$H_2$ for demethylation. With a plant of this capacity the reduction of the phenol made could therefore be brought about by separating one-hundredth of the total hydrogen in the gas. This would mean practically no diminution in the calorific value of the producer gas.

The possibility of such a recovery of hydrogen has been discussed by Fischer, Schrader and Jaeger.[110] Fig. 59 explains the principle of the method. In a welded sheet-iron vessel small contact rings of the Raschig or Lessing type are disposed on a grid of wire netting to a depth of 10 to 20 cm. Producer gas flows through the space below the grid whilst superheated steam passes over the contact rings in the opposite direction and with a slight positive pressure against the producer gas, the pressure being indicated by the gauge. The whole apparatus must be kept at 150° and well lagged so as to avoid condensation of steam.

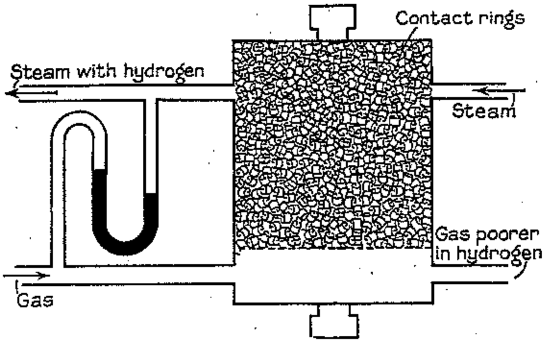

FIG. 59.

After condensation of the steam, hydrogen of high concentration can be obtained, even from gases of low hydrogen content.

### 5. *Benzine by Destructive Distillation of Primary Tar from Bituminous or Brown Coal*

It has already been shown in the section on "Chemical Changes on Distillation" that distillation under ordinary conditions and at atmospheric pressure leads to considerable chemical changes in primary tars, particularly in the high-boiling fractions. Broadly speaking, there are two ways of causing a scission of hydrocarbons of high molecular weight into lighter products by the action of heat at atmosphere pressure. The products are either vaporised and the vapours brought into contact with surfaces of considerably higher temperature, in which case there is a fairly wide margin of temperature; or else the hydrocarbons are submitted to a very protracted distillation, when decomposition takes place at a temperature at or below, and certainly not appreciably above, the boiling point of the product. The experimental conditions may be varied and modified in many ways. At higher temperature the reaction will proceed more rapidly and violently; at a lower temperature, more time is required to carry scission to the same extent. The temperature also influences the yield and properties of the products obtained.

Protracted destructive distillation of primary tars proceeds similarly to that of petroleum. It affects chiefly the constituents boiling above 300°, *i.e.*, viscous oils, paraffin wax and part of the high-boiling phenolic bodies.

It is well known that in the distillation at atmospheric pressure of oil mixtures, such as crude petroleum, more or less decomposition takes place according to the experimental conditions as soon as higher temperatures are reached. The higher fractions then do not consist of compounds which were originally present in the raw material, but of products derived from them by certain chemical changes. The temperatures at which decomposition sets in vary with the kind of crude oils; they lie, according to Engler,[111] between 200° and 250°. If the high-boiling constituents are to be obtained undecomposed, preserving conditions must be employed above these temperatures, such as distillation in a vacuum or in a current of superheated steam, or a combination of these two methods, a procedure which is practised in the manufacture of the lubricating oils from crude petroleum.

The break-down of compounds of high molecular weight into compounds of lower molecular weight may, on the other hand, be utilised for the purpose of enriching the lower fractions at the expense of the higher-boiling fractions, a practice originally introduced into petroleum refineries to secure higher yields of lamp oils.

A technical brown coal tar of the Riebeck Montan Works was subjected to destructive distillation.[112] This was not a true primary tar, but the results obtained will hold good for it, since previous work had shown that the distillation of primary tar conducted in the usual way yields products of the consistency and the general properties of commercial brown coal tar.

