through an autoclave which is charged with contact rings and molten metal. The tar bubbles are evenly distributed by the contact rings through the molten metal, without coming into contact with the steel shell, where they would be superheated. Fig. 62 shows diagrammatically the arrangement of the apparatus.[128] Whether the Blümner process will prove superior to the pressure cracking processes, which have been developed in the United States, and have stood the practical test, remains to be seen, also whether this method will yield only a small proportion of unsaturated hydrocarbons, as Burton claims for his process. The Burton process could no doubt be used for the production of benzine from primary tars and tar oils. The characteristic points of this process may therefore be outlined.

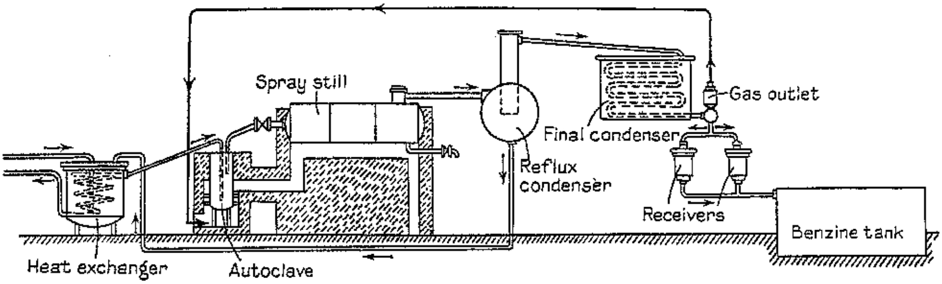

FIG. 62.

Benzine by the Burton Process [129]

The preparation of benzine by cracking under pressure gives less unsaturated compounds than when pressure is not applied.

In the method described above, pressure is set up by the vapours and gases liberated during the process. The cracking process is therefore started without pressure or, at any rate, without high gas pressure, this being developed during the experiment by the evolution of gas.

The Burton process differs from the above described in that the plant is started up with initial pressure. The permanent gases, which are liberated in every cracking process, are collected by Burton and forced by a compressor into the still at the beginning of a run, as soon as the removal of water from the oil is complete. The pressure applied is stated to be only 5 atm. Heating is continued under this pressure up to the cracking temperature, and as a result, the gasoline is claimed to be almost free from unsaturated compounds. The statements as to pressure and freedom from unsaturated compounds cannot be vouched for. Burton's process is distinguished from other cracking processes in use; he ingeniously presses the advantage of working under pressure to its logical conclusion, starting with compressed gas from the very beginning in order to obviate any tendency to decomposition. It is conceivable that the bulk of unsaturated hydrocarbons is formed in other cracking processes during the first stage, when the gas pressure is not high enough. If this view be correct, Burton's claim that his gasoline is better than others is perfectly intelligible. It would certainly be desirable to examine samples taken at different stages of the ordinary cracking processes for their degree of unsaturation of the benzines produced in relation to the pressure curve.

Benzine by Cracking and Simultaneous Hydrogenation under High Pressure

All benzines produced by cracking labour under the disadvantage of a high content of unsaturated compounds, which gives them an unpleasant smell and the undesirable property of darkening and gumming. This drawback seems to be partly or wholly avoided in the "Bergin" process, which Bergius [130] worked out and brought to a stage of high technical perfection in a large experimental plant at Rheinau, near Mannheim. Whether the yields of benzine from the same raw materials are greater than, for instance, in the Blümner process, can only be decided by exact comparative experiments. The part played by the hydrogen, which in the Bergin process is applied at a pressure of 100 atm., may be two-fold. The primary reaction in the Bergin process is probably the same as in any other cracking process. It is, however, conceivable that not only hydrogenation of nascent unsaturated compounds occurs, with suppression of the formation of coke, but also that the increase in total pressure caused by the hydrogen is of importance. It was stated, on p. 147, that in cracking under pressure the hydrocarbon chains are split about their middle with formation of liquid hydrocarbons, whilst at ordinary pressure scission takes place nearer the end of the chain, with copious evolution of gas. It is, therefore, quite plausible that the Bergin process with its high pressure more nearly approaches the object for which pressure is applied, and that it will therefore yield more liquid hydrocarbons and correspondingly less gas. Experiments with the Bergin process have so far mainly been made with petroleum products, but there is also some information on the Berginisation of tars. The impression given by statements that a practically complete* splitting-up of heavy oils into benzines is possible has not yet been confirmed.[131] This may, according to all experience, hold for certain selected and specially suitable fractions, but not for heavy oils generally. The laboratory apparatus which Bergius uses in his hydrogenation process, termed Berginisation, has a capacity of about 5 litres and is heated with gas. Temperatures are measured by means of a thermo-couple placed in the axial tube closed at one end. Fig. 63 shows diagrammatically the arrangement of the apparatus.

