CHAPTER III

HYDROGENATION OF COAL

(a) BY MEANS OF HYDRIODIC ACID UNDER PRESSURE ACCORDING TO BERTHELOT

MORE than fifty years ago Berthelot [148] first succeeded in converting natural coal into oils by hydrogenation. For this purpose he treated coal with about 100 parts of saturated hydriodic acid at 270° for about 24 hours. He described his experiments as follows : " I experimented with coal purchased from the 'Compagnie Parisienne.' The exact source was not known, but the coal was of a type which yielded 4 to 5 per cent. of tar. I collected the gas and liquor, and determined the iodine quantitatively. The residue was an agglomerate resembling bitumen, and represented a little more than one-third of the weight of the coal. The iodine liberated amounted to twelve times the weight of coal; the gases consisted mainly of hydrogen. The liquids amounted to 60 per cent. of the weight of coal, that is, their weight was twelve to fifteen times greater than that of the tar which this coal could have furnished; this is sufficient proof that the new hydrocarbons were derived from the coal substance. The liquids were submitted to two series of fractional distillation. I first isolated a small quantity of hexane, C_6H_{14}, boiling at about 70°; this hexane contained a little benzene, which I converted into nitrobenzene, aniline, etc. After the hexane, several hydrocarbons came over which showed the general properties of saturated hydrocarbons; the mixture was too complex to admit of accurate separation. The last products, still abundant, were oily."

Of Berthelot's further experiments on the liquefaction of solid fuels, the hydrogenation of a very young fuel, viz., wood, and further, charcoal and carbon itself, may be referred to.

" *Wood.*—Wood consists of various insoluble compounds which, in the main, may be regarded as sugar derivatives formed by gradual combination and molecular condensation. I made use of the wood of matches, and took the precaution to split it into thin splinters and to dry it. In contact with hydriodic acid, the wood blackened at once. I heated part of the substance with 80 parts of saturated acid for 24 hours to 280°. Apart from a trace of carbon, the wood was almost completely transformed into liquid hydrocarbons, which represented about two-thirds of the weight of wood used. The hydrogen liberated was measured; it contained only a small quantity of hydrocarbon vapours. If from the weight of iodine liberated (which was determined experimentally) the weight of iodine equivalent to the volume of hydrogen is deducted, there remain 1100 parts of iodine set free by the hydrogenation of 100 parts of wood, corresponding to 8·6 parts of hydrogen. I shall revert to this figure. The liquid hydrocarbons were fractionated by two series of distillations, which yielded :

(1) Hexane, C_6H_{14}, boiling about 70°, produced in appreciable quantity. It did not contain any benzene, and gave the usual reaction of methane hydrocarbons.

(2) Dodecane, $C_{12}H_{26}$, boiling about 200°, and amounting to about half of the product. It was analysed; it resisted the action of bromine, fuming nitric acid, fuming sulphuric acid, etc.

(3) An oily hydrocarbon of the methane series, of equal stability, but volatile at a high temperature, of composition $C_{24}H_{50}$.

" The formation of these hydrocarbons agrees with the composition of the principal proximate components of wood; their carbon is a multiple of six atoms, as that of the sugars and their derivatives. It also agrees with the amount of hydrogen fixed in the hydrogenation of wood. The wood used contained in the dry state :

" Carbon	49·0	per cent.
Hydrogen	6·0	,,
Oxygen	43·0	,,
Ash	2·0	,,

" To convert 43 parts of oxygen into water requires 5·4 parts of hydrogen. If it is assumed, on the other hand, that 49 parts of carbon have been converted into one hydrocarbon $C_{12}H_{26}$, the predominant product of the reaction the formula of which corresponds with the mean composition of the mixture of hydrocarbons obtained, then 8·9 parts of hydrogen are required, a figure agreeing with the iodine liberated. Altogether $5{\cdot}4 + 8{\cdot}9 = 14{\cdot}3$ parts of hydrogen are required to convert 100 parts of wood into saturated hydrocarbons. The wood contained already 6·0 parts of hydrogen, and it absorbs 8·6 parts, giving a total of 14·6 parts in agreement with the previous value.

