lower temperature, but that the products recovered are no longer pure phenols. The reason is probably that at 300° some of the hydrocarbons * possess the same solubility as the least soluble phenols.

The mode of operation to be adopted in any particular case will therefore depend upon whether the purity of the hydrocarbons, or of the phenols, is the main object. On the whole, the latter will be preferable as an undue reduction of the oil residue is avoided, and because it is technically easier to work at the lower temperature and pressure.

In any case it can be asserted that the extraction of phenols with superheated water offers a means of reducing the phenol content of primary tar oils sufficiently for their utilisation as motor fuels, without the application of any chemicals and without the production of waste products or waste liquors. The extraction will further remove any products which are soluble in water, even to a slight extent, and there is therefore no question of a corrosive action of the refined tar oils on the metal of engines, even in the presence of moisture.

4. *The Reduction of Phenols of Primary Coal Tar to Benzol and Toluol*

In the conclusion of the section on "The Utilisation of Phenols" it was pointed out that it would be of special value to convert the phenols of primary tar oils by chemical means into other more useful motor fuels. Two methods seem to be available for this purpose: hydrogenation and formation of the homologues of cyclohexanol, or the elimination of oxygen with formation of homologues of benzene. The former method is feasible with the use of catalysts. The method will hardly be adopted, as the oils would first have to be freed of sulphur compounds by means of metallic sodium, a course not feasible with phenols, nor practicable for economic reasons. Without this purification, the catalyst applied will be quickly poisoned and rendered ineffective.

The first mode of working can also be followed by dispensing with catalysts and making hydrogen react at temperatures of about 400° and at high pressure. Whether or not homologues of cyclohexanol can be produced in this way is not yet proved. In any case high pressures will be avoided as long as there is a method of effecting the conversion of the phenols into low-boiling hydrocarbons in other ways.

It is indeed possible to eliminate oxygen from phenols [100] by passing them, together with an excess of hydrogen, through iron pipes at a temperature of 750°. Ordinary iron pipes would not stand this treatment for any length of time, as they are rapidly burned through by the flame gases. There are, however, special kinds of cast iron which can be formed into resistant pipes. It is further possible to protect the external surface of common iron pipes

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* Whether this is a definite type of hydrocarbons remains to be seen.

by coating them with aluminium-bronze,[101] or by spraying-on aluminium, or by coating them by some process corresponding to sherardising.

Using such pipes, one soon notices that carbon is deposited, which after a time leads to clogging of the pipe. The yield of benzol and toluol is moreover very poor, evidently because part of the phenols, or part of the aromatic hydrocarbons already formed, is decomposed into carbon and hydrogen under the catalytic influence of the iron. Porcelain tubes being out of the question for works use, and fireclay pipes being too permeable to hydrogen, one seems to be tied down to the use of iron pipes. It has been found that catalytic action of the iron can be entirely suppressed by tinning the inside of the tube. The inner surface then turns, in the course of time, into a tin-iron alloy which no longer has the undesired property of iron itself to induce liberation of carbon catalytically. The iron forming a chemical compound with the tin no longer exists in the free state, and the tin-iron alloy is evidently unable to effect a catalytic deposition of carbon by a transient formation of carbide. Tin was selected for coating the inner walls of the tube because all tin compounds which might conceivably be formed would, under the experimental conditions, again be reduced by hydrogen to metallic tin at 750°, and because metallic tin is not volatile at that temperature. In the course of numerous experiments, it has been found that the protective action of the tin is maintained, provided the hydrogen used for the reduction of the phenols is pure. It is then possible to effect the conversion of phenols into benzene hydrocarbons without carbon deposition in an iron pipe, with a yield of almost 100 per cent. of the theoretical. If, however, the hydrogen is replaced by the cheaper water gas, the yields are much poorer and there is deposition of carbon in the reaction tube. This carbon might have been formed by the decomposition of carbon monoxide into carbon dioxide and carbon. But the reduction in the yield of aromatic hydrocarbons suggests that at least part of this carbon is derived from the decomposition of phenol or benzene homologues. On switching over from water gas to pure hydrogen, the disappointing observation is made that good yields are no longer obtained, and that there is deposition of carbon. The protective action of the tin has vanished, or has been reduced, obviously by some deleterious action of carbon monoxide upon the tin-iron alloy. On examining the interior of the pipe after removing the carbon dust, it is found that the tin-iron coating has peeled off in the form of a brittle, bright mass. This was observed in the case of the large tube which was used in the experiments to be described below, and it was feared that the inner surface of the iron, having apparently taken up a good deal of carbon, could not be retinned at all. Desiring to continue the experiments with the comparatively large tube already fitted up, the happy idea occurred to us to convert the inner surface of the pipe into iron sulphide.[102] It was to be supposed that the sulphur would inhibit the catalytic action of the iron, or iron carbides, on the deposition of carbon. The conversion of the iron into sulphide at high temperature, by means of hydrogen sulphide diluted with nitrogen, did not offer any difficulties. There remained the question how long the sulphide coating would last, and whether, in the reduction of phenols by hydrogen, iron sulphide would not be reduced in the course of time and sulphur be carried away as hydrogen sulphide. Preliminary experiments on a small scale demonstrated that an ordinary gas pipe which, without previous treatment, gave poor yields and carbon deposits when phenol vapours and hydrogen were passed through it at 750°, immediately showed a yield of 90 per cent. without formation of carbon after having been sulphided on the inner surface. This protective coating of sulphide remained efficient throughout the whole series of experiments.