The experiments discussed in the following lines were made to clear up two points. In the first instance, the yield and properties, particularly of the light products, obtainable by slow distillation down to coke, were to be ascertained. Secondly, it was of interest to know whether and to what extent by such cracking, if interrupted at the proper point, a concentration of viscous products in the residue would take place. This was to be expected from experiments made by Engler on the behaviour of unsaturated compounds, such as amylene and hexylene, when heated under pressure to 300–350° for long periods, and from experiments made in this Institute. Theoretically this might be explained by the thermal decomposition of high molecular compounds to saturated and unsaturated products of low molecular weight, which partly polymerise again, forming compounds of the character of lubricating oils.

The experiments were performed in a welded sheet-iron still of 1·5 mm. wall thickness, which had done good service before for the distillation of tar in bulk. As to the shape of the still, which has some bearing on the results, it consisted of a cylinder 50 cm. in diameter and about 18 cm. in height, with a conical top 13 cm. high (Fig. 60). To avoid superheating and to distribute the heat uniformly over the whole of the bottom, the still was not heated by gas burners, but was placed on an electric resistance heater and insulated by porcelain buttons. The cylindrical portion was lagged with a jacket of sheet-iron and asbestos; the conical portion was left bare for the purpose of re-condensing the undecomposed vapours and sending them back into the hot zone. The low-boiling products were taken off through a tube in the top of the cone, which was bent to avoid priming, and were passed through two Liebig condensers and a coil condenser in series. The temperature was taken with a thermometer or thermo-couple in the liquid, 0·5 to 1 cm. from the bottom. Vapour temperatures are not given, as, on account of the very slow distillation, fluctuations in the rate were unavoidable. The distillation was regulated so that a constant and slow drip of distillate was maintained for days without interruption. The specific gravity of the distillates was taken during the experiment as a guide to the progress of decomposition.

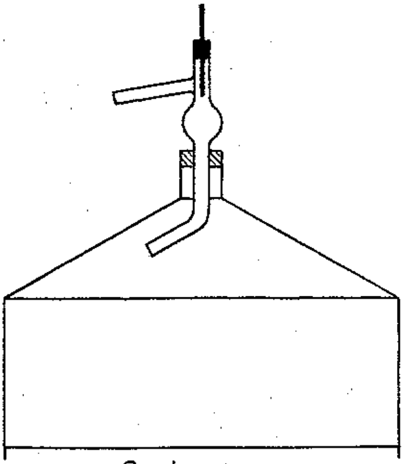
Scale. 1 : 10.

FIG. 60.

These researches have proved that the constituents of primary brown coal tar boiling above 300° are broken up to a considerable extent by slow distillation, only about 14 per cent. of the material treated still showing a boiling point above 300°. This does not necessarily represent unchanged raw material, but probably contains high-boiling constituents secondarily formed from primary decomposition products. The bulk (33 per cent.) of the material left after the removal of about 4 per cent. of tar acids and bases, boiled between 200° and 300°. Seven per cent. of benzine boiling below 150°, or 14 per cent. boiling below 200°, was obtained. The coke residue amounted to 12 per cent., the difference of about 23 per cent. representing gas and loss. The experiments proved further that a re-formation of high-boiling bodies of lubricating oil character took place simultaneously with the formation of low-boiling products.

The destructive distillation of primary tar from bituminous coal gave similar results.[113] A commercial low-temperature tar containing 45 per cent. phenols, of which 10 litres were submitted to very slow distillation which was continued for 5 days, yielded 5·2 kg. of oil, 3·6 kg. of coke, 2·7 cb.m. of gas and 700 c.c. of water. Fractional redistillation of the oil obtained gave 14 per cent. of benzine boiling below 200°, about 40 per cent. of oil from 200° to 250°, with a phenol content of 45 per cent., about 14 per cent. from

250° to 300°, with a phenol content of 25 per cent., and about 7 per cent. of semi-solid residue suitable for lubricants. The latter substance was formed by polymerisation as in the case of the brown coal tar. Low-boiling phenols do not disappear, but the higher fractions seem to have been diminished.

