13; + 30; − 57; − 2; − 4; Mean = − 8 Calories.
(*b*) Bituminous Coal II: − 26; + 12; − 10; Mean = − 8 Calories.
(*c*) Brown Coal I: + 52; + 60; + 35; Mean = + 49 Calories.
(*d*) Brown Coal II: + 60; + 35; + 45; + 54; + 64; + 98; + 25; + 80; + 49; + 54; Mean = + 54 Calories.
(*e*) Lignite: + 103; + 109; + 112; Mean = + 108 Calories.
(*f*) Wood: + 118; + 366; + 178; + 165; + 323; + 276; + 190; + 232; Mean = + 231 Calories.

The upper curve of Fig. 9 represents graphically the relation between the oxygen percentage of an ash-free, dry fuel and its gross heat of carbonisation. With an oxygen content above 12 per cent. the value is positive; with lower oxygen it is negative.

In practice, however, not the gross but the net value is in question, since the distillation products are liberated, not as liquids, but as vapours. The latent heat of the condensate must therefore be deducted from the gross heat of carbonisation, to arrive at the net values. By this calculation the higher grade of brown coal is found to approach bituminous coals, *i.e.*, fuels subject to endothermic decomposition.

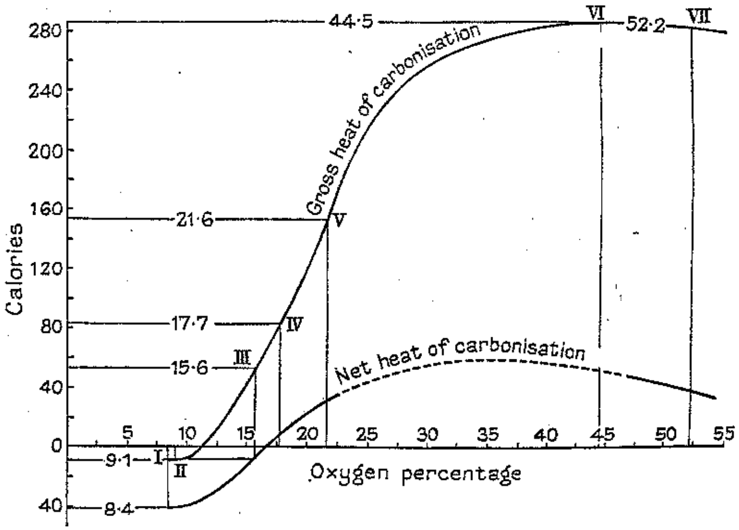

FIG. 9.

The lower curve of Fig. 9 represents the course of the net heats of carbonisation. Here the demarcation between an exothermic and endothermic heat balance is shown by an oxygen content of the fuel of 17 per cent.

Strache and Frohn [65] summarise their conclusions as follows: Bituminous coal and good brown coal require for their carbonisation a sustained supply of heat, whilst low-grade brown coal, wood and cellulose liberate heat. With increasing oxygen percentage, therefore, the calorific value and the heat required for carbonisation diminish.

These statements, of course, hold only for completely dry fuel preheated to the temperature at which carbonisation begins. The difference becomes noticeable only at that stage when materials relatively poor in oxygen require a continued supply of heat for their complete degasification; whilst with the decomposition of materials richer in oxygen, degasification proceeds spontaneously with more or less liberation of heat. Starting, however, with fuel of a natural moisture content, the position is altered inasmuch as external heat must be supplied both for drying and thermal decomposition, and the differences in the total heats required will then not be those between the net heats of carbonisation. Let us assume a poor brown coal containing 50 per cent. moisture (quite a common value), and let us further assume the coal to be free of ash. The heat of carbonisation liberated by 2 kg. of this coal corresponding to, say, 1 kg. of ash-free dry fuel may be 50 Calories; but about 600 Calories would be required for vaporising the 1 kg. of water contained in 2 kg. of raw coal. Hence, in practice, the endothermic carbonisation of bituminous coal, which contains little moisture, required less heat than the intrinsically exothermic carbonisation of brown coal, if the latter is used in its raw state containing up to 50 per cent. of moisture. Since carbonisation is always preceded by drying, external heat must needs be supplied when fuels in their natural moist state are carbonised.