Fundamental Experiments on a Small Scale [103, 104]

It appeared useful to ascertain in the first instance what yields of benzene or toluene might be expected in the reduction of the individual phenols. Reduction in molecular weight may be produced not only by splitting off oxygen in the form of water, but also by a scission of the methyl group in the form of methane. In the case of cresol, for instance, the following reactions may occur :—

$$CH_3{\cdot}C_6H_4{\cdot}OH + H_2 = CH_3{\cdot}C_6H_5 + H_2O$$
$$CH_3{\cdot}C_6H_5 + H_2 = C_6H_6 + CH_4$$

TABLE XXX

Yield from	Molecular Weight.	Xylene. %	Toluene. %	Benzene. %
Xylenol	122	87	75	64
Cresol	108	—	85	72
Carbolic acid	94	—	—	83
Xylene	106	—	87	74
Toluene	92	—	—	85

The theoretically possible yields of xylene, toluene and benzene, starting from the different phenols, are summarised in Table XXX. Xylenol, it will be seen, can yield at the most 64 per cent. of benzene by splitting off two methyl groups in the form of methane and one atom of oxygen in the form of water. Conditions are somewhat more favourable with cresol, which gives a theoretical yield of 72 per cent. by weight. The table also gives the hydrocarbons xylene and toluene as raw materials for benzene. Xylene may yield 74 per cent. by weight of benzene; toluene, 85 per cent. From the theoretical yields mentioned in the following tables, the absolute yields may easily be calculated with the help of Table XXX.

TABLE XXXI

Suitability of different Phenols

	Crude benzol.		Gas.	
	% of theory.	% of quant. used.		
Carbolic acid	65	—	Coal gas	Tinned iron tube
m-Cresol	99	—	H_2	
Xylenol	72	—	H_2	
Primary tar phenols from :				
Bituminous coal 200–250°	—	66	H_2	
,, ,, 250–340°	—	15	H_2	
Brown coal 200–240°	—	50	H_2	

How the different phenols behave when treated with hydrogen in the tin-coated iron tube is shown in Table XXXI. The figures are minimum values which might possibly be raised by the adoption of other temperatures or rates of flow. " Optimum " conditions were worked out for *m*-cresol, and all the other phenols were studied under the same conditions. The upper half of Table XXXI, which concerns definite chemical compounds, gives theoretical percentages; in the lower half, dealing with commercial mixtures, results are expressed in percentages of quantities used. It will be seen that the primary tar fractions 200—250°, which, by their boiling points, correspond to the cresols and xylenols, gave very favourable results whether obtained from bituminous or from brown coal. As Table XXX shows, xylenols can theoretically never yield more than 64 per cent. of benzene. The conversion of the low-temperature phenols, boiling between 200° and 250°, *i.e.*, the bulk of the phenols, into benzene, is therefore very promising. The higher-boiling phenols undoubtedly give a smaller yield of benzene. The actual yield of 15 per cent. represents about 25 to 32 per cent. of the theoretical, and modifications in the experimental conditions will possibly lead to improved results.

Table XXXII shows the behaviour of various hydrocarbons in the tinned iron tube at a temperature of 750°.

Only 7 per cent. of the hexane used is converted into benzene. This figure is quite in accord with older experiments of Haber,[105] and finds its explanation in that benzene is not formed from hexane by dehydrogenation and closure of the ring, but synthetically from the gases such as acetylene, liberated upon the decomposition of hexane. Similar considerations apply to the other petroleum products mentioned in Table XXXII, and also to the hydrocarbons of the primary tar from coal which in general resemble petroleum.

TABLE XXXII

Suitability of Hydrocarbons

	Tinned iron tube with H_2. Benzol at 750°
Aliphatic hydrocarbons.	
Hexane (benzine)	7·2% of quantity used
Petroleum	16·0% ,, ,, ,,
Wietze crude oil	18·0% ,, ,, ,,
Primary tar hydrocarbons from bituminous coal 275–300°	16·0% ,, ,, ,,
Aromatic hydrocarbons.	
Toluene	100% of theory
Toluene and hexane	47% of quantity used
Para-cymene	74% of theory
Solvent naphtha I	61% of quantity used
,, ,, II	44% ,, ,, ,,
Anthracene oil	11% ,, ,, ,,
Diphenyl	95% of theory
Naphthalene	unaltered
Anthracene	,,

Table XXXIII gives some information concerning the influence of temperature in the use of the tinned iron tube. There is no reduction below 700°, but above 800° decomposition is considerable with formation of naphthalene. A temperature of 750° has so far been found the most favourable.

TABLE XXXIII

Influence of Temperature

Tinned iron tube	below 700°	Unchanged cresol.
10 times theoretical amount of hydrogen	750°	Benzene and toluene.
o-Cresol	above 800°	Decomposition with formation of naphthalene.

Another series of experiments was made to ascertain whether hydrogen is replaceable by other gases. Table XXXIV indicates that a mixture of carbon monoxide and hydrogen in equal proportions, *i.e.*, water gas, answers as well as hydrogen, if applied in large excess in an internally-glazed porcelain tube. Carbon monoxide, instead of hydrogen, gave only 47 per cent. of the theoretical yield. Even in the absence of reducing gases, working in an atmosphere of nitrogen, 41 per cent. of the theoretical yield of benzene was obtained. The explanation is probably that the decomposition of part of the cresol furnishes the hydrogen for the reduction of another part. Further experiments were made with the tinned iron pipe, when 99 per cent. of the theoretical yield was obtained with hydrogen, and 75 per cent. with town's gas.

TABLE XXXIV

Influence of Kind of Gas

Cresol at 750°.

	Benzol % of theory.
In porcelain tube.	
H_2	72
N_2	41
CO	47
$CO + H_2$	78
In tinned iron tube.	
H_2	99
Coal gas	75

In the previous experiments in porcelain tubes we worked with a very large excess of hydrogen. It was of importance to ascertain how far this excess might be reduced, and how close the theoretical proportion of hydrogen could be approached. The practical importance of an approximately theoretical hydrogen requirement is that the benzene will separate spontaneously on cooling, and that only a small volume of gas need be washed for the complete recovery of the benzene. Although absorbents, such as activated carbon, are now available for the removal of the last traces of benzene, it is always advantageous to restrict the volume of gas to be submitted to this process. Table XXXV shows that 2 mols. of hydrogen are required per 1 mol. of cresol to convert it into benzene, methane and water. How closely that figure can be approached, without undesirable secondary reactions, will be seen from the fact that 99 per cent. of the theoretical yield of benzene is obtained using 10 mols. of H_2, *i.e.*, 5 times, and 95 per cent. with 3 mols. of H_2, *i.e.*, 1·5 times the theory.