" *Charcoal.*—I selected fragments, well carbonised to the core, of a very light and porous charcoal (Charbon de fusain) such as artists use for sketching. The high porosity of this material, and the relatively low temperature at which it had been made, seemed to make it most suitable for my purpose. This material is known to contain considerable quantities of hydrogen and oxygen. One part of this charcoal was heated to 280° with 100 parts of hydriodic acid. The gases and liquids were collected, and the iodine was estimated quantitatively. About one-third of the charcoal had resisted the attack, or to be more correct was changed into a lumpy, bitumen-like mass, richer in hydrogen. The gas was hydrogen mixed with a small quantity of a highly volatile hydrocarbon. The liquids, which amounted to 70 per cent. of the original coal, were fractionated twice, and I isolated :

> (1) Hexane, C_6H_{14}, in small quantity, boiling at about 70°, showing the characteristic properties of this body.
>
> (2) Dodecane, $C_{12}H_{26}$, the chief product, boiling at about 200°, of the composition and properties stated above.
>
> (3) An oily, almost solid, hydrocarbon, about one-third of the product, giving the reactions of methane hydrocarbons. It is probably the hydrocarbon $C_{24}H_{50}$.

" By deducting from the weight of the iodine obtained that corresponding to the gas, I found that 100 parts of drawing charcoal had, by its hydrogenation, liberated 1270 parts of iodine. The weight of iodine equivalent to that of the hydriodic acid required for complete hydrogenation of 100 parts of charcoal would be about 1410 parts. As stated, about one-third of the charcoal had been merely transformed into a bituminous mass ; there is, therefore, no discrepancy between the results obtained and the theory.

" It should be noted that the hydrocarbons yielded by charcoal are identical with those from wood ; this shows that even so violent a reaction as charring does not completely destroy the chemical structure of the proximate constituents of wood. In other words, the compounds contained in wood still represent certain condensed derivatives of the compounds, *i.e.*, the sugars, contained in wood. I shall presently show that, up to a point, the same conclusion holds good for pure carbon, if it is derived from charcoal.

" *Pure Carbon.*—When charcoal is submitted to progressively intensified calcination, it is less and less attacked by hydriodic acid as it approaches the state of pure carbon. Coke is no longer attacked by this reagent, nor is natural graphite. The carbon produced by the decomposition of sodium carbonate with phosphorus at red heat resists the reaction, as does the carbonaceous matter which results from the treatment of aromatic compounds at 280° with an insufficient amount of hydriodic acid. (Berthelot, *Les carbures d'hydrogène*, III, pp. 144, 146, 147). The charcoal ceases altogether to be attacked by hydriodic acid if it is completely deprived of its hydrogen, which can be effected by the action of chlorine at red heat. Yet the carbon derived from charcoal and other organic compounds retains some trace of its origin, and of its chemical as well as physical structure. I have indeed succeeded, by the aid of the two following wet reactions, in transforming pure carbon into hydrocarbons.

" I have observed that pure carbon, as prepared by the action of chlorine on artists' charcoal at red heat, has the property of being slowly dissolved by nitric acid at 80°. A brown soluble substance is formed which I have so far not been able to convert into any known organic compound. Hydriodic acid had the desired effect. Under the conditions described, it converted the compound at 280° into methane hydrocarbons, C_nH_{2n+2}, similar to those obtained from wood. Owing to scarcity of material I could not study these compounds in detail, but characterised them in a general way. This experiment is, I believe, the first example of the formation, below 300° and in an aqueous medium, of a hydrocarbon from pure carbon. The experiment shows that pure carbon retains something of the organic structure of the bodies from which it was produced, and of which it represents a derivative defined by molecular condensation."