(o) *The Development of Commercial Primary Tar Production.*

It should at once be pointed out that primary tar production has by no means assumed final shape, as high-temperature coking has done. It is still in a state of development and of the various systems known, those which seem most likely to meet all requirements have to be perfected. The first aim in distillation processes in which gasification or combustion of the semi-coke plays no part should be to obtain a tar free from dust and water. It might also be possible to effect, with a well-conducted distillation process, a fractional condensation of the oils, which would admit of withdrawing pitch, viscous oils, fuel oils and benzine at suitable stages. With a continuous process, this should be far easier than in coke-ovens, in view of the smaller make of gas in low-temperature carbonisation relative to the quantity of oil obtained. The coking process is intermittent, and the production of gas and tar is therefore not uniform, as is necessary for a fractional condensation of the tar constituents. Fractional condensation is rendered much more difficult when the tar vapours are diluted with many times their volume of non-condensable gas. If, therefore, the adoption of fractional condensation has been a qualified success only in a few coke-oven plants (Feld process), it may be more promising in low-temperature carbonisation. In the coking process, some 250 cb.m. of gas are made per ton of coal carbonised, together with about 3 per cent. of tar, or, say, 30 kg. per ton. Before being condensed the 30 kg. of tar vapours will therefore be diluted with 250 cb.m. of gas. In the low-temperature coking of gas coal, on the other hand, a ton of coal will yield 50 cb.m. of gas and 10 per cent., or 100 kg., of tar. In this case 100 kg. of tar vapours will be diluted with 50 cb.m. of gas before entering the condenser. The concentration of tar vapours in the gas is therefore more than fifteen times as large, and the conditions for fractional condensation will be correspondingly more favourable. As the working cost of the fractional condensation is no higher than those for the condensation of the total tar as now practised, it is obvious that a plant for the production of low-temperature tar will be more economical, if it is able to supply four finished products instead of an emulsion of tar, dust and water, which must subsequently be worked up at additional costs, as is still frequently the case.

Many critics of primary tar production have rightly emphasised that the semi-coke amounting to 70 per cent. of the coal is not obtained in a readily utilisable form. This objection is met easiest by carbonising only such coals as yield a firm semi-coke. Such coals are known and many others may be found. The possibility of compressing the semi-coke during its production has already been discussed, as well as its utilisation as powdered fuel (p. 50). In general, however, it will be obtained in a form unsuitable for direct use. It must be either briquetted, or ground for powdered fuel. Semi-coke would appear to be directly applicable only as producer fuel, where it even offers advantages. In Chapter IV of this book it will be shown that a combination of primary tar production with the Synthol process via water gas from semi-coke constitutes an ideal method of oil production from coal.

When speaking of primary tar production as being still in the stage of development, the working-up of the oils obtained must be considered. For what use would it be to produce various kinds of crude oils if they have to be freed, by costly methods, of constituents objectionable for certain purposes and if no use can be found for these? For example, the fuel oils from the low-temperature carbonisation of gas coal, the richest in tar yield, contain not less than 50 per cent. of phenols. That these phenols can be removed by inexpensive processes and that they can be converted into useful products I shall show in two further chapters which will deal with the extraction of phenols by superheated water and with the reduction of phenols to benzene and toluene by the aid of hydrogen. I shall also point out that the hydrogen required for this purpose can be prepared from water gas or producer gas by means of a special process based on diffusion against steam. I am firmly convinced that primary tar production will only be placed on a sound basis when the different requirements mentioned are satisfied.

In reviewing the development of commercial primary tar production, I shall first indicate the various methods opened up by scientific experience and technical possibilities, and I shall then describe plants corresponding to each type. I shall, however, refrain from mentioning all the innumerable patents, and from reproducing drawings in as far as they offer no particular interest.

(1) *Distillation Apparatus with External Heating.*—Distillation apparatus in which the semi-coke is not further worked up may be divided into two

classes depending upon external heating, where the heat is transmitted from outside through a wall, and internal heating where carbonisation is directly effected by hot gases passing through the charge.

The apparatus for external heating may be further divided into stationary and rotary furnaces.

The stationary furnaces may be shaft furnaces, horizontal retorts or tunnel kilns.

Vertical Retorts.—If the production of low boiling benzine and gas is aimed at, the coal is best distilled by applying external heating. The relatively low temperature of 400° to 500° required for this purpose admits of the use of retorts of steel or cast-iron, which are preferable to refractory material on account of their impermeability to gas and greater thermal conductivity. Stationary retorts offer the advantage over rotary furnaces that they do not require a power drive. The rate of distillation depends upon the thermal conductivity of the walls and the thickness of the layer of coal. In view of the low thermal conductivity of coal and the resulting semi-coke, that layer should be as thin as possible, so as to keep the carbonising period at the low temperature gradient reasonably short and provide for an economical throughput of the retort. An attempt to raise the throughput by more intense heating of the retort wall would lead to superheating the tar vapours, diminish the tar yield and lower the quality, *i.e.*, its hydrogen percentage. In other words, a product would result which in quantity and character would approximate to coke-oven tar. This is a defect of all processes which profess to produce primary tar, but claim at the same time to realise very high yields of ammonia. These become possible only at temperatures from 600° to 800°, whilst in the normal low-temperature tar production most of the nitrogen remains in the semi-coke. It may be subsequently recovered as ammonia by gasification of the semi-coke much more completely than would be possible by applying higher carbonising temperatures.