Considering that almost half of the original tar consisted of phenols, the proportion of low-boiling products obtained could not be very large, for it may be assumed that their parent substance can only be the hydrocarbons of the tar.

*Benzine by Cracking of Primary Tar at Ordinary Pressure.*

As was pointed out in the preceding section, the scission of high-boiling constituents in destructive distillation occurs chiefly in the liquid phase. Since the temperature of the liquid cannot be raised above its boiling point, except when working under pressure, the point of decomposition may not be reached.

If the action on the hydrocarbons is to be intensified at atmospheric pressure, the vapour phase must be superheated, a process known as "cracking." The production of benzine from brown coal tar may be cited as an example.

The pyrogenic decomposition of brown coal tar oils at atmospheric pressure has been the subject of various researches. Several short papers were published in 1878 by C. Liebermann and O. Burg,[114] M. Salzmann and H. Wichelhaus [115] and a few others.[116]

As a result of these investigations it was proved that the pyrogenic decomposition of the less valuable high-boiling fractions of brown coal tar yields products which contain, like ordinary tar, aromatic compounds such as benzene, toluene and anthracene. The most favourable working conditions were investigated.

With a different object in view, the fractions were divided, which makes comparison with our results difficult. The yield of low-boiling products was certainly lower than that realised in the experiments to be described.

In order to facilitate comparisons with the previous work, the raw materials for our experiments [117] were brown coal paraffin and brown coal tar from the Riebeck Montan Works. Further experiments were made with a brown coal producer tar, and with a tar oil fraction boiling between 200° and 300°.

The apparatus used (Fig. 61) consisted of an iron still A of 1 litre capacity, and the superheater tube B (40 cm. long, 5·5 cm. internal diameter) screwed into the cover of A; the cover was clamped to the still, an asbestos joint being interposed. A thermometer well was fixed to the cover with its closed end 1 cm. from bottom of the still. The superheater tube was closed by a screwed plate in which an iron tube was fixed to carry a thermo-couple. The wire gauze netting, on which a catalyst for the superheater was placed in a layer of 30 cm. thickness, rested on three iron studs fixed immediately above the opening connected to tube D, leading to the cooler E. Another tube C connected the top portion of B with the cooler E, which had approximately the same dimensions as B and was mounted at a distance of 14 cm. from the latter. The tube D was U-shaped and was provided with a drain cock, the liquid collecting in it serving as a seal between E and B. At the top, E was closed by a screw plate which was drilled to carry cylinder F, 30 cm. high and 4 cm. internal diameter, with a clearance of 0·8 cm. between its outer wall and the cooler E; it was charged with a liquid of definite boiling point, *e.g.* xylene, so that the vapours rising in E would be cooled to the boiling point of xylene, and only those boiling below this temperature would distil over through take-off tube G. A reflux condenser mounted on F prevented the evaporation of xylene.

