

poured out from the receiver; the remainder was carefully boiled off so that tar could be weighed directly. Table LXI shows the tar yield.

TABLE LXI  
*Destructive Distillation of Hydrogenated Brown Coal*

Expt. No.	Coal from Expt. No. (Table LV).	Kind of distillation.	Product of distillation.	
			Tar % of ash-free dry coal.	Coke % of dry coal.
1	1	ordinary	27.3	—
2	2	"	26.6	—
3	3	"	23.2	48.8
4	3	"	23.0	50.3
5	3	"	26.6	—
6	4	steam	35.1	53.1
7	5	—	21.9	61.1
8	5	steam	30.0	51.3

These tar yields are very high. Some equal the yields obtainable by ether extraction, one (Expt. 6) even exceeding them by about 10 per cent. The preservative action of steam upon the tar yield (Expts. 6 and 8) is very marked. Incidentally steam counteracts the tendency to intumescence.

The tar of Expt. 1 was redistilled, yielding 1 c.c. of a rather mobile oil, 1 c.c. of a mass which congealed to ointment consistency and 1.7 grams of a thicker pasty residue of very high boiling point.

The residue was soluble in hot alcohol, with the exception of a little brown matter; on cooling, a large quantity of yellow scales separated out. The hydrogenation of diverse coals and plant products thus confirms the facts observed by various experimenters that the yield is inversely proportional to the geological age of the fuel treated. The ether-soluble reaction products are, throughout, substances of high boiling range. By distillation and partial decomposition they can be transformed into oily products, still of high boiling point. The properties of the undistilled ether-soluble products will be discussed later, in connection with the experiments of Bergius. It should be emphasised that hydrogenation of coal, by means of sodium formate under our experimental conditions, resulted in no case in a completely liquid product.

(d) HYDROGENATION BY MEANS OF CARBON MONOXIDE AND WATER

The following experiments were made in a steel autoclave of 118 c.c. capacity, with Rhenish brown coal (Union briquettes), as in the formate experiments. The results of the first series are given in Table LXII.

In the first experiments brown coal was heated by itself; in the second

experiment water was added to the extent of twice the weight of the coal. The yields, 4.8 per cent. and 7.6 per cent. of ether-soluble products, agree with the previous result with smaller quantities in that the presence of water favours the formation of ether-soluble matter.

In the presence of hydrogen (Expts. 3 and 4) yields were still greater, 11.1 and 13.5 per cent., and this time, again, the higher figure was obtained when water was present. Expt. 5 shows the effect of carbon monoxide upon brown coal in the absence of water, when 12.5 per cent. of ether-soluble products was obtained, approximately the same as with hydrogen. The hydrogenating effect of carbon monoxide in the absence of added water must be ascribed to the moisture in the coal, and to the water formed by decomposition.

TABLE LXII

*Comparative Hydrogenation of Rhenish Brown Coal (Union Briquettes) with Hydrogen and Carbon Monoxide.*

20 grams brown coal heated for 3 hours to 400° in iron autoclave of 118 c.c. capacity; gas pressure at room temperature.

Expt. No.	Added.		Ether-soluble reaction product.		Carbonaceous residue.				CO <sub>2</sub> formed. l.
	Gas.	H <sub>2</sub> O. c.c.	g.	% of ash-free dry coal.	g.	Ash. g.	Organic substance. g.	Solubility in pyridine. %	
1	—	—	0.75	4.8	10.25	0.17	10.08	little	1.67
2	—	40	1.20	7.6	8.87	0.79	8.08	„	1.29
3	H <sub>2</sub> at 130 atm.	—	1.75	11.1	8.51	1.03	7.48	much	2.34
4		40	2.13	13.5	8.13	0.98	7.15	45	1.20
5	CO at 140 atm.	—	1.98	12.5	9.39	1.33	8.06	much	5.38
6		40	4.7	29.7	6.31	0.94	5.37	53	7.02

The amount of ether-soluble products was very much greater, practically 30 per cent., when the coal was treated with carbon monoxide in the presence of water. We believe the superior efficiency of carbon monoxide to be due to the action of nascent hydrogen formed by the reaction between carbon monoxide and water vapour. More carbon dioxide was formed in this experiment than in any other.

Expt. 6 offers particular interest, and may be described in detail. Almost the whole of the water was, at the end of the experiment, found floating on the other products, and could be poured off. Below the water was a layer, yellow-brown in colour, and of the consistency of vaseline, with some dry, uncaked coal powder at the bottom.