Bergius gives the following details of the method of working: "In making experiments in the 5-litre bomb, the vessel is gripped in a vice and charged with the weighed quantity of raw material. The cover is then put on, and the

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* The loss by formation of permanent gases is stated not to exceed a few per cent.

vessel is mounted on plummer blocks, and is connected with the hydrogen feed-pipe and filled with the desired amount of hydrogen as measured by a gauge. After closing the valve, the hydrogen pipe is disconnected; the thermo-couple is inserted into the inner tube, and the apparatus is rotated.

A temperature record is always kept for the control of the apparatus. The gas burners and pressure gauge are watched from outside. After a given time the heating gas is turned off and the apparatus is allowed to cool; the bomb is then again put into the vice and the gas pressure is released. The gases are collected in a gasholder, and are examined for condensable and non-condensable hydrocarbons. The cover is then removed, and the contents of the bomb poured out and worked-up. The pouring losses may be estimated from experience. Part of the losses is due to matter adhering to the walls of the bomb; another portion consists of condensable gases which are present in the relatively large volume of unconsumed hydrogen. These losses can be determined by cooling or washing.

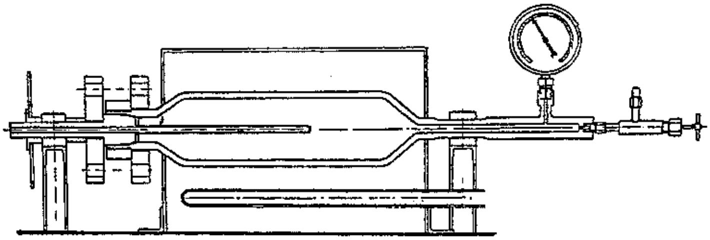

FIG. 63.

"This intermittent mode of working served us and is still being used for, the technical study of the hydrogenation of various raw materials. For industrial uses the method is manifestly not suitable; for these a continuous method had to be worked out. A continuous apparatus was used by us at Hanover as early as 1914, and has since been further developed. Fig. 64 explains the arrangement now in use. Hydrogen is circulated by means of a pump through the high-pressure apparatus, and serves both as a reacting medium and as a carrier for the resultant products. The hydrogen and the raw material, which is forced into the apparatus by a pressure pump, are first heated in a separate preheater to the working temperature in order that the reaction chamber itself may be properly utilised. The reaction vessel is a steel cylinder of about 40 litres capacity, fitted with stirring gear. The raw material and hydrogen enter at one end, and hydrogen charged with oil vapours leaves at the other end. A reflux condenser returns the entrained heavy products into the apparatus, whilst the lighter products are condensed, collected in a pressure vessel and separated from hydrogen. The cooled hydrogen returns to the pump, and is again fed into the apparatus after having passed through the preheater. The products are discharged from the receiver in which they are kept under working pressure, and are separated from the dissolved gases which are liberated on expansion. A lead bath supplies the heat required for heating-up and for maintaining the temperature."

A commercial plant is now in operation at Rheinau, of 4 cb. m. reaction space and a rated capacity of 20,000 tons of raw material per annum. The numerous visitors to this installation speak most highly of the supreme excellence of the mechanical arrangements. The reaction chamber is double-walled, and is heated by forcing hot compressed nitrogen through the jacket space and back to the heater disposed in a lead bath. Several advantages are claimed for this mode of heating. The nitrogen, being under pressure, compensates hydrogen pressure on the inner wall of the reaction chamber. This pressure-balance is particularly desirable, as compressed hydrogen at a temperature of 400° dissolves carbon in the form of methane from the iron and steel, thereby diminishing the tensile strength of the metals. The outer wall of the reaction chamber, which has to bear the pressure difference against the atmospheric, is not endangered by the chemical action, being in contact with compressed nitrogen.

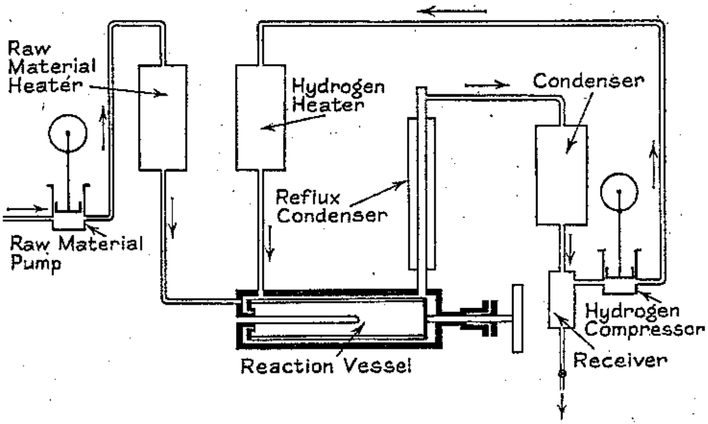

Fig. 64.