TABLE XXXV

Influence of Quantity of Hydrogen for m-*Cresol in Tinned Iron Tube, at* 750°

Theory requires 2 mols. H_2 for

$$CH_3C_6H_4OH + 2H_2 = C_6H_6 + CH_4 + H_2O.$$

10 mols. H_2 . . .	99% benzene
3 ,, ,, . . .	95% ,,

The aromatic hydrocarbons behave somewhat differently, and are still more readily converted into benzene. Toluene can be converted with a theoretical yield of 100 per cent. A mixture of equal parts of toluene and hexane yields 47 per cent., as much as can be expected, and *p*-xylene gives 74 per cent. A good yield is also obtained from the two solvent naphthas.

Whilst diphenyl combines with 1 mol. of hydrogen giving the theoretical yield of 92 per cent. of benzene, the yield from anthracene oil is very small; naphthalene and anthracene are not converted at all under these conditions. Table XXXVI shows the suitability of various low-temperature tar oils, that is, fractions of primary tar which contain hydrocarbons as well as phenols and small quantities of bases.

For the reasons stated the yields are given in percentages of the material used. The fractions boiling between 200° and 250° are again seen to give the best results.

Table XXXVI

Suitability of Primary Tar Oils

	Crude benzol % of quantity used.	Gas.	Tube.
Primary tar oils, below 305°	20	H_2	Tinned Fe
,, ,, (bituminous coal) 250–270°	15	H_2	Porcelain tinned nails
Middle oil (coke-oven tar) (29% phenols)	45	H_2	Tinned Fe
Brown coal primary tar	29	H_2	
Primary tar oils (bituminous coal) 200–250° (50% phenols)	40	H_2	
Primary tar oil (bituminous coal) 250–300° (40% phenols)	30	H_2	

The treatment of the whole tar with hydrogen at 750° in the tinned iron tube for the benzol recovery may, under certain conditions, be advisable. In that case the low-boiling constituents of the tar should be distilled off in the first instance.

Table XXXVII gives an indication of the relative stability of the benzene homologues with respect to the scission of methane.

Table XXXVII

Stability of Benzene Homologues at 650°

Reduced to benzene with CH_4-formation.

Cymene	almost completely.
Xylene	partly.
Toluene	hardly.

Cresol forms at 700° benzene and some carbolic acid.

Methane is split off at 650°, the easier the higher the methylation of the material.

So far a reduction to benzene only has been discussed. In reality some toluene will always be present. Table XXXVIII shows that in general a mixture of approximately 5 parts of benzene and 1 part of toluene will result, which as a motor fuel is superior to pure benzene, on account of the liability of the latter to crystallise in the cold. The term benzol here designates all those products boiling between 80° and 95°; toluol, those boiling between 95° and 115°.

TABLE XXXVIII

Ratio of Benzene to Toluene

From cresol	15·5 : 2·7	5 parts benzene to 1 part toluene.
,, primary tar phenols .	15·6 : 3·4	

Fraction 80–95° calculated as benzene, 95–115° as toluene.

Experiments on the Large Scale [106]

On the strength of these preliminary experiments, the following experiments, on a larger scale, were carried out in the apparatus illustrated in Figs. 55 and 58.

The apparatus consists of three main portions:

(1) Vaporiser and oil feed.
(2) Tinned iron tube and furnace.
(3) Condensers.

(1) *Vaporiser and Oil Feed.*—In the vaporiser, Fig. 55, the material to be reduced is converted into vapour and at the same time mixed with the reducing gas. It consisted of an iron cylinder, 5 mm. thick, tapering at both ends. One end was closed by a screw-cap to make the interior accessible for cleaning. The other end was welded to a tube which could be connected by means of a union to a short pipe projecting from the cover of the large reduction tube. A thermometer pocket was provided for temperature readings in the middle of the cylinder. As shown in Fig. 55, two inlet tubes passed into the vaporiser vertically from above; one for the oil vapour, the other obliquely, for the gas. The latter was bent so as to set up turbulence in the cylinder for the intimate mixture of the oil vapours with the gas. A glass funnel was cemented with talcum and silicate of soda into the vertical oil feed pipe, by means of which the rate of flow of the phenols could be observed. The vaporiser was heated by a row of high-pressure burners. The cylinder was provided for a length of about 30 mm. with an asbestos-lined sheet-iron jacket, in which a number of holes were drilled for the ready escape

of the gases. A feed bottle, provided with a syphon pipe closed by a full-bore stopcock, was mounted about 1·5 metres above the vaporiser. The lower end of the pipe was attached by means of india-rubber tubing to a capillary syphon which was fixed into the glass funnel with the aid of a rubber stopper. The bore of the capillary was chosen according to the desired rate of oil feed; the feed-bottle had a constant-pressure device so as to maintain an even oil feed.