These findings indicate that at 400° not only the water, but all the oily

constituents had been in the vapour phase, from which, on cooling, they were condensed above the coal.

The oily products, soluble in ether, were distilled with superheated steam in the aluminium retort. The fractions collected consisted of a brown mobile oil (15 per cent.), a yellow substance of butter consistency (40 per cent.) and a dark brown pitch-like but soft substance (12 per cent.); a dark varnish (32 per cent.) remained in the retort. On extracting 1 gram of the coal residue, insoluble in ether, with boiling pyridine, 0.53 gram was dissolved; a portion of the residue then remaining was dissolved in boiling dilute hydrochloric acid, leaving 0.37 gram of a black powder undissolved; the gas generated contained a good deal of sulphuretted hydrogen.

*Comparative Hydrogenation of Various Coals*

The comparative experiments were extended to the semi-coke from the Lohberg Colliery gas flame coal, to this coal itself and to a semi-coke from Saxon brown coal. The semi-cokes were examined because we assumed that the CO<sub>2</sub> found in the gas after heating was a reaction product of the CO, and not of the coal, and that the CO<sub>2</sub> was therefore a measure of the CO conversion. This assumption, it will be seen, proved erroneous in the case of the semi-coke from brown coal. The gas flame coal was selected for having given the highest yield by hydrogenation with formate.

With both semi-cokes, as Table LXIII shows, the treatment with hydrogen

TABLE LXIII

*Comparative Hydrogenation of different Coals with Hydrogen and Carbon Monoxide*

20 grams coal heated with 20 c.c. H<sub>2</sub>O for 3 hours to 400° in iron autoclave. Gas compressed to 90 atmos. at room temperature.

Expt. No.	Coal.	Gas.	Ash-free dry coal used. g.	Soluble in ether.		Carbonaceous residue.		Gas blown off.		
				g.	% of ash-free dry coal.	g.	% of dry coal.	l.	CO <sub>2</sub> in gas.	
									%.	l.
1 } 2 }	Semi-coke from bit. coal.	{ CO	17.22	0.10	0.58	18.14	94.58	9.80	36.6	3.59
		{ H <sub>2</sub>	17.22	0.04	0.23	18.09	94.32	7.00	4.4	0.31
3 } 4 }	Gas flame coal	{ CO	17.57	2.32	13.20	15.20	78.55	10.26	30.4	3.12
		{ H <sub>2</sub>	17.57	1.84	10.47	14.92	77.11	8.05	12.2	0.98
5 } 6 }	Semi-coke from brown coal	{ CO	14.84	3.32	22.37	12.53	66.86	14.80	44.2	6.54
		{ H <sub>2</sub>	14.84	0.22	1.48	16.15	86.18	8.16	11.4	0.93

was only slightly successful, and the yield of ether-soluble products from gas flame coal did not even come up to the tar yield in ordinary low-temperature carbonisation of the coal. The application of carbon monoxide, on the other hand, increased the quantities of ether-soluble products in all three cases. The superiority of CO was most striking in the case of brown coal semi-coke, where the amount of ether-soluble products increased fifteen times. When hydrogen was used, the quantity of carbon monoxide, which here must have been derived from the coal, was relatively high, but much smaller than that formed in the carbon monoxide experiments.

#### *Influence of Pressure*

In experiments made on the hydrogenation of Rhenish brown coal with carbon monoxide and with hydrogen, an increase of pressure, from 50 to 90 atm. (in the case of the carbon monoxide, from 90 to 150 atm.), was found to exert only a moderate influence on the yield of ether-soluble products. The figures are given in Table LXIV.

TABLE LXIV

#### *Influence of Pressure on Hydrogenation with Carbon Monoxide or Hydrogen*

20 grams Union briquettes and 20 c.c. water heated for 3 hours to 400° in iron autoclave of 118 c.c. capacity.