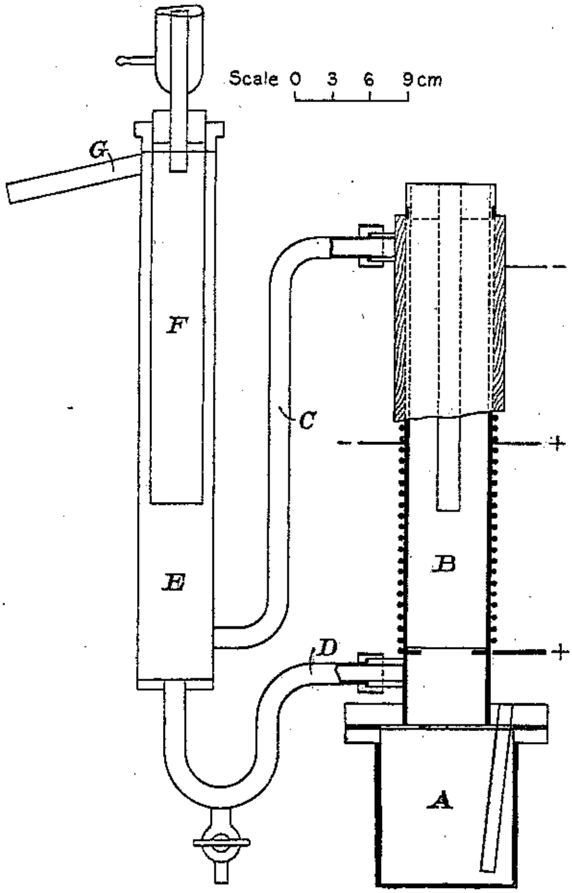

FIG. 61.

The distillation proceeded as follows: The vapours liberated in A passed through the superheated tube B, and then through C into the cooler E. The more volatile constituents escaped through G, whilst the portions of higher boiling range were condensed and returned through D into the superheater B. The latter was electrically heated. Temperatures were first measured by means of a thermo-couple mounted inside the tube. Afterwards two wires of copper and nickel were soldered to the outer wall of G and connected with a millivoltmeter. This did not indicate the highest temperature in the tube, because the turns of the heating coil were pitched farther apart at this point. The hottest portion was about three-quarters of the distance up the tube, where the temperature was from 50° to 60° higher. For purposes of comparison, observation of the wall temperature rendered good service; the maximum temperature was taken at the same time.

After charging the still with tar, and the superheater with the catalyst, the apparatus was assembled; container F was filled with xylene and fitted with a cork stopper which carried a Liebig condenser. Another Liebig condenser was joined to the off-take G, and was connected by an adapter to a flask serving as first receiver. The second receiver was an Erlenmeyer flask, the inlet tube of which reached close to the bottom. These two receivers were cooled by means of a freezing mixture. There followed a third vessel, cooled in some experiments by means of liquid air, and finally a gas meter. The iron still, which was surrounded by a protective shield, was heated by means of gas burners, and the superheater was brought up to 400° at the same time. After the liquid had started boiling, the temperature of B was gradually raised until the appearance of white, more or less dense fumes and the escape of gases indicated decomposition. As soon as the temperature dropped, the formation of fumes ceased; if it rose too high, they turned brown. These signs facilitated the maintenance of the correct temperature range. This was not always easy, because the gradual increase in temperature required, for instance, in the case of brown coal tar, caused fluctuations in the vapour velocity through B, and hence temperature variations. Yet the apparatus worked satisfactorily enough for comparative experiments. It was noticed that the gases carried a good deal of high-boiling products through the cooling tube. The substitution of water for xylene made as little difference as the charging of the cooling tube with broken brick, which ought to have facilitated fractionation owing to its great surface.* Heating was continued until the bottom of the still was red hot and the still contained only coke. After completion of the experiment, the liquid still contained in D was drawn off by means of the tap. In the tables

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* Although broken brick, on account of porosity, was not very suitable for this purpose, a preliminary experiment showed that the temperature inside the cooling tube at a level with the take-off was about 68–70°. Yet, the condensate consisted of about equal fractions boiling below and above 200°. The generation of gas prevented a proper fractionation.

this portion of the liquid is termed "liquid" residue. An experiment took from two to three hours. The distillates in the two receivers were weighed and combined. Very little liquid was usually found in the second receiver, at the utmost 5 per cent. of the total distillate. The coke was taken from the still at the end of each experiment, and weighed.