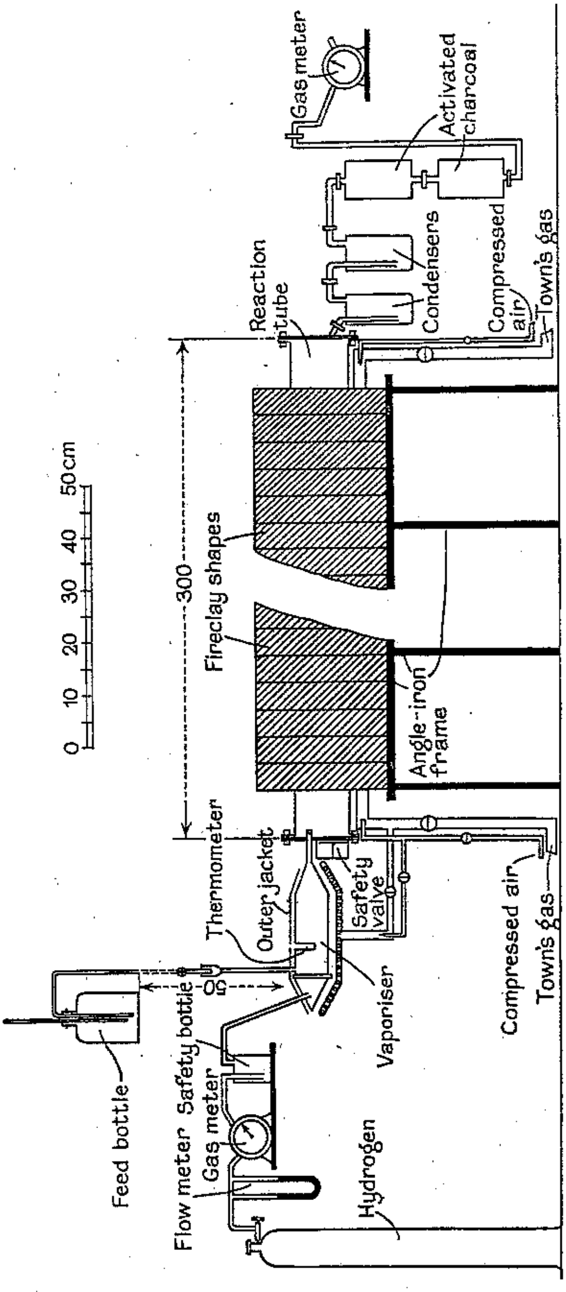

Fig. 55.

(2) *The Tinned Iron Pipe.*—The iron tube was 3 metres long, 28 cm. internal diameter, and had a wall thickness of 10 mm. The inner surfaces of the tube and cover were tinned by a competent firm. The coating was bright and apparently very uniform. The covers were flanged and bolted to both ends of the pipe. The cover nearest the vaporiser was provided with a safety-valve, made by cutting into it a hole of 18 cm. diameter, over which an iron plate with projecting edge was ground. This plate was pressed against the cover by a spring held by a strap. The joint was kept gas-tight by means of oil and graphite. The reaction tube rested on a frame of angle iron, forming two supports which also carried the fire-clay shapes surrounding the reaction tube. One of these

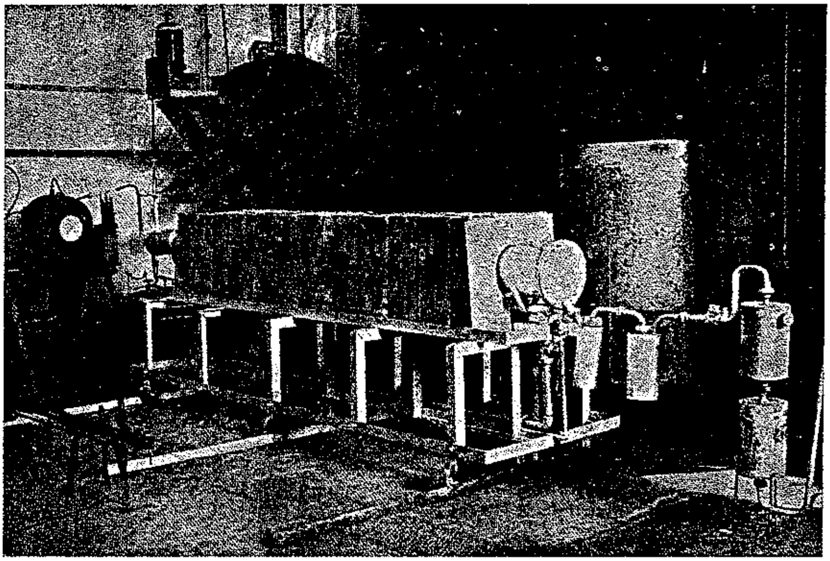

FIG. 56.

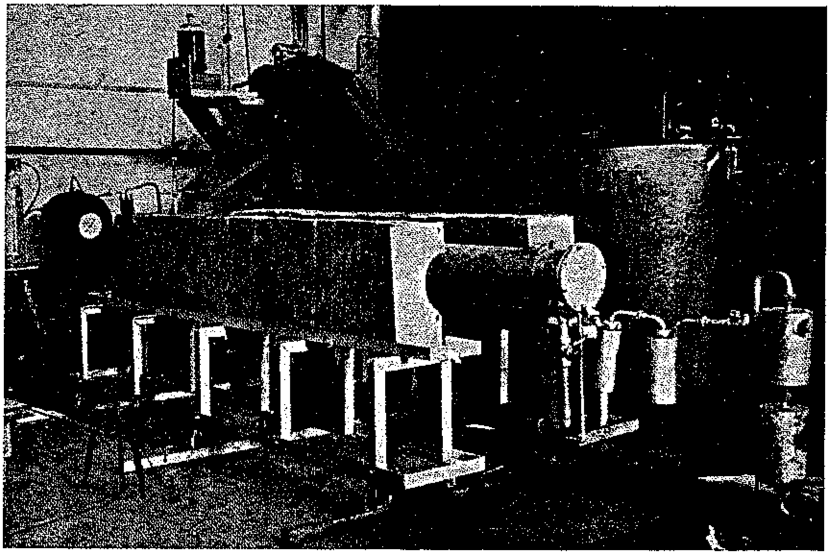

FIG. 57.

supports was mounted on wheels, so that the tube was easily accessible (Figs. 56 and 57). In order to ensure a uniform distribution of heat, two independent sets of gas burners were used, each row heating half the length of the reaction tube, and being controlled by gas and compressed-air taps fixed at the ends of the frame. The burner pipes had a diameter of $1\frac{3}{4}$ inches, and were provided with three rows of staggered holes, 3 mm. diameter, 10 cm. centres. Fig. 58 illustrates the shape and dimensions of the fire-bricks. They were held in position on the angle iron frame by iron wire. The reaction tube projected from the bricks at each end by about 40 cm. In order to prevent its destruction by oxidation, the tube was given a coat of aluminium-bronze.[101] This behaved very satisfactorily, and throughout the series of experiments conducted at temperatures between 700° and 800 the tube was hardly attacked.