The experiments of Berthelot make it clear that his hydrogenation is only successful if carbon is treated, not as such, but in form of carbon compounds, such as wood or coal, or partially calcined charcoal. That coal, in spite of its high carbon percentage, does not contain free carbon, but only highly carbonaceous compounds, is evident from the fact that free carbon has never been observed on treatment with a variety of solvents. Further, coal, but not carbon, can be easily oxidised by means of ozone to compounds soluble in water. The possibility of Berthelot's intensive hydrogenation also supports this view. He was only able to hydrogenate carbon itself after converting it by oxidation into compounds. Hydrogenation offered no difficulties in the case of lightly calcined charcoal; this is easily understood, for by determining the electrical conductivity it has been found that charcoal must be heated to 700° before it loses sufficient hydrogen to form practically free carbon.[149]

(*b*) COMPARATIVE HYDROGENATION OF DIFFERENT COALS WITH HYDRIODIC ACID

The experiments of Berthelot were extended by Tropsch,[150] who investigated the hydrogenation of coals of different geological ages with the aid of hydriodic acid and phosphorus. He did not succeed in liquefying coal completely, but was able to show that the solubility of hydrogenated coal in chloroform was greater the younger the coal. This solubility in chloroform before and after hydrogenation is given in his laboratory notes as follows :

1. *Anthracite, Gottfried Wilhelm Colliery, Mausegatt Seam* (*Coke yield* 89 *per cent.*)

0·52 per cent. of chloroform extract was obtained from anthracite. Two grams of anthracite were mixed with 2 grams of red phosphorus, and were heated with 5 c.c. of hydriodic acid of spec. grav. 1·7 in a sealed tube for 12 hours to 200°. There was gas pressure in the cooled tube. The contents were diluted with water and filtered. A black, sandy product of the reaction remained on the filter which did not differ in appearance from anthracite; but the phosphorus had disappeared. The product was exhaustively extracted with chloroform, the extract was evaporated, and the residue heated in a vacuum on the water bath until the weight remained constant. 0·243 gram of extract was obtained, representing 12·1 per cent. of the weight of the anthracite.

2. *Semi-bituminous Coals (Esskohle), Rosenblumendelle Colliery, Girondelle Seam (Coke yield* 85 *per cent.)*

Chloroform extract 0·55 per cent.

Two tubes, each charged with 0·8 gram of coal, 0·8 gram of red phosphorus and 3 c.c. of hydriodic acid (1·7 spec. grav.), were heated to 200° for 12 hours and treated as described. The filter residue was washed with bisulphite to remove iodine. The product again did not much differ from the original coal; but the phosphorus had disappeared. Extraction of the dried residue with chloroform gave 0·2826 gram of extract, 17·7 per cent. of the coal.

3. *Fat Coal, Osterfeld Colliery, Albert Seam (Coke yield* 78 *per cent.)*

Chloroform extract 0·71 per cent.

The quantities used and treatment were as in 2. The product was a scaly black mass which was filtered, washed with bisulphite, dried and extracted with chloroform. The residue gave 0·8732 gram of extract, 54·6 per cent. of the coal.

4. *Gas Flame Coal, Bismarck Colliery (Coke Yield* 64 *per cent.)*

Chloroform extract 1·5 per cent.

Quantities used and treatment as in 2 and 3. After heating, the content caked; it was fused by means of warm water, powdered after cooling, washed with bisulphite and dried, giving 1·124 grams of extract, 70·3 per cent. of the coal.

By a modification of Berthelot's process, we succeeded eventually in obtaining liquids of hydrocarbon character by heating the coal with hydriodic acid and phosphorus to 280°. For 0·5 gram of extracted gas flame coal (Rheinbaben Pits), 1 gram of red phosphorus and 10 c.c. of hydriodic acid (spec. grav. 1·7) were used. On account of the high pressure we heated the sealed tube in a steel tube, half filled with water so as to equalise the pressure. After 6 hours the reaction was completed and the phosphorus had disappeared. Droplets of oil, coloured by free iodine, floated on the hydriodic acid. After adding sulphurous acid, and steam distillation, about 30 per cent. (of the weight of coal) of a colourless petroleum-like liquid was obtained; the non-volatile residue was a bituminous mass, mostly soluble in chloroform.