TABLE XLII

| Raw material. | Superheater tube B charged with broken brick. | | | Superheater tube empty. | |
|---|---|---|---|---|---|
| | Paraffin wax. | Carbonising tar from Central German brown coal distilled to 200°. | | Carbonising tar. | |
| | | Expt. I. | Expt. II. | Expt. I. | Expt. II. |
| Quantity used . . . . | 200 g. | 360 g. | 205 g. | 329 g. | 214 g. |
| Total distillate . . . . | 51·8% | 53·2% | 50·2% | 47% | 55% |
| Liquid residue in apparatus | 6% | 4·2% | 6·3% | 3% | 5·6% |
| Coke residue in still . . | 0·8% | 8·1% | 8·6% | 9·4% | 6·5% |
| Gases condensed with liquid air . . . . . . . . | 36·4% | 20·6% | 29·9% | 25·8% | — |
| Measured in gas meter . . | 8·5 l. | 15 l. | 13 l. | 14 l. | 45 l. |
| Results of Fractionation of Total Distillate obtained. | | | | | |
| 40–100° | 20·5% | 17·1% | 10·0% | 8·7% | 6·2% |
| 100–150° | 13·9% | | 6·5% | 7·7% | 7·3% |
| 150–200° | 11·4% | 11·6% | 8·4% | 10·2% | 10·4% |
| 200–300° | 5·6% | 17·4% | 18·9% | 20·3% | 32·8% |
| above 300° | | 6·6% | 8·4% | | |

In testing the catalytic effect of various catalysts, we impregnated broken brick of nut size with a concentrated solution of the substances and expelled the water either in a drying oven, or, preferably, in the superheater before assembling our apparatus. The mode of procedure was the same as before. The raw material in these comparative experiments was a lignite tar, from which the fractions boiling below 200° had been distilled off. The catalysts enumerated in Table XLIII had no appreciable influence upon the temperature of decomposition. It would therefore appear that the decomposition must be regarded as a purely thermal process. The effective temperature measured at the wall in these experiments was as in the previous ones, between 530° and 560°.

Table XLIII shows that the yield of products boiling below 150° amounted to 14–16 per cent., and that of the products below 200° to 24–28 per cent. The

TABLE XLIII

*Summary of Experiments on Decomposition of Brown Coal Tar in the presence of Catalysts*

| Catalyst | Al | Fe | Coke | Bauxite | NaOH | $H_3PO_4$ | $MnCl_2$ | $CrCl_3$ | $BaCl_2$ * | $ZnCl_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | %. | %. | %. | %. | %. | %. | %. | %. | %. | %. |
| Total distillate | 43·2 | 48 | 51 | 53 | 54 | 46 | 49·5 | 42·6 | 43 | 24 |
| Residue | 3·4 | 8·8 | 9·5 | 3·1 | 9·4 | 5·4 | 8·5 | 7·4 | — | 45 |
| Coke | 13 | 9·5 | 7·4 | 5·1 | 6·7 | 13·7 | 8 | 7·4 | — | 8·3 †<br>15 ‡ |
| Condensed in liquid air | 23·2 | — | — | 14·3 | 20·3 | — | — | 26·9 | — | — |
| Measured in gas meter | 22 l. | 48 l. | 51 l. | 66 l. | 13 l. | 49 l. | — | 18 l. | 46 l. | 32 l. |
| Results of Fractionation of Total Distillate. | | | | | | | | | | |
| below 100° | 7·9 | 8·2 | 7·6 | 7·0 | 7·1 | 8·3 | 7·1 | 7·7 | 6 | 3·2 |
| 100–150° | 7·3 | 7·2 | 6·6 | 8·8 | 7·0 | 7·3 | 6·7 | 5·6 | 5 | 2·4 |
| 150–200° | 8·2 | 10·1 | 9·0 | 11·6 | 10·7 | 8·3 | 11·8 | 9·3 | 6 | 5·9 |
| 200–300° | 12·9 | 16·5 | 17·0 | 19·1 | 22·1 | 14·1 | 16·8 | 15·0 | 23 | 4·9 |
| above 300° | 4·4 | 8·8 | 10·0 | 5·2 | 10·2 | 6·3 | 8·2 | 5·3 | | 1·9 |

fluctuations within these narrow limits are hardly due to specific effects of the catalysts, but chiefly to difficulties in controlling experimental conditions.§ Chromic chloride and zinc chloride catalysts behaved somewhat differently. With the former, some coking took place in the superheater. With zinc chloride, coking was so pronounced that part of the superheater was completely blocked. For that reason the total distillate amounted only to about 25 per cent., while 50 per cent. of oil was withdrawn from the U-tube. The coke in the superheater amounted to about 15 per cent. It is known that thick viscous oils are formed on boiling brown coal tar oil with zinc chloride. Similar reactions probably occur in the superheater tube and lead to the copious deposition of coke.