A maximum margin of safety in working is claimed for this arrangement against the risk of fracture of the walls. Provision is further made that the nitrogen in the jacket is at all times at somewhat higher pressure than the hydrogen in the chamber, so that in case of any damage to the inner wall, which is slightly thinner than the outer wall, there would be no escape of hydrogen, but the nitrogen would rush into the chamber. The installation is fitted with the requisite heat exchangers.

The arrangements for the production of hydrogen do not come within the scope of this work, but the results obtained with producer tar from brown coal are of great interest.

TABLE XLV

Brown Coal Producer Tar

Density = 1·045. Solidification point = 28°.

Ordinary distillation.	110–300°	>300°. Solidif. pt. 38°. Density = 1·042.	
After Berginisation.	Berginol. Visc. = 1·35° E. Density = 0·922		
After distillation of Berginol.	75–210°	210–300°	>300° Solidif. pt. 15°. Density = 1·04
	20 40 60 80 100 kg.		

According to Table XLV, which is taken from the paper by Bergius, 100 kg. of producer tar from brown coal yielded on Berginisation the following results: 25 kg. of oil boiling from 75° to 210°, which may be called benzine, and about 40 kg. of oil, boiling from 210° to 300°. The difference of 35 kg. includes oils boiling above 300°, of solidification point 15° and density 1·04, and loss. The loss cannot well be estimated, as the total weight of the resultant liquid products cannot be clearly seen from the table, but there certainly was some loss. It is not possible to see from the table whether the Bergius process would be capable of converting, by repeated treatment, the high-boiling portion completely into benzine, *i.e.*, whether 100 kg. of brown coal producer tar would yield 100 kg. of benzine. According to the general experience of cracking brown coal tar under pressure, which process gives the best yields, one may expect a maximum of 35 per cent. benzine boiling below 200°. Bergius's value of 24 per cent. for benzine boiling below 210°, or say 20 per cent. below 200°, lies far below the figure of 35 per cent. The reason may be that the table gives results of a single treatment. With repeated treatments of the residue the benzine yield would be higher. This assumed analogy between the processes of cracking under pressure and of Berginisation is unfortunately not explained by the graph (Fig. 65), which gives the pressure curves for cracking and Berginisation. The diagram shows that the pressure rise in the Berginisation ceases with the end of the heating-up period, and that at constant temperature a slow diminution of pressure takes place, due to the absorption of hydrogen by the unsaturated compounds formed by cracking, and doubtless also to the formation of methane. The significance of the methane formation will be discussed in connection with the hydrogenation of coal by means of hydrogen. The corresponding pressure curve of the cracking process shows a continuous rise. This rise will presumably continue until a pressure is reached which prevents the further liberation of gases at a given temperature. If the cracking experiments had been made with a more complete filling of the reaction chamber (attention has been drawn by Snelling to the importance of free space in the autoclave, see p. 147), the pressure rise would have been much more rapid. If enough tar had been put into the autoclave to leave only a quarter of the gas space allowed by Bergius, the pressure curve would have approached the Berginisation curve more closely. The difference would be that the curve would commence at zero, as the initial hydrogen pressure of 100 atm. would be missing, and the pressure would eventually remain constant and not show a drop.

A comparative study of the pressure cracking process and Berginisation is exceedingly interesting. For a strict comparison, the cracking should begin with a nitrogen pressure of 100 atm., as Bergius commences with hydrogen at that pressure; the pressure curves, as well as the products obtained, could then be directly compared. This has not yet been done, although the reaction would not be seriously disturbed by the formation of ammonia from nitrogen at these temperatures. If such data were available, the hydrogen consumption of Berginisation and its nature generally would become much more apparent.

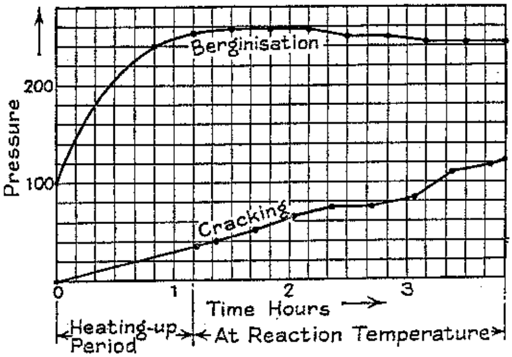

FIG. 65.—Typical pressure diagram comparing Berginisation and cracking experiments at approximately equal temperature.