(3) *Condensers.*—The right end cover of the tube carried a tube inclining downward, which was joined to the condensers by a union. The condensers consisted of two sheet-iron pots for the reception of the liquid condensate, and two cylindrical drums to be charged with activated carbon. The first condenser was cooled by means of water, to retain the less volatile products; the other by a freezing mixture of ice and salt, to condense the more volatile constituents.

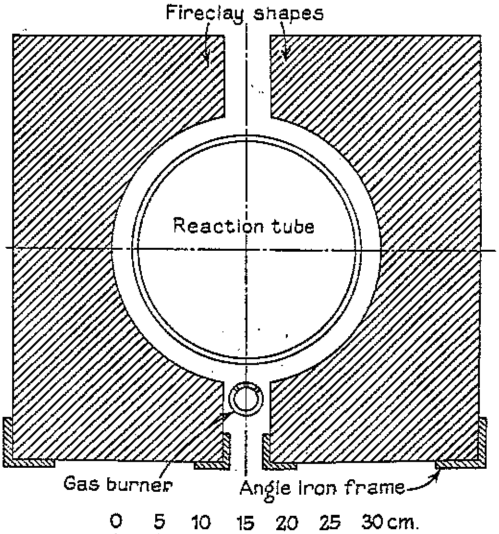

FIG. 58.

The gases leaving the second condenser were passed through the two absorbers charged with activated carbon, for the extraction of benzol vapours. The gases were then passed through a gas meter and burned. The internal arrangements of the drums, shown in Figs. 56 and 57, were the same as in the large drums to be mentioned below, but the wire gauze and feed-pipe in the middle were dispensed with. The end of the gas intake pipe, which reached a few centimetres into the drum, was closed by a plate, but provided with a ring of lateral perforations which distributed the gas uniformly over the whole surface of the drum. The carbon was placed between nets of wire gauze. Openings, closed with caps, were provided at the sides for charging the drums with the charcoal. The different parts of the condensers were assembled with screw connections.

This condensing arrangement was inadequate for experiments at high rates of flow, and a larger plant was installed. It had in the place of the two condensers a water-cooled coil with receiver, to which the two large drums charged with activated carbon were joined.

Experimental Data.

The gas used in the reaction, which was generally taken from a steel cylinder, passed through a flow meter and a gas meter, as shown in Fig. 55.

The experiments were conducted in the following way :—

All the air having been expelled from the apparatus by means of coal gas, the apparatus was tested for leaks with a flame. The tinned iron tube was then heated to 750°, while the coal gas was kept flowing. The temperature had to be raised very slowly, since the lower side of the pipe would heat up quicker than the upper, thus causing bending of the long tube owing to the expansion of the lower side, and possibly fracture of the fire-bricks. Temperatures were continuously observed by means of a Wanner pyrometer directed on the upper portion of the tube through the opening between the fire-bricks. When the temperature had remained constant for some time, the current of coal gas was replaced by the reaction gas. The vaporiser had meanwhile been heated up and the oil feed tap was opened. After the completion of the experiment the oil tap was closed, and the gas meter was read. A little more gas was passed through the tube in order to expel the reaction products from it. The amount of phenol oil used was ascertained by weighing the feed-bottle before and after the experiment, and the increase in weight of the condensers was also determined. The working-up of the oil condensed in the first two vessels will be explained below. Besides ascertaining the increase in weight of the carbon filters, in most cases we expelled the benzol absorbed, by means of superheated steam. For this purpose it proved necessary to raise the temperature at the outlet of the charcoal drum to 250°. This steaming took two hours from cold, and finally a slow current of air was passed through the drum to displace the water vapour. The results obtained with this apparatus will be described subsequently, but it may be mentioned here that the throughput of our tube was as much as 12 kg. per hour, or about 300 kg. of oil in 24 hours. For larger capacities the diameter of the tubes could be increased, or a number of them could be arranged as in a setting of horizontal gas retorts. Further experience might also suggest the advisability of a vertical reaction tube. With this outfit the following experiments were conducted.[107]

Experiment 1.—In Experiment 1 with cresol, the rate of drip was so adjusted that the throughput amounted to only 200 grams per hour. The rate of hydrogen feed was set to 1½ times the theoretical. We obtained 90 per cent. of the theoretical yield of crude benzol. Apart from small leaks, which were easily stopped, the apparatus proved perfectly satisfactory. No carbon was deposited in the reaction tube.

Experiments 2 *and* 3.—We then directed our attention to the material which claimed it first and foremost, viz. the phenols from primary tar. In Experiments 2 and 3 the drip rate was adjusted so that from 200 to 300 grams of substance passed through the tube per hour. The raw material of Experiment 2 was the primary tar phenols from Röchling producer tar, fraction 150–250°, prepared by extraction with water under pressure as described on p. 110. The phenols had been redistilled after extraction and boiled between 190° and 250°. In Experiment 3 we used phenols likewise prepared from crude producer tar by extraction with water and therefore representing a mixture of primary tar phenols of higher and lower boiling points. To render the experiments more simple with a view to subsequent technical application, the phenols were not redistilled, but used as obtained by extraction and mechanical separation. The quantity of material, 441 grams, available for Experiment 2, was rather small for the large apparatus. In order to ascertain the conditions for maximum yields, we worked with 2½ times the theoretical amount of hydrogen. The total yield of crude benzol, which consisted of 205 grams of benzene, 48 grams of toluene, and 5 grams of xylene, amounted to 58·5 per cent. of the quantity used. Allowing for minor leakages in this experiment, one may reckon upon an average yield of 60 per cent. Assuming that the phenols from primary tar consist of cresols and xylenols, which by scission of the hydroxyl groups and side-chains form H_2O and CH_4 and could give only 64 to 68 per cent. of benzol, the yield obtained must be considered very satisfactory. Unchanged phenols were not found in the condensate. Small quantities of solid hydrocarbons, chiefly naphthalene, were found in the distillate even at lower temperature; above 180°, the distillates congealed completely. Higher-boiling constituents continued to come over up to and beyond 360°. They consisted mainly of naphthalene, and probably of higher aromatic hydrocarbons, such as had always been observed in small-scale laboratory experiments. In Experiment 3 the yield of benzol, which consisted of 315 grams of benzene, 41·5 grams of toluene, and 7 grams of xylene, dropped to 39·6 per cent. This was to be expected, since we had started from a mixture of higher and lower boiling phenols and, according to our preliminary experiments, the higher phenols give only a low yield of benzene (about 15 per cent.) by thermal reduction with hydrogen. This experience was confirmed by Experiment 4 in the large apparatus. The yield of Experiment 3 may therefore also be considered relatively satisfactory.