The discrepancy between our results and Berthelot's may be due to the different coals used, although other unknown factors may play a part in the reaction.

Brown Coal.—We then studied the action of hydriodic acid and phosphorus on brown coal. The brown coal came from the Riebeck Montan Works, and gave on carbonisation 48·3 per cent. of coke, 17·3 per cent. of tar and 10·0 per cent. of liquor, all related to coal dried at 105°. 18·2 per cent. of bitumen could be extracted from it with benzene. We used coal extracted with benzene under pressure.

Three tubes, each containing 1·2 grams of brown coal, 1·2 grams of red phosphorus and 5 c.c. of hydriodic acid (spec. grav. 1·7) were heated to 200° for 12 hours. The product of reaction was a soft brown mass, which on steam distillation gave a small amount of an oily liquid and some iodine. The distillation residue solidified to a brittle yellow-brown mass, from which chloroform extracted 2·17 grams, or 60 per cent., leaving a light yellow substance behind. The chloroform extract had about the same properties as the products obtained from bituminous coal under equal conditions.

The experiments described proved that hydrogenation of coal by means of hydriodic acid can be effected more easily the younger the coal. Hydrogenation is also successful with brown coal, and its resulting products resemble those from bituminous coal. Whilst at 200° the products obtained are bitumen-like, of high molecular weight and soluble in chloroform, working under special conditions and at higher temperatures yields liquids of petroleum character. Instead of hydriodic acid which Berthelot, and after him, Tropsch, had used in their hydrogenation experiments, Fischer and Schrader [151] first tried sodium formate, which, on heating, readily liberates hydrogen, and later a mixture of carbon monoxide and steam, which yields hydrogen at high temperature. Whether in these two cases hydrogen was actually liberated in the first instance, or whether formic acid, present or formed, acted as hydrogen carrier, remains as yet undecided.

(c) HYDROGENATION BY MEANS OF SODIUM FORMATE

The autoclaves used in the experiments with formate, and subsequently with carbon monoxide as hydrogenating agent, were of the type of the apparatus illustrated in Fig. 68. They were drilled out of a block of Siemens-Martin steel, and the same drill conveniently served later to remove the reaction products completely from the cylinder. The autoclave [152] was closed, as in previous cases, with the aid of a sleeve with left and right-handed thread pressing the head against the cylindrical body. The joint was made either by means of the conical seat shown in the diagram, or of a collar and groove into which a ring of copper or iron was fitted. For the purpose of charging the cylinder with compressed gases and releasing them, a valve was provided in the head. The spindle of this valve was made very long; the passage leading from the small opening in the interior of the autoclave could thus be kept very short, and any products condensed in this part would offer little resistance to the escape of the gases. The upper portion of the cylinder was filled up with an iron piston so as to place the heated reaction chamber in the lower part of the apparatus. Thus, the surface of the joint was not exposed to the high temperatures. A thermometer or thermo-couple was inserted into a hole drilled through the cover and wall of the cylinder. The dimensions adopted admitted of heating up to 450°, at pressures of several hundred atmospheres.

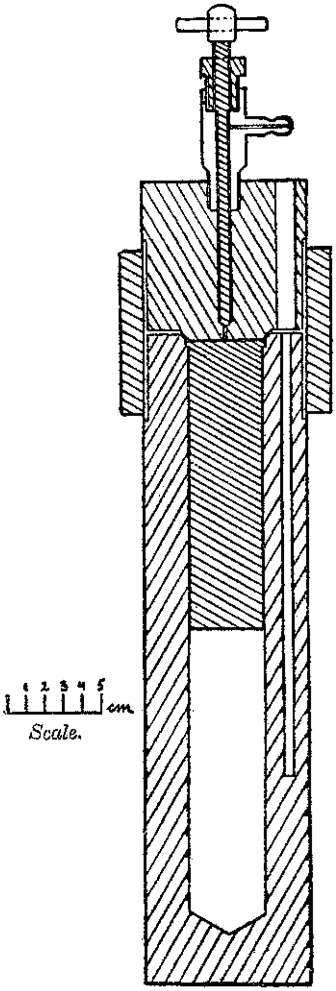

FIG. 68.