A paper by Waterman and Perquin,[132] on comparative experiments with cracking under pressure and Berginisation, is an interesting contribution to this problem. The paper deals with the behaviour of paraffin wax,* and is here of interest for the study of the behaviour of brown coal tar, because paraffin wax is an essential component of this tar and of all its constituents that give the best benzine yields on cracking. The paraffin applied had the following properties: $D^{15} = 0{\cdot}913$, solidifying point 50·6°, bromine value 0·5.

300 Grams of paraffin wax and 300 grams of pebbles were shaken in a steel autoclave which was heated to 435° and maintained at this temperature. The pressure rose continuously in the way indicated by Bergius. The corresponding

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* Berginisation would show up better in the case of asphalt, which cannot be cracked to oil and gas as readily as paraffin wax.

experiment, according to Bergius, was made with an initial hydrogen pressure of 40 atm., as Fig. 66 and Table XLVI show. The curve becomes flatter, once temperature has become constant, but there is no indication of a decrease of pressure after 4 hours. The initial pressure of 40 atm. applied by Waterman may have been too low, and the reaction therefore too slow. Bergius, in the experiment illustrated by the graph, used an initial hydrogen pressure of 100 atm. Possibly the absence of the accelerating effect of the iron oxide, about 5 per cent. of which Bergius always adds, made itself felt, although, according to Bergius, this oxide is not to act as a catalyst but simply as a desulphuring agent—a statement which could easily be verified by experiment.

Possibly Waterman's temperature was too high. He may have adopted a high temperature in order to accelerate the reaction, other accelerating factors being insufficient. An argument against this latter assumption is the fact that Waterman was perfectly aware of the importance of maintaining exact temperature limits.

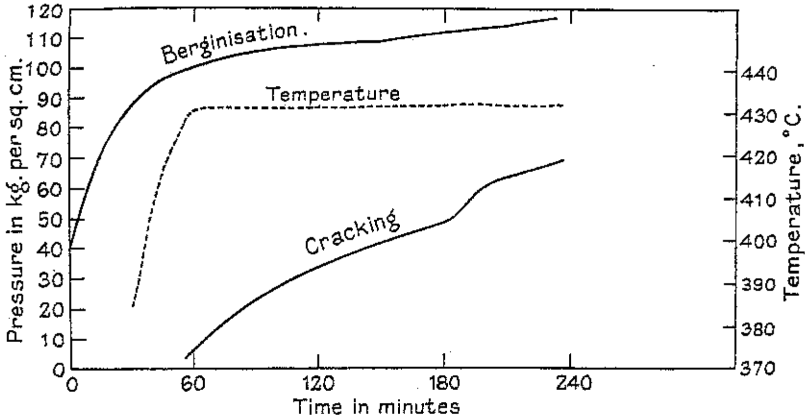

FIG. 66.

He states (*Chimie et Industrie,* Numéro special, May 1913), at the conclusion of his paper, that the influence of temperature upon the reactions is very important. In the Berginisation of a fraction (D = 0·993) of a heavy asphaltic oil from Borneo, he had observed, when using a stationary autoclave, that a temperature of 388° was too low, and 420° too high. Fairly favourable results had been obtained between 403° and 410°. At too high a temperature (in his case 420°) the cracking process predominated; at too low a temperature the intensity of the Berginisation was too feeble, because at that temperature cracking (a necessary preliminary then) was still inappreciable.

It is further known that the optimum temperature varies with the raw material. This is intelligible, for the thermal decomposition (cracking)