Experiment 4.—This experiment, particulars of which are given in Table XXXIX, was made in order to ascertain whether the higher-boiling phenols from primary tar, 210–270°, would give better benzol yields when operating on a larger scale. Having meanwhile ascertained by Experiments 5 to 9 that the experiments may be performed at a much accelerated rate of feed of the phenols to be reduced, without detriment to the benzol yield, we raised the input to 4 kg. per hour and kept the hydrogen supply at an excess of about 1½ mols. of the theory, taking the average molecular weight of the phenols as 100, which is probably too low. The yield obtained was 33·3 per cent. of the amount used. The experiment therefore indicated, in confirmation of our previous experience, that the phenols boiling above 250° give a much lower yield in benzol than those of lower boiling point. For the fairly good results of Experiment 4, dealing with fraction 210–270°, credit must be given to that portion boiling below 250°.

The result of the last three experiments on a large scale confirms the small-scale experience, that the phenols of primary tar boiling below 250° may be reduced, like cresols, by means of hydrogen at high temperature with good yields. With the higher-boiling phenols the yields drop off considerably.

Experiments 5 *to* 9.—Experiments 5 to 9 were undertaken for the purpose of ascertaining how far the capacity of the apparatus could be increased. They were made with a commercial cresol mixture. The rate of feed was doubled at the end of each hour, 99 litres of hydrogen being finally passed through the tube per minute. The original absorption apparatus could not deal with such large volumes of gas, and was replaced by the larger apparatus already mentioned.[105] Owing to the strong cooling action of the gas, and in order to increase the velocity of reaction between phenols and hydrogen, it proved necessary to raise the temperature of the tube to 800°, lest a considerable portion of unreduced phenols should be found in the condensate.

Even the enlarged apparatus did not prove quite sufficient for the last experiments, Nos. 7, 8 and 9, and a quantitative collection of the benzol was dispensed with. We contented ourselves with the estimation of unreduced material in the condensates, as a measure of the extent of phenol reduction. Table XXXIX shows that the proportion of unreduced raw material increased with the higher throughput. With a throughput of 12·3 kg. per hour, this proportion amounted to 16·2 per cent. It was higher in Experiment 8, where the temperature was too low. The experiments prove at any rate that a plant of the size of ours will, with proper temperature control, convert about 12 kg. of cresol per hour into benzol with a good yield.

Experiment 10.—Experiment 10 of Table XXXIX was made in order to see whether hydrogen might be replaced by a cheaper gas, such as coal gas. The coal gas at our disposal was a coke-oven gas containing about 50 per cent. of hydrogen. The available gas supply not being sufficient for our rates of feed, the gas was compressed in a steel cylinder to 150 atm. The gas rate was regulated in such a way that, considering that half of the coal gas consisted of hydrogen, we had about 2½ mols. of hydrogen at our disposal. Table XXXIX shows that we limited the throughput to less than 1 kg. of cresol per hour, so as to allow for the increased gas volume to be dealt with by the absorption train. The benzol yield was 73 per cent. of the theoretical, *i.e.*, 17 per cent. less than in Experiment 1 with hydrogen. This diminution was evidently connected with the deposition of a little soot on the tin-coated iron, the cause

TABLE XXXIX

Reduction of Cresols and Primary Tar Phenols with Hydrogen or Coal Gas at 750–800° in the large Apparatus

No.	Substance used.			Gas.		Condensates.						Condensates contain.					Remarks.
	Kind.	Amount.	Through-put per hour.	1 mol. subst. in mol. gas.	Rate per min.	Receiver.		Act. charcoal.			Total.	Crude benzol 80–180°.			Un-decomp. raw material.	Hydro-carbons boiling above 180°.	
						I.	II.	I.	II.	III.		Total.	% of theory.	% of quantity used.			
		g.	g.		l.	g.	g.	g.	g.	g.	g.	g.			%	g.	
	Experiments with hydrogen.																
1	Tri-cresol .	510	219	3·4	12	103	115	214	23	—	455	330	90·0	64·7	—	—	
2	Primary tar phenols 190–250°	441	220	4·25*	14·5	103·1	15·5	170·5	77·5	—	366·6	258	—	58·5	—	55	*100 g. substance in mol. gas.
3	Phenols from total primary tar.	919	290	5·2*	—	161	219·3	296·3	38·5	—	715·1	363·5	—	39·6	—	208·5	
4	Primary tar phenols 210–270°.	945·5	3,790	3·7*	21	108·9	113	55·3	292	10	579·2	315	—	33·3	—	200	See remark to 6–9.
5	Tri-cresol	1,075	815	2·25	8	241·5	103	253	0·5	—	598	395	50·9	36·7	—	135	
6	,,	890	1,330	4·45	36	192	101	283	9	—	585	402	62·5	45·2	0·4	110	Benzol yield inaccurate through inadequate absorption.
7	,,	886·5	3,100	2·83	37·3	72	99	294	121	21	607	523	81·7	59·0	0·6	48	
8	,,	2,088·4	8,300	2·95	75	782	—	588	300	—	1,670	—	—	—	18·7	391	
9	,,	2,475	12,300	2·77	99	950	—	508	402	—	1,860	—	—	—	16·2	550	
	Experiments with coal gas.																
10	,,	330	890	6·4	16	41·2	31·1	128·4	40·6	—	241·3	174	73·0	52·7	—	40	Slight separation of soot.