The electric furnace used for heating the autoclaves consisted of an iron tube wound with iron wire on asbestos lagging; the tube was placed vertically in a box filled with sand to the upper edge of the pipe. The lower edge of the sleeve of the autoclave rested on the furnace tube. Long wires connected the thermo-couple with a millivolt meter mounted in a shelter at a safe distance. Two blank experiments, made to show the behaviour of coal without an addition of formate, gave the results tabulated in Table LIII. Heated in the autoclave without water, the coal yielded 1·3 per cent. of ether-soluble products; with twice the weight of water, the yield rose to 10·1 per cent. of the coal substance.

Expt. 1, Table LIV, shows that in the presence of formate, but without water, the oil yield was 44 per cent. against 1·3 per cent. in Expt. 1, of Table LIII. With addition of water in the presence of formate in Expt. 2, Table LIV, no further increase in the yield was observed.

The material used was 4 grams of powdered Union briquettes, containing 3·16 grams of ash-free dry coal and 8 grams of sodium formate. In the experiment without water an intimate mixture was obtained by evaporating the formate solution stirred into the coal. The iron autoclave, 31 c.c. capacity, was heated to 400° for 3 hours, after which there was a moderate gas pressure. The oil formed was taken up with ether, and the solution which showed intense yellow-green fluorescence was dried with sodium sulphate, and evaporated. A mass of ointment consistency, reddish-brown in thin layers, and smelling of tar was obtained. The residue, insoluble in water and ether, was collected on a filter and dried at 105°. The residue from the experiment without water was brownish-black, and yielded, on heating, a further fairly large amount of pasty tar; whilst the residue from the experiments in presence of water was a light yellow-brown powder, and nothing but the ash appeared

Table LIII

Heating 4 grams brown coal * (Union briquettes) under pressure for three hours at 400° in autoclave of 31 c.c. capacity without addition of formate.

Expt. No.	Addition.	Ether soluble.		Residue. g.
		g.	% of ash-free dry coal.	
1	no water	0·04	**1·3**	2·04
2	8 c.c. ,,	0·32	**10·1**	1·73

Table LIV

Influence of Water $NaCHO_2$

4 grams brown coal (Union briquettes) and 8 grams sodium formate heated for 3 hours at 400° in autoclave of 31 c.c. capacity.†

Expt. No.	Ash-free dry coal used. g.	Water present. c.c.	Ether soluble.		Residue. g.
			g.	% of ash-free dry coal used.	
1	3·16	—	1·39	**44·0**	0·87
2	3·16	8	1·42	**44·9**	0·53

to remain. It still contained some organic substance, however, and when heated turned black and gave a little oil.

The hydrogenation experiments summarised in Table LV give a further proof that the presence of water does not increase the oil yield. The sodium formate employed in these experiments was not the pure salt used in the first series, but a 91·5 per cent. preparation. Here, again, the presence or absence of water made little difference in the oil yield.

The superior results realised with formate must, therefore, be ascribed not to the presence of the water, but to the hydrogen and carbon monoxide generated by the decomposition of formate, and compressed. This point will be discussed below. The favourable effect might be due to the slower decomposition of the formate under pressure, so that the nascent hydrogen is not liberated faster than it can combine with the coal.

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* The ether extract from untreated Rhenish brown coal was 1·6 per cent., the montan wax extracted with benzene in a Soxhlet was 3·5 per cent.

† This autoclave was not yet provided with the valve described on p. 179, hence the gases formed could not be measured.

TABLE LV

Hydrogenation of Brown Coal (Union Briquettes) with Commercial Sodium Formate (91·5 *per. cent.*)

75 grams brown coal heated to 400° with 75 or 150 grams sodium formate for 3 hours in autoclave of 255 c.c. capacity.