TABLE XLVI

Comparison of Berginisation and Cracking at + 435°

No. of the experiment.		Time required to reach the temperature in minutes.	Duration of the proper experiment in minutes.	Initial pressure in atmospheres.	Maximum pressure during the experiment.	Final pressure after complete cooling.	Obtained oils in grams.	Bromine content (addition).	Distillation of the oil obtained according to Engler.					Gases.		
									Weight % of the distilled oil.				Sp. G. residue 15°/15°.	Quantity in Litres.	Sp. Gr. compared with air.	Hydrogen %.
									to 220°.	to 300°.	residue > 300°.	Loss.†				
35	Berginisation	60	60	40	110·5	37·5	260 *	16·4	24·9	41·0	56·3	2·7	0·846	—	0·24	85·8
37		60	60	40	108·5	37·5	272 *	16·1	22·8	37·9	59·0	3·1	0·854	—	0·20	89·5
36		60	120	40	107	31	272	19·0	36·6	56·6	38·7	4·7	0·838	—	0·37	74·6
33		60	180	40	117	30	256	20·8	51·7	72·1	22·4	5·5	0·852	—	0·56	56·9
46		75	240	40	118	28	250	21·0	58·9	79·6	14·8	5·6	0·836	63	0·63	47·5
48		75	240	40	120	28	249	20·7	59·7	79·2	13·8	7·0	0·838	62·5	0·63	46·5
40	Cracking	80	60	0 Atmospheric pressure	30	± 2	271 *	21·6	23·0	39·0	60·1	0·9	0·854	—	0·99	—
45		70	120	0	51·5	< 4	270	27·6	41·9	63·7	32·0	4·3	0·855	—	0·80	—
34		60	180	0	71	5	246	26·1	56·5	76·5	17·5	6·0	0·900	—	1·10	2·3
49		75	240	0	72	7·5	238	23·9	56·8	76·9	16·2	6·9	0·902	29	0·94	3·7

* The product obtained was still solid and had to be melted out, which gave rise to extra losses of weight.
† Belongs to the lowest fraction.

of different kinds of molecules of the various raw materials sets in at different temperatures,* and only then can Berginisation take place.

The result of Waterman's experiments was that all paraffin wax was invariably converted into oil and gas, whether he worked under hydrogen pressure or not. Further, the yields of benzine were the same in both cases. The density was, however, always lower in the Bergius experiments than in the corresponding cracking tests, as Table XLVI shows.

The final pressure in the Bergius experiments, which was always lower than the initial pressure, as well as the composition of the resulting gases, demonstrate that a considerable proportion of the hydrogen had been consumed. The bromine value of the products, *i.e.*, their degree of unsaturation, was smaller with the Bergius process than with the cracking process.

Although it would have been better in the experiments both of Waterman and of Bergius if cracking had been tried with an initial nitrogen pressure of 40 atm. (argon would have been still better), the comparison demonstrates that the benzine yields did not differ in the two cases. The products differed only as to quality, a fact which confirms an assumption expressed on a previous occasion.[133]

There was no noteworthy difference as regards the deposition of " carbon," which was very small in both cases. In this respect, paraffin wax seems less suitable for comparison than asphalt, for instance. All the same, the experiments of Waterman are very valuable for the study of the Bergius process.

In mixtures of compounds such as tars and tar oils, hydrogenation is, of course, not limited to the saturation of unsaturated fragments of molecules formed by cracking. A reduction of oxygenated compounds to hydrocarbons is likewise conceivable, and a hydrogenation of the same, *e.g.*, of the phenols, to hydro-aromatic alcohols is still more probable. This problem will be discussed in the following sections.

6. *The Hydrogenation of Primary Tars, Tar Oils and Phenols*

With Catalysts.

A more complete hydrogenation of the constituents of primary tars and tar oils would no doubt be possible if one could work at temperatures considerably below the temperature of 400°, at which Bergius operates. Without the use of catalysts the reaction velocity is, however, too small at temperatures between 200° and 300°. In practice, one would be compelled to work, as in the manufacture of tetralin, at these lower temperatures with the aid of hydrogen under strong pressure, and finely divided nickel as catalyst. As the nickel catalyst is poisoned very quickly by sulphur, the tar oils must be submitted to an intensive preliminary purification for the elimination of sulphur com-

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* There is surely an analogy with ignition points, which are preceded by a loosening of the molecules.

pounds. In the preparation of naphthalene for hydrogenation into tetrahydronaphthalene (tetralin), this purification is effected by means of metallic sodium with perfect success, but only after thorough refining of the naphthalene by physical processes.

Preliminary purification of the tar oils by means of crystallisation need hardly be considered. A purification with sodium could only be applied to the hydrocarbon fraction of the tar oils, and would necessitate the previous separation of the phenols. In the presence of phenols in tar oils, which may contain one-half of them, metallic sodium would simply dissolve with generation of hydrogen and formation of phenolates, and the consumption of sodium would assume fantastic dimensions. Considering all these factors, it will be seen that the hydrogenation of the technical tar oils by means of catalysts is practically out of the question. Recognition of this fact may explain why the Tetralin Works at Rotleben have acquired a licence under the Bergius patents for the industrial hydrogenation of tar products rich in sulphur, which, owing to this sulphur and to their general properties, are not amenable to purification by catalysts.

Without Catalysts.