Briefly recapitulating the results of these experiments, it is shown, in accordance with other researches, that decomposition by superheating at atmospheric pressure favours the liberation of gases to an extraordinary degree. The catalysts used had no appreciable influence either on the temperature of decomposition or on the yields. The experiments with brown coal tar gave on average 15 per cent. of benzine boiling from 35° to

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* This experiment was not completed, being very similar to that with $MnCl_2$.

† In the still.

‡ In the catalyst tube.

§ It is not known whether the iodine numbers of corresponding fractions tally; for other purposes these fractions were combined to be worked up.

150°, as against 25 per cent. with application of pressure. 3 to 4 per cent. of the benzine was carried away with the gases. The products obtained resembled in smell and in appearance those resulting from heating under pressure, but the specific gravity was somewhat higher, and they differed from the latter products in their extremely high percentage of unsaturated compounds. The products could be readily refined, as regards smell and colour, by treatment with caustic soda, and more effectively with zinc chloride.

In the selection of the raw material for these decomposition processes preference will naturally be given, not to the primary tars of brown coal rich in bitumen, which can be more economically worked up for paraffin, but to the primary tars obtained from coal poor in bitumen, which by improvements in plant are produced in ever-increasing quantity and of superior quality.

Corresponding experiments on primary tar from bituminous coal have not yet been published. This tar should, on cracking, behave similarly to the primary tar from brown coal, but would probably differ by a still lower proportion of cracked benzines, owing to its lower hydrocarbon content. Phenols, when their vapours are superheated, do not yield benzine any more than by decomposition of the liquid phase, as has been shown in the last section.

Superheating experiments with primary tar from bituminous coal at ordinary pressure have been made under somewhat different conditions. It was then found [118] that the carbolic acid, originally present only in small quantity, was increased by the decomposition of higher-boiling phenols. The appearance of acetone in some commercial primary tars from coal may also be due to superheating. For no acetone was found in the primary tar carefully prepared from the same coal in the laboratory rotating drum.[47] That the primary tar from coal is highly sensitive to distillation, even at ordinary temperature, was mentioned on p. 93.

There appears to be no possibility of hydrogenating tar or tar oils at temperatures between 300° and 500° without the application of high pressure, even when catalysts are used. Catalysts are not likely to induce sufficient hydrogenation to counteract the liability to scission of hydrogen at these temperatures.

I therefore regard the process of Melamid,[119] who sprays the material to be hydrogenated by means of hydrogen into hot reaction chambers containing catalysts, merely as a cracking process, though the addition of hydrogen may possibly be an advantageous modification. It is not impossible that an atmosphere of hydrogen alone at ordinary pressure would suppress the liberation of hydrogen from the oil, and that limiting the reaction time would lead to molecular fragments richer in hydrogen.

The process of Melamid is mentioned here as being, in my opinion, a modified cracking process at ordinary pressure.

*Benzine by Cracking under Pressure.*

The observation that high-boiling, solid hydrocarbons of the paraffin series, by being heated in closed vessels, are split into liquid products of lower boiling points with a small evolution of gas, was made long ago by Thorpe and Young.[120] These investigators distilled paraffin wax from the hot portion into the cold portion of a two-limb closed tube, and observed that the paraffin wax after repeated distillation had assumed the consistency of butter and could be liquefied by the heat of the hand, and that after twelve distillations the bulk of the products remained liquid at ordinary temperature.