To avoid hanging-up of the charge of highly caking or swelling coals and difficulties in discharging, the vertical retorts are given a suitable taper.

The English "Coalite" process was probably the first to be commercially applied for the low-temperature carbonisation of coal.[66]

Fig. 10 gives two longitudinal sections and a cross-section of the retort.

The above applies to this process in particular. It should be mentioned, however, that the Coalite process was not designed for the production of oil, but essentially for the production of a smokeless fuel.

The process of the Premier Tarless Fuels, Ltd., is based on similar principles and aims at the same object (Fig. 11). As in the Coalite process, cast-iron vertical retorts are used, but they are formed into annular carbonising chambers. Experiments were made as early as 1900 on the Coalite process, and working on a large scale started in 1906. Later the use of cast-iron retorts proved unsatisfactory. Under the influence of heat the cast-iron began to "grow," the connections developed leaks, and the retorts cracked, became porous and had to be replaced at short intervals. Although the retorts were tapered, the coke could only be discharged with the aid of rods and other tools to the detriment of its quality and size. A tendency to spontaneous ignition of the semi-coke also caused difficulties. Heavy quenching proved necessary, which made it water-logged and increased its brittleness. For these reasons fire-clay retorts were adopted, and quenching of the semi-coke with water was abandoned and replaced by cooling in water-jacketed

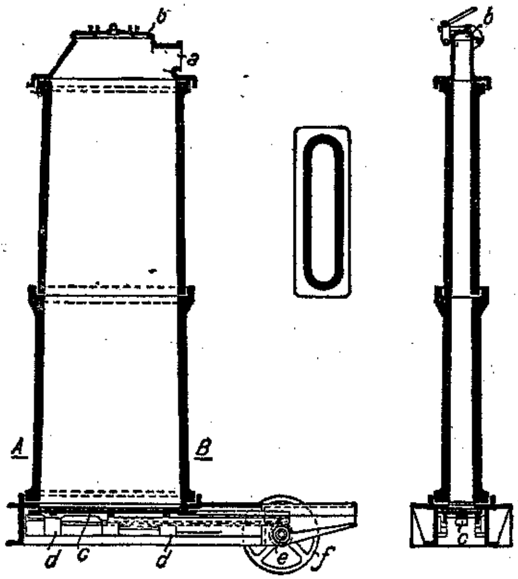

FIG. 10.

FIG. 11.

chambers, in the absence of air. Details of these modifications have been described in the literature.[67]

Another system in which vertical retorts are employed is that of Greene-Laucks, at Denver (Colorado).[68] The retorts are of cast-iron, 5·5 metres high and 0·4 metre diameter. As Fig. 12 shows, an external spiral rib is cast on the retort to serve in conjunction with the setting as a flue. An internal screw conveyor is intended to keep the coal in motion, and its hollow shaft is perforated to allow the distillation gases to escape. Apparently the plant is of an entirely experimental character.

The large-scale test plant, consisting of horizontal steel retorts, at H.M.

Fuel Research Station, Greenwich,[69] was designed by the late Sir George Beilby, mainly for the purpose of correlating laboratory and works results. It was intended for experiments in which tons and hundredweights could be dealt with under standard conditions which could be reproduced at will on an industrial scale.

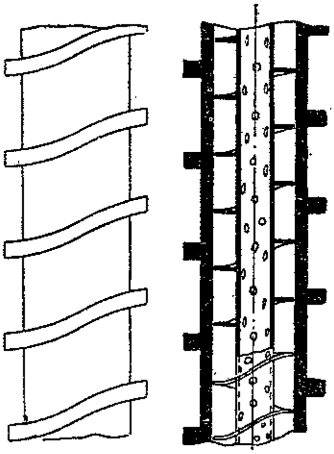

FIG. 12.

Whilst the processes mentioned so far concern the production of primary tar and semi-coke from bituminous coal, retorts for the treatment of brown coal and of oil shales have long been used. These materials present no difficulty by caking or swelling, and if they are very rich in tar, the properties of the solid residue are of no consequence for the economy of the system as in the case of coal. The plants were not designed for producing primary tar. There was no interest in undecomposed bitumen, and the object was the production of well-crystallised paraffin wax, gas oil and fuel oil. Even the production of benzine from the carbonising gas was not a decisive factor in these older processes. Three of the most important types used may be mentioned.

In the Central German carbonising industry, the Rolle furnace has been used for many years. It is intended for the use of raw brown coal, which, air-dried by suitable storage, admits of continuous working. The height of the retorts reaches 10 metres.

The retort is built of firebricks and is surrounded by flues. The coal slides down between the walls of the retort and an inner cylindrical body, built up Venetian-blind fashion, of a series of bells resting upon one another, through which the gases and vapours find an outlet. Large numbers of such retorts have been in operation for many years in Central Germany.