To carry out the hydrogenation without the aid of catalysts requires, as has already been explained, temperatures near 400°, say between 350° and 450°, to ensure a measurable reaction velocity. Since, however, hydrocarbons rich in hydrogen, hydro-aromatic or aliphatic, are very liable, even at these temperatures, to split off hydrogen and to be converted into compounds poorer in hydrogen, hydrogenation can only be successful if conducted under hydrogen pressures which exceed the dissociation pressure of hydrogen in the products to be formed at any given temperature of reaction. Thus, one is compelled towards hydrogenation at high pressure, as first applied by Ipatiew to numerous compounds, and later by Bergius to mixtures such as commercial oils and coal. The latter process, as has been pointed out, is really a continuation of hydrogenation with preliminary cracking.

Scientific information concerning the real nature of hydrogenation by the Bergius process not being available so far, we can only communicate the results obtained in the hydrogenation of primary tar oils and primary tar phenols by the aid of sodium formate, and with carbon monoxide + steam, *i.e.*, with nascent hydrogen.[134] The experiments, conducted at 400° in a steel autoclave, demonstrated that the hydrocarbon portion of primary tar, which had previously been distilled at ordinary pressure down to coke, and the hydrocarbon fractions of primary tar thus treated, did not undergo any modification which affected the boiling points. On the other hand, the phenol portion of primary tars, no matter whether treated by itself or in the presence of the hydrocarbons, was converted into oils partially insoluble in alkali.

Phenols boiling below 250° proved to be not amenable to hydrogenation under the conditions stated, whilst phenols from primary tar boiling between 250° and 340° could be hydrogenated under the most diverse experimental conditions. The reaction products had apparently not parted with their oxygen. There had merely been an addition of hydrogen, converting the phenols into hydro-aromatic alcohols, which were thus rendered insoluble in alkali.

7. *Summary of the Recovery of Light Motor Spirits from Primary Tars*

The possibilities of recovering light motor spirits from the primary tars of bituminous and brown coal in the various ways described may be summed up as follows :

(a) *Low-boiling Constituents of the Gases of Low-temperature Carbonisation.*

It has been shown that the gases of low-temperature carbonisation contain benzines. The figures reproduced in Table XLVII were obtained by compressing large volumes of low-temperature carbonisation gas in steel cylinders previously charged with kerosene. The benzine absorbed was subsequently recovered by distillation. At the present time the recovery by means of activated carbon is more convenient and, perhaps, more promising, particularly for the stripping of highly-diluted benzine from producer gas. The proportions of such benzine are considerable; they amount to one-third per cent. of the weight of the coal.

TABLE XLVII

	% by weight of coal.
Low-boiling gas benzine from fat coal (Ruhr)	0·17
,, ,, ,, ,, fat coal (Minden)	0·3
,, ,, ,, ,, gas flame coal (Lohberg)	0·3

(b) *Alcohol from Low-temperature Carbonisation Gas.*

There are other ways of utilising the gases from low-temperature carbonisation for the production of liquid fuels. They contain up to 10 per cent. of ethylene and its homologues. The higher olefines can be absorbed by concentrated sulphuric acid, and subsequently ethylene by chlorsulphonic acid (according to W. Traube, easily and quantitatively); decomposition with water yields the corresponding alcohols.

Table XLVIII gives the amounts of unsaturated compounds in the gas obtained by carbonising the upper portion of the fat coal seams Catharina du Matthias, Preussen I Colliery. Propylene, butylene, and the other homologues of ethylene are almost instantaneously extracted by concentrated sulphuric

TABLE XLVIII

Carbonising stage.	Unsat. compounds sol. in cold conc. H_2SO_4. % by vol.	Unsat. compounds insol. in cold conc. H_2SO_4 but sol. in SO_3HCl. % by vol.	Total unsat. compounds. % by vol.
400°	5·6	6·4	12·0
425°	5·6	8·4	14·0
450°	3·2	5·2	8·4
475°	2·0	2·4	4·4

acid in the cold;* the action of chlorsulphonic acid on ethylene was equally rapid and satisfactory.

(c) *Low-boiling Constituents of Primary Tar.*

It is convenient to speak of tar benzines as distinct from gas benzine. Whether the benzine will be found in the gas or in the tar will mainly depend upon the mode and efficiency of condensation.

The proportions of the more volatile benzines of several low-temperature tars are given in Table XLIX. The tar of the gas flame coal contains up to 10 per cent. of constituents boiling below 200°; as the coal yields about 10 per cent. of primary tar, that figure represents 1 per cent. of tar benzine in coal.