TABLE

Reduction of Tri-cresol and Brown Coal Creosote

	Substance used.			Gas.		Condensates.					
						Receiver.		Act. Charcoal.			
No.	Kind.	Amount. g.	Throughput per hour. g.	1 mol. subst. contained in mol. gas. g.	Rate per min. g.	I. g.	II. g.	I. g.	II. g.	III. g.	Total. g.
1	Tri-cresol . . .	1843	3000	2¼	23·5	360	—	400	470	—	1230
2	,, . . .	2719	3000	2¼	23·5	275	701	500	400	—	1876
3	Brown coal creosote	2082	2000	—	19	134	267	650	300	—	1351
4	,, ,, ,,	1888·5	2000	—	19	120	250	600	450	—	1420
5	,, ,, ,,	1620·1	2000	—	19	30	75	480	310	—	895

of which could not be ascertained definitely, although the decomposition of the ethylene and similar constituents of coal gas was suspected. Another explanation is that iron carbonyl, which is present in gas containing carbon monoxide, particularly after compression in steel cylinders, upon decomposition at high temperature into metallic iron, catalytically induces the deposition of carbon.

It has already been mentioned that water gas when used instead of hydrogen spoiled the iron tube. The following Experiments, 3 to 5, Table XL, were made[102] with the tube after revivification by sulphiding, with a brown coal creosote placed at our disposal by the Deutsche Erdöl A.-G. The creosotes, practically free of neutral oils, were first distilled down to pitch to remove the high-boiling constituents which are of little use for this reaction. Thirty-one per cent. of pitch was left on distilling the creosote from 200° to 240°. The experiments were made with hydrogen and a throughput of 2 kg. of creosote per hour. Assuming that the creosote consisted mainly of xylenols, the hydrogen rate was adjusted on the basis of an excess of $\frac{1}{4}$ mol. over the theoretical requirement. Table XL shows that the yield was about 40 per cent. of the quantity used, in agreement with the results of previous experiments. The benzol was brown in colour, smelled of pyridine and had a specific gravity of 0·89. Distilled by Spilker's method, it gave the fractions :

Below 85°	68 per cent.
85–95°	18 ,,
95–113°	3 ,,

The product then consisted largely of benzene, with very small pro-

XL

with Hydrogen at 750–780° *in the large Apparatus*

Condensates contain					Gas analysis.						Calorific value of reaction gas.
Crude benzol 80–180°.			Undecomp. raw material.	Hydrocarbons boiling above 180°.	CO_2.	O_2.	CO.	H_2.	CH_4.	Unsat. hydro-carbon.	
Total. g.	% of theory.	% of quantity used.	%.	%.	%.	%.	%.	%.	%.	%.	Cals.
1090	81·9	59	—	not det.	0·4	0·8	12	58·8	19·6	—	3412
1510	76·9	55·5	—	,,	—	—	—	—	—	—	—
855	—	41	—	,,	0·6	0·8	17·8	46·8	23·2	—	3876
790	—	41·8	—	,,	—	0·2	15·6	50·2	20·8	0·6	—
630	—	38·8	—	,,	—	0·2	13·2	54·0	23·4	1·2	3794

portions of higher homologues. It should be mentioned that a high cresol velocity favours the formation of toluene, whilst at a slower rate benzene predominates. This observation is explained by the fact that for a complete removal of the methyl group the molecules must be kept at high temperature for prolonged periods.

It should, therefore, be possible to obtain in commercial working a product richer or poorer in toluol by modifying the mode of procedure. We had to content ourselves with a slow throughput of creosote in order to be able to absorb the benzol quantitatively in our condensation plant. In working-up the reaction products of all the experiments of which details are given in Table XL, we proceeded in the manner already described.[107] The figures given for benzol in the table apply to crude benzol obtained by steaming the activated carbon of the absorption drum and "topping" the products collected in the receivers.

A few experiments were made with the object of replacing the reducing action of hydrogen by that of coke. This had not been attempted before, as it was feared that the mineral constituents, and particularly iron compounds, would induce deposition of soot. Since the favourable influence of sulphur had been established, it seemed promising, by a sulphiding treatment, to make the impurities in coke innocuous.

For this purpose semi-coke was treated in our iron tube by passing hydrogen sulphide over it for 3 hours at a red heat. "Tri-cresol" vapour was then passed through the tube together with a very gentle current of hydrogen sulphide. The benzol yield was 30 per cent. of the "tri-cresol" used. No soot was definitely found on the semi-coke at the end of the experiment. A second experiment conducted in the same way, but with the addition of steam, gave an appreciable improvement in the yield. In this experiment again a deposition of soot could not be established with certainty. Owing to the low pressure of the town's gas mains at the time, the temperature of the experiment did not exceed 700°.

The object of some final experiments was to ascertain whether the reaction could be appreciably accelerated by enlarging the contact surface. The absorption capacity of our large apparatus being inadequate for these experiments, we had to proceed on a small scale in the following manner. We passed vapour of "tri-cresol" mixed with $2\frac{1}{2}$ mols. of hydrogen per mol. of cresol through the sulphided pipe, only half the length of which was heated to 750°, at a velocity which exceeded the capacity of the apparatus, so that 20 per cent. of undecomposed cresol was condensed along with benzol and other reaction products. We then charged the pipe with sulphided iron turnings which approximately doubled the contact surface, and passed an equal amount of cresol vapour through the pipe under the same conditions. In this experiment only 13 per cent. of undecomposed raw material was collected in the receivers. A comparison of the proportions of unreduced cresols obtained in the first experiments shows,[108] in confirmation of previous results, that, by increasing the contact surface, the reaction velocity and the capacity of the reaction tube had been raised by one-third only. The observation justifies the supposition that the reaction is not influenced catalytically, but is entirely due to thermal decomposition.