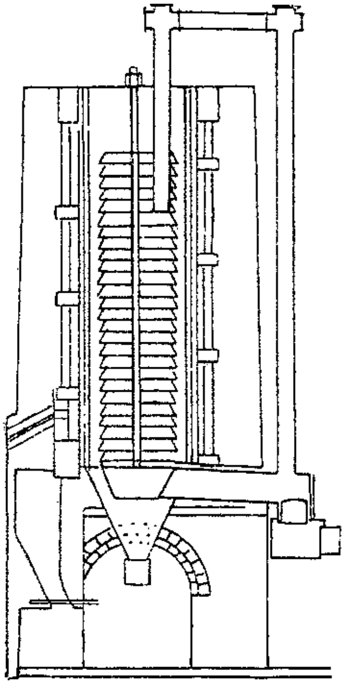

FIG. 13.

Another retort system is in use at Gewerkschaft Messel, near Darmstadt, where shale in lump form is carbonised. The Rolle furnace, which is designed for powdered material, would be less suitable in this case. The large size of the Messel shale permits of the application of superheated steam to facilitate carbonisation. Fig. 14 explains the principle of this retort; further details will be found in Scheithauer, "Die Gewinnung der Schwelteere," 2nd edition, p. 50.

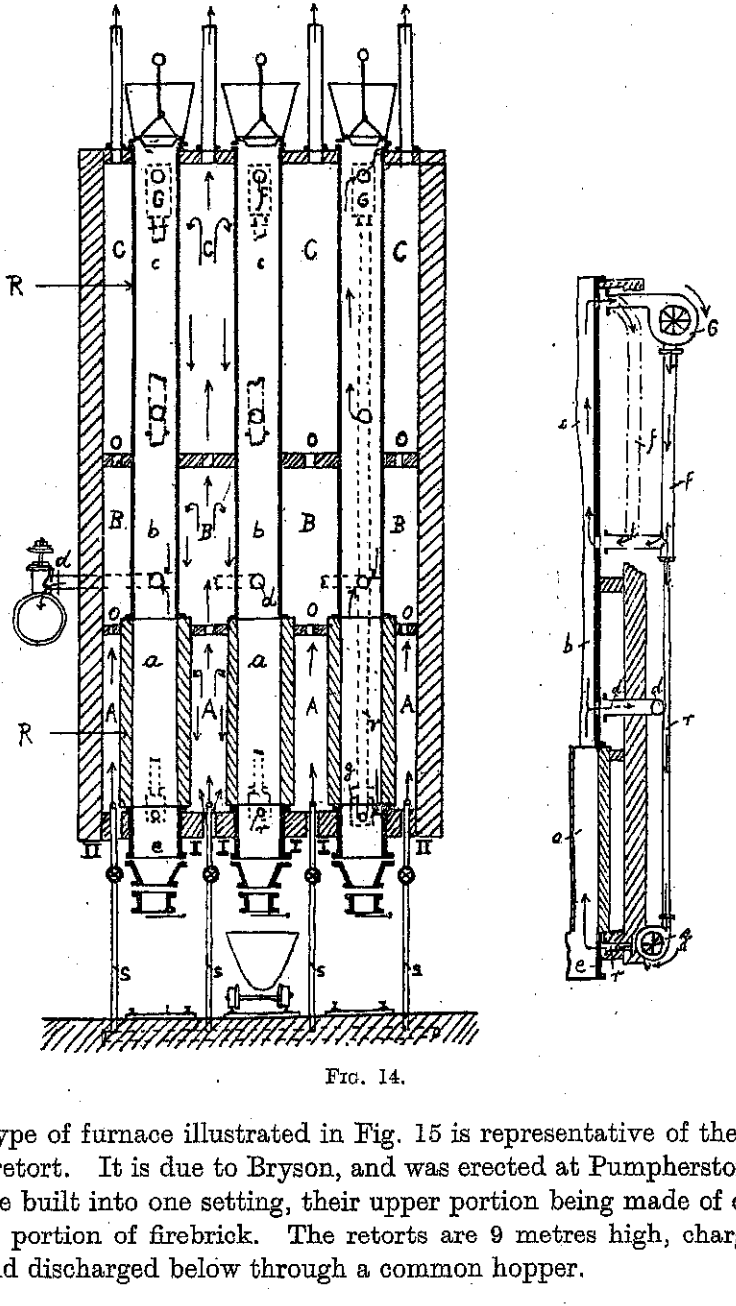

FIG. 14.

The type of furnace illustrated in Fig. 15 is representative of the Scottish oil-shale retort. It is due to Bryson, and was erected at Pumpherston. Four retorts are built into one setting, their upper portion being made of cast iron, the lower portion of firebrick. The retorts are 9 metres high, charged from above, and discharged below through a common hopper.