TABLE XLIX

		% of tar.
Tar benzine of various primary tars, boiling below 200°.	Gas flame coal	10
	Rhenish brown coal	3·4
	Saxon carbonising coal	6

(d) *Benzine by Thermal Decomposition of High-boiling Tar Hydrocarbons.*

Prolonged heating of the hydrocarbons of low-temperature tars, especially of those boiling above 300°, to that or a higher temperature, leads by way of molecule scission to the formation of gases and of low-boiling hydrocarbons of the benzine type. A considerable portion of the latter are unsaturated and pass, by absorption of oxygen, or by polymerisation, into resinous products. For many purposes, it is advantageous to operate in such a way as to keep the proportion of unsaturated compounds as low as possible, allowing them to be hydrogenated.

The first three groups of Table L summarise the results of experiments to which W. Schneider submitted a Saxon brown coal tar; various cracking methods were applied. The third group also gives the low-boiling constituents

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* Tropsch and v. Philippovich [135] found later that an 87 per cent. solution of H_2SO_4 is most suitable for the absorption of ethylene.

of the tar before treatment: 0·5 per cent. below 100°; 1·1 per cent. 100° to 150°; and 8·7 per cent., 150° to 200°.

In destructive distillation, and taking the high-boiling portions over at a very slow rate, this tar yielded 7 per cent. of fractions boiling below 150° against 1·6 per cent. before treatment.

When the vapours were passed through a tube heated to 600°, the fraction boiling below 150° amounted to 15 per cent.

Heated several times above 400° in an autoclave, the tar yielded 25 per cent. boiling below 150°. By the third method the proportion of unsaturated compounds was notably lower than by the two first ones.

TABLE L

Thermal Decomposition of Saxon Brown Coal Primary Tar

(*Yields in % of Tar.*)

	Destructive distillation.			
60–100°		2·6	7	14
100–150°		4·3		
150–200°		7·1		
	Scission at ordinary pressure.			
below 150°			15	26
150–200°			11	
	Scission under high pressure.			
	before	after		
below 100°	0·5	11·6	25	35
100–150°	1·1	13·6		
150–200°	8·7	11		
	Bergius process with brown coal producer tar.			
	before	after		
below 210°	20	25		
210–300°		39		
above 300°	80			

A comparison of the fractions up to 200° shows a rise from the original of 10 per cent. to 14 per cent. by the first, 26 per cent. by the second and 35 per cent. by the third method.

The fourth group of Table L reproduces the data published by Bergius [131] in his paper on a "New Method for the Working-up of Mineral Oils from Coal." From a brown coal tar he obtained 25 per cent. boiling below 210°. In Table L, the fraction boiling below 200° by the other methods was 14, 26, and even 35 per cent. As regards quantity, the Bergius process gives, therefore, no striking result. The advantage of his method may lie in the absence of unsaturated compounds, but this cannot be judged from the data. The fact that Bergius did not obtain more than 25 per cent. (as against 35 per cent.) boiling below 200° may be ascribed either to his use of a tar of less suitable quality, or to the fact that only a single treatment was given.

The first three groups of Table L are an extract of the results of extensive researches conducted by W. Schneider in this Institute some years ago. I now proceed to deal with researches conducted by myself chiefly in conjunction with Hans Schrader and his assistants.

(e) *Benzol and Toluol by Reduction of the Phenols from Primary Tar.*

The chief raw materials so far considered for the production of low-boiling spirits have been the hydrocarbons of the tar and gas of low-temperature carbonisation. The following is a summary of experiments on the reduction of phenols. Table LI shows that both the total phenols of primary tar and their individual fractions can be converted into benzol and toluol by reduction with hydrogen in an iron tube, internally tinned or sulphided as described on p. 117.

TABLE LI

Suitability of Different Phenols

		Crude benzol.		Tube.
		% of theory.	% of quant. used.	
m-Cresol		99	72	Tinned iron tube
Bit. coal primary tar phenols .	200–250°	—	66	
,, ,, ,, ,, ,, .	250–340°	—	15	
Brown coal primary tar phenols .	200–240°	—	50	

TABLE LII

Summary of Light Motor Fuels from Gas Coal

	% of	% of tar.	% of coal.
Gas benzine			0·25
Tar benzine		10	1
Cracking benzine . . .	Hydrocarbons 15	8	0·8
Benzol	Phenols about 40	20	2·0
Alcohols	12 g. from 50 l. primary gas		1·2
Alcohols	from cracking gas.	?	?
	Total light motor fuels		5·25

The phenols boiling below 250° are most amenable to this treatment, giving a yield of 66 per cent. Much higher yields cannot be expected, because both the oxygen and the methyl groups are split off in the form of water and of methane, as has been pointed out before.

Table LII finally reviews the total yield of light motor fuels obtainable from gas flame coal according to the experience so far gained.