Expt. No.	Formate used. g.	Water used. c.c.	Gas formed. l.	CO_2 formed. l.	Oil volatile in steam. c.c.	Ether soluble part of solid product. g.	Ether soluble part of solid product. % of ash-free dry coal.	Carbonaceous residue. g.	Carbonaceous residue. % of dry coal used.	Formate left over g.
1	75	—	13·75	4·02	0·4	17·9	30·2	25·9	41·3	5·27
2	75	25	14·42	6·22	0·3	16·5	27·8	30·0	47·8	0·3
3	75	75	8·94	3·29	0·3	15·5	26·2	30·7	49·0	0·5
4	150	50	12·82	4·10	0·1	14·5	24·4	33·4	53·2	0·52
5 *	150	50	8·81	3·22	—	18·2	30·7	30·0	47·8	0·26

* Heated for 6 hours.

Influence of Temperature upon the Hydrogenation of Brown Coal

The experiments with brown coal (Union briquettes) at 400° were supplemented by two further trials at 350° and 450°, details of which are given in Table LVI.

TABLE LVI

4 grams brown coal, 8 grams sodium formate, 8 c.c. water heated for 3 hours in iron autoclave of 31 c.c. capacity.

Temp.	Ether-soluble. g.	Ether-soluble. % of ash-free dry coal.	Residue. Total. g.	Residue. Ash content. g.	Residue. Organic substance. g.	Residue. Organic substance. % of ash-free dry coal.
350°	0·91	28·8	1·27	0·25	1·02	32·28
400°	1·42	44·9	0·53	0·32	0·21	6·64
450°	0·25	7·9	0·59	0·21	0·38	12·02

The maximum yield of substances soluble in ether was therefore obtained at 400°; at 350°, the yield decreased to 64 per cent.; at 450°, to 18 per cent. of the maximum.

At 350°, the ether-soluble portion was a reddish-brown, highly viscid mass. The dark-brown coal residue intumesced strongly on heating, and liberated gas, but hardly any tar. At 400°, the ether extract was of pasty consistency,

TABLE LVII

Hydrogenation of Coals and Plant Materials with Sodium Formate

4 grams substance heated with 8 grams Na-formate and 8 c.c. H_2O for 3 hours to 400° in autoclave of 31 c.c. capacity.

No.	Substance.	Original coal.			Hydrogenated coal.					
					Sol. in ether.		Residue.			
									Organic substance.	
		Ash. %.	Moisture. %.	Org. subst. g.	g.	% of org. subst. used.	g.	Ash.* g.	g.	% of org. subst. used.
				Bituminous coal.						
1	Semi-coke from Lohberg gas flame coal	7·3	3·8	3·56	0·35	9·8	3·07	0·42	2·65	74·5
2	Anthracite: Lauerweg pit, Merl seam	5·4	0·7	3·76	0·06	1·6	3·89	0·30	3·59	95·5
3	Lean coal: Roland colly., Geitling seam	3·7	0·8	3·82	0·41	10·7	3·11	0·26	2·89	74·7
4	Fat coal: Osterfeld colly., Albert seam	4·3	0·8	3·80	0·35	9·2	2·86	0·25	2·61	68·7
5	Gas flame coal: Lohberg colly. near Dinslaken	8·9	3·3	3·52	1·38	39·2	2·04	0·39	1·65	46·9
6	Fat coal(spont.comb.): Trier colly. Radbod pit No. 14 seam	6·7	1·1	3·69	0·97	26·3	2·45	0·55	1·90	51·5
7	Cannel coal: Deutscher Kaiser colly. Rhein I pit, No. 5 seam	13·8	1·0	3·41	0·96	28·2	1·38	0·62	0·76	22·3
				Brown coal.						
8	Semi-coke from Saxon brown coal	19·5	6·3	2·97	0·96	32·4	2·03	0·94	1·09	36·7
9	Saxon brown coal: Riebeck Montan Works	12·9	9·8	3·09	1·34	43·4	0·74	0·59	0·15	4·9
10	Rosenthal coal: Preichow-Wellmitz	10·6	11·7	3·11	1·13	36·3	0·89	0·72	0·17	5·5
11	Rhenish brown coal: Union briquettes	4·6	16·3	3·16	1·42	45·0	0·53	0·32	0·21	6·6
12	Lignite: Bad Oybin, near Zittau	5·1	16·7	3·13	0·84	26·8	0·60	0·28	0·32	10·2
13	Ulmic acid from Rosenthal coal by NH_3	13·1	12·6	2·97	1·10	37·1	1·02	0·88	0·14	4·7
				Peat, Wood, Lignin, Cellulose, Sugar.						
14	Peat (Oldenburg)	1·2	13·1	3·43	0·83	24·2	0·59	0·43	0·16	4·7
15	Wood charcoal	5·3	6·0	3·55	0·21	5·9	3·27	0·44	2·83	79·7
16	Beech sawdust	0·9	9·9	3·57	0·70	19·6	0·26	0·18	0·08	2·2
17	Fir sawdust	0·3	9·6	3·60	0·70	19·5	0·26	0·17	0·09	2·5
18	Lignin (Goldschmidt)	3·3	12·6	3·36	0·75	22·3	1·67	0·48	1·19	35·4
19	Cellulose (Kahlbaum)	0·3	7·0	3·71	0·48	12·9	0·39	0·27	0·12	3·2
20	Cane sugar	—	—	4·00	0·69	17·3	0·44†	0·37	—	—