Having noticed a smell of butadiene when steaming out the activated carbon, we investigated whether di-olefine hydrocarbons were formed by thermal reduction. In preliminary experiments we attempted to ascertain in the crude benzol the proportion of constituents boiling below 70°. For this purpose we fractionated 200 c.c. of benzol in a Dufton[109] spiral column, and obtained 2·1 c.c. of compounds which smelled strongly of isoprene and absorbed bromine readily. These figures are not final; further investigation of this problem and an exact estimation had to be postponed, since only part of the reaction products could be condensed in our apparatus.

To sum up: it has been demonstrated that a thin coating of iron sulphide protects the iron reaction tube, heated to 750°, during the thermal reduction of phenols to benzol, from the deposition of soot as effectively as a tin coating. No deleterious influence of the iron sulphide upon the reaction was noticed. A series of experiments with "tri-cresol" and with brown coal creosote gave yields in the sulphided tube as favourable as those obtained in a tinned tube. Coke which, owing to its ferruginous mineral constituents, deposits soot, lost this property after having been sulphided for several hours. Phenols may be reduced to benzol by sulphided semi-coke in a gentle current of hydrogen sulphide, with a yield of 30 per cent. The yield is increased to 40 per cent. by the addition of steam to the mixture. Doubling the contact surface of the reaction tube raises the reaction velocity by one-third.

Benzol by Reduction of Brown Coal Primary Tar Phenols

The same apparatus served, while the internal tin coating was still intact, for experiments in which the preparation of benzene and its homologues from creosote of brown coal primary tar, was investigated. Numerous preliminary experiments on a small scale having proved quite satisfactory, they were tried on a larger scale.[107]

The raw material was a new consignment of technical brown coal creosote from the Deutsche Erdöl A.-G. The material was first distilled down to pitch in an iron pot, the oil boiling from 180° to 240°. Higher distillates were not obtained. The pitch residue amounted to about 20 per cent.; the water in the distillate to 3·4 per cent. The distilled oils were completely soluble in caustic soda, and, therefore, were free from neutral constituents. According to information supplied by the Works, this creosote had been extracted by caustic soda.

TABLE XLI

Reduction of Brown Coal Creosote with Hydrogen and Coal Gas at 750–780° *in the large Apparatus*

No.	Oil used.		Gas.		Condensates.						Condensates contain		
					Receiver.		Act. Charcoal.			Total.	Crude benzol 80–180°.		Hydro-carbons boiling above 180°.
	Amount.	Through-put per hour.	100 g. oil contd. in mol. gas.	Rate per Min.	I.	II.	I.	II.	III.		Total.	% of quant. used.	
	g.	g.		l.	g.	g.	g.	g.	g.	g.	g.		g.
Experiment with Hydrogen.													
1	1299	3890	2·7	21	159·9	178·8	401·5	80·8	34	855	612	**47·1**	210
Experiment with Coal gas.													
2	975	1950	7	21	111·8	107·5	329·7	66·1	15·0	630·1	390	**40**	60

The first experiment was made in a current of hydrogen; the second in a current of coal gas. In Experiment 1 an excess of hydrogen of ½ mol. was used, and the creosote feed was adjusted to a throughput of about 4 kg. per hour. The furnace temperature was kept between 760° and 780°. 47·1 per cent. of crude benzol boiling from 80° to 180° was obtained as calculated on the material used; the benzol produced was of a light yellow colour and smelled strongly of pyridine.

These experiments confirmed the results previously obtained on a smaller scale. Brown coal phenols may be reduced with hydrogen to benzene and small quantities of other hydrocarbons boiling below 180°, up to 50 per cent. of the original weight. In terms of calorific value, the yield is considerably higher, for the oxygen of the phenols has no calorific value. For example, 1 kg. of benzene has a calorific value of about 10,000 cals., 1 kg. of phenol $C_6H_5{\cdot}OH$ a value of about 7800 cals.; 78 kg. of benzene are therefore equivalent in calories to 100 kg. of phenol.

The light spirits formerly available, *i.e.*, benzol in aromatic coal tar and benzine from brown coal, have had benzine from bituminous coal added to their number in recent years. We have now established the conditions under which benzol may be produced from brown coal.

The benzine from the distillates of bituminous coal,* brown coal and peat is a decomposition product of bitumen; some benzine exists preformed in coal. Benzol may be obtained from these fuels by our process of reducing the phenol of primary tar. The phenols themselves are not derived from bitumen, but from the ulmic constituents of coal. Benzol recovery from the gas and the ordinary tar of high-temperature carbonisation of bituminous coal, as practised in coke-ovens and gas retorts, is possible because, under the conditions prevailing there, primary phenols are reduced.

Production of Hydrogen by the Diffusion Process.

After it had been shown that phenols could be extracted from primary tar oil by means of superheated water, and reduced by extremely simple methods with hydrogen to benzene and toluene (which, it should be noted, is free from thiophene), it remained to find a cheap process for the supply of the requisite hydrogen. To replace hydrogen by coal gas or water gas did not prove feasible. It was found that hydrogen could be obtained from producer gas or water gas by a process of diffusion.

Producer gas will be available where primary tar is made in generators, or could be made from the semi-coke of low-temperature carbonising plant in sufficient quantity. There is no need to separate all hydrogen from a producer gas: it is quite sufficient to extract a few per cent. of hydrogen as long as this is of high concentration and contains as little carbon monoxide as possible.

In the case of a plant gasifying lignite briquettes in generators, 1 ton of briquettes would produce 100 kg. of tar containing 20 per cent. of phenol, say 20 kg. of phenol. Of these only one-half, *i.e.*, 10 kg., can be reduced. Let us assume a yield of 3000 cb. m. of producer gas per ton of briquettes, containing a total of 450 cb. m. of hydrogen. For reduction and demethylation to benzol, 10 kg. of cresols require about 4 cb. m. of hydrogen at the rate of 44·8 litres per gram-mol. of cresol (*i.e.*, 108 grams), this being 1 mol. H_2 for reduction and 1 mol.

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* This is only partly true in the case of bituminous coal. Vide section "Extraction."