In the last column of the table the yields are referred to the weights of coal, when their values shrink to more modest figures. Taken absolutely, the figures still remain quite considerable, for a ton of coal gives 50 litres of a light motor spirit in addition to semi-coke, gas and the unused portion of tar.

The manufacture of cracked benzines will not be undertaken unless their value exceeds the loss of the corresponding much larger quantity of high-boiling hydrocarbons utilisable as fuel oil. Not allowing for benzine by cracking, a rough estimate shows about 4·4 per cent. referred to the weight of coal, of light motor spirit, and 5 per cent. of hydrocarbons applicable partly as lubricants and partly as fuel oil.

8. *Purification of Primary Tar Oils by Oxidation under Pressure*

Problems of oil refining are important in the petroleum industry as well as in the tar industries, and a good deal has been written on the subject. The chemical treatment with concentrated sulphuric acid and caustic soda is customary both for the removal of resins and of acid constituents. A restriction in the use of chemicals for refining liquid fuels would undoubtedly be desirable. Recent work proves that tar oils, especially the primary tar oils from brown coal, can be refined by oxidation under pressure.[136] An outline of the method and of the chief results will be sufficient in this place; for experimental detail the original paper should be consulted. Brown coal tar was fractionated, and the fractions were subjected to oxidation by compressed air in a steel shaking-autoclave (Fig. 67) at a temperature of 200°, and a total pressure of 35 atm. The compressed air entered the autoclave from a steel cylinder, through a reducing valve, and passed out through a vertical cooler. The cooler was made of steel; the condensation could thus take place while the vapours to be condensed and the air were still under pressure, the air leaving through a valve at the top. After a treatment of only 1½ hours the smell of treated oil underwent a characteristic change, the tar smell giving way to a pleasant odour. Fractional distillation left oxidation products of high molecular weight in the residue. The distillates were of light colour and had no tendency to subsequent darkening when left in the air, as unrefined oils always have. The less stable constituents of the original oils are oxidised and probably polymerised; they certainly have higher boiling points than before, and on distillation remain in the residue. The advantage of pressure oxidation over "blowing" tar, which is likewise an oxidation by air at an elevated temperature, is that the reaction proceeds more rapidly, the oxygen of the air is better utilised, and there is no loss of oil vapours by entrainment.

The acid constituents of the original oils, otherwise extracted with caustic soda, are considerably reduced in quantity. The phenols are probably oxidised to higher-boiling compounds which remain in the residue. A complete removal of the phenols, however, could not be effected. Before pressure oxidation, the various fractions had the following phenol contents :—

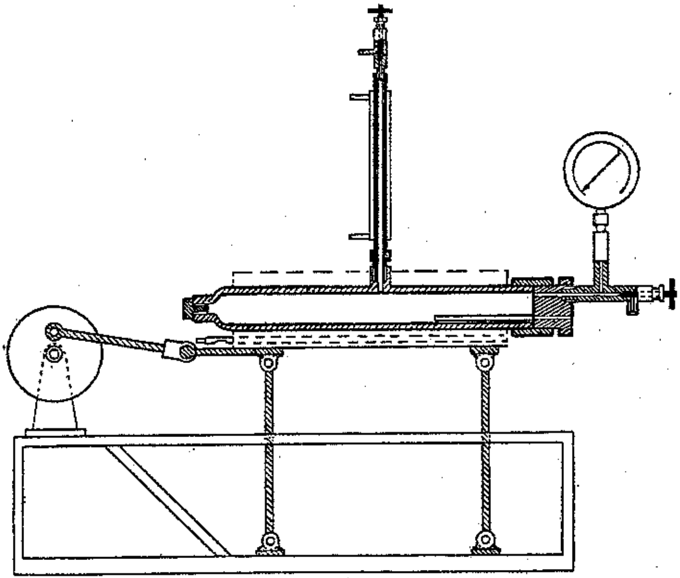

FIG. 67.

Fraction	150–200° . . .	12 per cent.
,,	220–250° . . .	10 ,, ,,
,,	250–270° . . .	8 ,, ,,
,,	270–300° . . .	5 ,, ,,

After oxidation under pressure, and subsequent distillation from the residues, the percentages of acid constituents were :—

	Soluble in sodium carbonate.	Soluble in sodium hydroxide.
Fraction 150–220°	0·8%	3·5%
,, 220–250°	1·6%	3·0%
,, 250–270°	1·5%	2·0%
,, 270–300°	1·8%	3·0%

The reduction in the low-boiling fraction is thus very striking, and points to the commercial applicability of pressure oxidation to the refining of