Similar reactions have been applied in the petroleum industry, particularly in America, for the purpose of converting heavy high-boiling oils into lighter lower-boiling oils. The original object was to increase the yield in lamp oil, but of late years petrol production has been the object. The consumption of motor spirit has increased to an extraordinary extent, whilst the production of oils of the paraffin type has decreased in the Eastern American States, though the production of asphaltic oils has much increased in California and Mexico. The former type of petroleum yields ample proportions of petrol. The latter contains much smaller quantities of lower-boiling constituents, or none at all.[121] The destructive distillation or cracking, introduced for the purpose of splitting hydrocarbons of high molecular weight into compounds of lower molecular weight, is based upon scission of the molecules by superheating, and it necessitates subjecting the oils either to prolonged heating or to heating at considerably higher temperatures. Conducted at atmospheric pressure this mode of procedure yielded favourable results, as long as the object aimed at was an increased production of kerosene, but it does not appear to have been found satisfactory for the production of petrol. Distillation under pressure was therefore resorted to; although this treatment does not yield a benzine of full value, the low-boiling product obtained is an acceptable substitute, and this mode of cracking has by now been practised for a long time in the American Oil Industry. Some two million gallons per day of benzine are produced in this way by the Burton [122] process. This application of distillation under pressure is not new. Young applied it in his factory fifty years ago, and Krey in Germany worked out patents in 1887 for the production of lamp oils from the heavy paraffin oils of brown coal tar by distilling the high-boiling constituents under a pressure of 6 atm. For economic reasons the process did not come into continued operation at that time, nor did the process of Graefe and von Walther, who used much higher pressures for the decomposition of brown coal tars.

The nature of the reactions involved in this destructive distillation remains on the whole obscure. It is certain that the chains of the larger molecules are split into fragments of lower molecular weight with partial formation of unsaturated compounds, and that there is, on the other hand, polymerisation of very small fragments to compounds of greater size. In the ordinary decomposition by distillation, the molecules are split near the ends of chains, and gases and oils of relatively high molecular weight are formed. When pressure is applied the splitting takes place nearer the middle of the chain.[123]

An autoclave of 1·2 litres capacity was filled to about one-third or half its volume.[124] A pressure gauge, a long thermometer sheath dipping into the liquid, and an outlet tube were attached to the cover of the autoclave.

According to Snelling,[125] heating of paraffin wax under pressure gives the best results when the vessel is more than one-tenth, but less than half full. The autoclave was rapidly heated by three burners, and the temperature in the vessel was read as soon as pressure was set up, heating being continued until the desired pressure had been attained. After complete cooling and discharge of the gas, the contents of the autoclave were distilled, and the products passing over below 150° were well cooled by means of a freezing mixture. During this distillation, temperature readings were taken immediately below the cover. The residue at 150° was then several times submitted to the same heating process in the autoclave. For the sake of simplicity oils boiling below 100° may be called light benzines; the fractions 100° to 150°, heavy benzines; and the fractions 150° to 300°, middle oils. It need hardly be pointed out that the products so designated are not identical with the benzine fractions which are obtained from petroleum, and which contain large quantities of unsaturated compounds.

TABLE XLIV

*Experiment with Brown Coal Tar*

Used: 500 grams Tar

| Repeated heating. | Approx. duration of heating up to beginning of pressure. Min. | Temp. at beginning of pressure. °C. | Heating period from beginning of pressure to maximum pressure. Min. | Maximum pressure. Atm. | Pressure after heating. Atm. | Distilled below 150°. g. |
|---|---|---|---|---|---|---|
| I. | 15 | 300 | 20 | 29 | 1–2 | 33·0 |
| II. | 15 | 350 | 25 | 32 | 4 | 41·6 |
| III. | 15 | 345 | 30 | 30 | 4 | 32·7 |
| IV. | 10 | 320 | 45 | 30 | 3 | 30·3 |
| V. | 20 | 320 | 43 | 33 | 2 | 26·0 |
| VI. | 20 | 293 | 50 | 32 | 2 | 23·0 |
| | | | | | | 186·6 |

After heating six times, the autoclave was opened, the liquid was syphoned off, and the residue, which at the bottom formed an adhering coke, but was loose and still moist in the upper part, was weighed.