* The ash in the residue is not identical with the ash in the original sample, as it is partly converted into carbonate and has picked up some iron oxide from the autoclave.

† The residue is soluble in dilute hydrochloric acid except for a small amount of black carbonaceous powder.

and the coal residue on heating gave some oil. At 450°, very little oil, light reddish-brown, mobile and nearly clear, was produced; the black-brown residue did not intumesce, and gave no oil. Owing to the high temperature the bulk of the oil formed had been gasified. On opening the autoclave a large quantity of gas escaped, burning, as in other cases, with a luminous flame.

Comparative Hydrogenation of Coal, Peat, Wood, Lignin, Cellulose and Cane Sugar

After preliminary experiments as to the efficiency the method was applied to a series of fossil and younger plant materials; the results are tabulated in Table LVII.

All experiments were performed under identical conditions. In each case 4 grams of the material were heated together with 8 grams of sodium formate and 8 c.c. of water, to 400° for 3 hours, in the steel autoclave of 31 c.c. capacity. The reaction product was exhaustively extracted with ether. The solution, which always displayed a beautiful yellow-green fluorescence, was dried with sodium sulphate and evaporated; the quantity of residue so obtained is entered as "ether-soluble" in Table LVII. In Table LVIII the materials

TABLE LVIII

Materials arranged according to yield of Ether-soluble Products of Hydrogenation

(in per cent. of organic substance used)

Bituminous coal.		Brown coal.		Peat, wood, etc.	
Anthracite	1·6				
				Charcoal	5·9
Fat coal	9·2				
Semi-coke	9·8				
Lean coal	10·7				
				Cellulose	12·9
				Cane sugar	17·3
				Fir wood	19·5
				Beech wood	19·6
				Lignin	22·3
				Peat	24·2
Fat coal (liable to spont. ignition)	26·3				
		Lignite	26·8		
Cannel coal	28·2				
		Semi-coke	32·4		
		Rosenthal coal	36·3		
		Ulmic acids	37·1		
Gas flame coal	39·2				
		Saxon carbonising coal	43·4		
		Rhenish brown coal	45·0		

submitted to hydrogenation are arranged in the order of the percentage of ether-soluble obtained, grouped for coal, brown coal, peat, etc.

In the case of bituminous coal, the percentage of the ether-soluble products of hydrogenation under the conditions applied agrees approximately ("fat" coal and "lean" coal excepted) with the geological age, the youngest coal giving the highest yields. The yields of oil vary widely, from 1·6 per cent. in anthracite up to 39·2 per cent. in gas flame coal (ash-free, dry basis). It is noteworthy that the semi-coke of gas flame coal still gives 10 per cent. of ether-soluble products.