Raw products obtained :—

| | |
|---|---|
| (i) distilled from the autoclave up to 150° | 187 grams |
| (ii) syphoned off | 176 ,, |
| (iii) coke residue | 60 ,, |
| Total | 423 ,, |

The total yield of 423 grams of weighable products represents about 85 per cent. Liquid (ii), on standing for some time, deposited 30 grams of tarry matter. The fractional distillation of 177 grams of liquid (i) yielded, after separation of water :—

| | |
|---|---|
| (1) 40–100° | 58 grams. |
| (2) 100–150° | 68 ,, |
| (3) residue boiling above 300° | 50 ,, |

Liquid (iii) was added to the oil syphoned from the autoclave, and distilled; the fractions were :—

| | |
|---|---|
| 150–200° | 54·2 grams. |
| 200–300° | 90·0 ,, |
| above 300° | 50·0 ,, |

The total result is therefore the following :—

500 Grams of brown coal tar yielded 11·6 per cent. of light benzine, 13·6 per cent. of heavy benzine, 29 per cent. of middle oil, 10 per cent. of constituents boiling above 300°, 2 per cent. water, 6 per cent. tarry matter, and 12 per cent. of coke; a total of 84·2 per cent.

The properties of these products were as follows :—

(1) *Light Benzine.*—The distillate which was originally almost colourless turned gradually pink and darkened more and more. After six days some red-coloured matter had deposited on the walls and on the bottom of the receiver. The liquid itself had now only a faint yellow colour and a faint unpleasant smell.

(2) *Heavy Benzine.*—This fraction also gradually turned to a pink colour. The colour then changed into a light brown, and there was some deposit on the walls of the receiver. The liquid finally was darker than the oil (i).

(3) *Middle Oil.*—The middle oil had a reddish-brown colour.

The following table records the results obtained with, and without, pressure :—

| | Ordinary distillation. | After repeated heating under under pressure. |
|---|---|---|
| Below 100° | 0·5% | 11·6% |
| 100–150° | 1·1% | 13·6% |
| 150–200° | 8·7% | 11·0% |
| 200–300° | 35·7% | 18·0% |

| | Light benzine. | Heavy benzine. | Middle oil. |
|---|---|---|---|
| Spec. grav. at 22° | 0·684 | 0·765 | 0·844 |
| Calorific value (Berthelot-Mahler Bomb) | 10399 | 10853 | 10636 cals. |
| Flash point (Pensky-Martens) | below 30° | below 30° | 41° |
| Iodine number (Hübl) | 69 | 64 | 39 |

The iodine number of heavy benzine from ordinary brown coal tar (obtained without heating under pressure) is, according to Graefe,[126] 61 before and 59 after treatment with $H_2SO_4$.

Our iodine values were determined on products which had been kept standing for a year for another purpose, and were then poured off from the resinous deposit, and redistilled. The iodine numbers tabulated above are, therefore, not directly comparable with those of freshly prepared products.

Under the conditions of repeated heating under pressure, brown coal tar yields considerably higher quantities of low-boiling products than by destructive distillation, or by cracking at ordinary pressure. The products are at the same time superior to those from the latter two processes. The highest yield of low-boiling products is obtained from those primary or ordinary brown coal tars which are poorest in phenolic constituents, and, therefore, richest in viscous oils and paraffin wax.

The commercial production of benzine from brown coal tar is, of course, not conducted in the above-described primitive way of alternate heating in an autoclave and redistillation of the low-boiling products. The process must be continuous, the liquid being discharged from the autoclave while still hot, and the apparatus should be so arranged that the low-boiling constituents are boiled off and condensed, whilst the higher-boiling constituents are returned to the autoclave, possibly mixed with a suitable quantity of fresh tar. The same treatment may be applied to fractions of brown coal tar, which should be particularly suited for benzine recovery.

A technical process of this class is Blümner's,[127] in which an exact maintenance of the optimum temperature of 450° to 500° is ensured by forcing tar