The figures of the two other groups come closer together. The yields from the brown coals range from 27 per cent. for lignite, to 45 per cent. for Rhenish brown coal. An examination of this group shows that the yields of ether-soluble products are not dependent upon the original bitumen content of the material. The Rhenish brown coal, which is poor in bitumen, gives higher values than the Saxon carbonising coal richer in bitumen. Hydrogenation evidently affects the non-bituminous constituents derived from lignin, and, therefore, of aromatic structure. That would also explain the resemblance in ultimate composition of the products in Table LIX to that of similarly hydrogenated primary tar phenols, which contained carbon 82·3 per cent. and hydrogen 8·9 per cent.

TABLE LIX

No. in Table LVII.	Ether soluble hydrogenation products from	C. %.	H. %.
5	Gas flame coal	86·7	7·6
11	Rhenish brown coal	86·0	8·6
—	Ulmic acid (at 200° from lignin) . . .	84·1	7·7
15	Beech wood	84·0	8·8
17	Lignin (pure)	85·0	8·2

To what extent the ether-soluble hydrogenation products contain, beside aromatic products derived from lignin, constituents of bitumen, that is, aliphatic compounds, has not yet been settled. In the case of cannel coal, a large portion of the bitumen seems to be gasified under our experimental conditions, owing to the prolonged heating to 400°; for this coal gave about 50 per cent. of gas and water as against 22 per cent. or less of volatile matter from other coals. Brown coals of various bitumen content do not exhibit such a difference.

The materials of the third group, mainly representing the plant skeleton, yield from 13 to 24 per cent. of ether-soluble hydrogenation products. Charcoal, having at the high temperature of its manufacture assumed a dense chemical structure, which is not prone to the re-formation of smaller fragments of its molecules, yields only 6 per cent. of ether-soluble. Of the other materials, cellulose gives the lowest yield, followed by cane sugar, pine wood and beech wood arranging themselves quite properly between cellulose and lignin, according to their composition. Peat, in which ulmic constituents are already concentrated, leads on to the brown coals, beginning with lignite at 27 per cent.

In an experiment made on a somewhat larger scale in an autoclave of 116 c.c. capacity, 20 grams of powdered Union briquettes were heated with 40 grams of sodium formate and 20 c.c. of water to 400° for 3 hours.

The solid products of the reaction consisted of an oil-impregnated mixture of white salt and a dark mass. The salt was dissolved in water, and gave 8·23 grams of formate. The residue was extracted with ether, and then with water.

The ether solution was dried with sodium sulphate, and the ether evaporated. The extract yielded on distillation the following fractions:

TABLE LX

Distillation of Ether-soluble Portion of Hydrogenated Brown Coal

Temperature	g.	%.	Property of distillate.
100–200°	0·28	4·1	mobile.
200–250°	0·64	9·4	limpid.
250–300°	0·71	10·4	thicker.
300–350°	3·31	48·6	thin paste.
Residue	1·87	27·5	solid, dark, opaque.
	6·81	100·0	

The distillates darkened on exposure to air; the fraction from 100° to 200° turned dark yellow; the higher fractions, red with a brownish tint. On allowing the residue in the flask to "sweat" for some time over a small flame, a gentle decomposition took place and lower-boiling products continued to condense in drops; this indicates a possibility of transforming at least part of the residue into oil.

The brown coal used contained 16·3 per cent. of moisture and 4·6 per cent. of ash; 6·8 grams of ether-soluble products were obtained, representing 43 per cent. of the ash-free, dry coal substance.

A larger quantity of brown coal was then hydrogenated in the same way, but instead of extracting it with ether, 30 grams of it were directly submitted to distillation in the aluminium retort (see p. 23), the temperature being raised very gradually.

The first drops of a rather mobile tar appeared at about 300°; the later portions were of pasty consistency. The temperature was finally kept at 500° until the end of the distillation. Most of the distilled water could be