Expt. No.	Gas.	Pres- sure.  Atm.	Ether-soluble product.		Carbonaceous residue.		Gas blown off.		
			g.	% of ash-free dry coal.	g.	% of dry coal.	l.	CO <sub>2</sub> in gas.	
								%.	l.
1	CO	140	4.7	29.7	6.3	37.63	13.5	52.0	7.02
2	"	90	3.95	25.0	7.30	43.61	10.35	41.8	4.33
3	"	50	3.51	22.2	7.47	44.62	6.27	42.4	2.66
4	H <sub>2</sub>	90	3.45	21.8	6.72	40.14	8.00	22.8	1.82
5	"	50	2.76	17.4	7.53	44.98	5.13	28.8	1.48

The further study of this problem is important, particularly for the design of apparatus required for industrial hydrogenation.

#### *Influence of Temperature*

Comparative experiments on the influence of temperature were conducted at temperatures of 400°, 350°, and 450°. Details are given in Table LXV. The experiments "A" were made in an autoclave of steel; the experiments "B" in one of copper. The object was to study the influence of the material on the reaction between carbon monoxide and hydrogen, a factor to be discussed in the next section.

TABLE LXV

*Comparative Hydrogenation of Brown Coal (Union Briquettes) with Hydrogen and Carbon Monoxide at different Temperature*

20 grams brown coal and 20 c.c. water heated for 3 hours. H<sub>2</sub> and CO compressed to 90-100 atmos. at room temperature.

Expt. No.	Temp. ° C.	Gas.	Ash-free dry coal used. g.	Ether-soluble product.		Carbonaceous residue.			Gas blown off.			
				g.	% of ash-free dry coal.	g.	% of dry coal used.	Solubility in pyridine.	I.	CO <sub>2</sub> in gas.		
										%.	I.	
A. In iron autoclave * (capacity 118 c.c.).												
1	350	H <sub>2</sub>	15.82	2.06	13.0	9.71	58.0	a little higher than at 400° and 450°.	8.0	18.3	1.47	
2	350	CO	15.82	4.07	25.7	7.87	47.0	small	9.2	38.2	3.52	
3	400	H <sub>2</sub>	15.82	3.45	21.8	6.72	40.1	very small	8.0	22.8	1.82	
4	400	CO	15.82	3.95	25.0	7.30	43.6	small	10.4	41.8	4.33	
5	450	H <sub>2</sub>	15.82	4.05	25.6	5.73	34.2	very small	7.4	23.0	1.70	
6	450	CO	15.82	4.48	23.3	5.02	30.0	small	10.9	57.5	6.29	
B. In copper autoclave * (capacity 130 c.c.).												
1	350	H <sub>2</sub>	15.82	3.15	19.9	8.85	52.9	about $\frac{1}{2}$	8.8	18.8	1.65	
2	350	CO	15.82	3.83	24.2	8.30	49.6	very small	11.5	39.6	4.55	
3	400	H <sub>2</sub>	15.82	3.30	20.9	7.25	43.3	" "	8.1	13.3	1.08	
4	400	CO	15.82	3.67	23.2	7.40	44.2	" "	10.5	39.6	4.16	

\* A steel autoclave completely lined with copper.

Table LXV (A) shows that the use of carbon monoxide resulted in much higher yields of ether-soluble products than the use of hydrogen at the same temperatures. A comparison of the values obtained at 400° with those of Expts. 4 and 6 of Table LXII shows that the yield with hydrogen was here exceptionally high in spite of the lower pressure (90 atm. against 130 atm.), being 21.8 per cent. against 13.5 per cent.; the yield with carbon monoxide increased, with the increase in pressure, from 25.0 to 29.7 per cent. The smaller amounts of solid coal residue found in the CO experiments corresponded to the greater yield of ether-soluble products; this residue differed from that of the experiments with hydrogen by being soluble in pyridine to the extent of one-third of the substance.

The figures of Table LXV (B) are surprising in that the yields realised at 350° were nearly as high as those obtained at 400°; in the carbon monoxide experiment a slightly higher yield was actually obtained at 350°. Here,

again, the values for carbon monoxide are higher than those for hydrogen. No experiments were made at 450° because the copper autoclave developed leakage at the higher temperature owing to the softening of the copper.

The influence of temperature was further studied in a series of experiments made with carbon monoxide at a pressure of 140 atm. between 300° and 400° (Table LXVI).

TABLE LXVI

*Hydrogenation of Brown Coal with Carbon Monoxide at different Temperatures*

20 grams Union briquettes, 40 c.c. H<sub>2</sub>O, CO under 140 atmos. pressure heated for 3 hours in iron autoclave of 118 c.c. capacity.

Expt. No.	Temp. ° C.	Ether-soluble reaction product.		Carbonaceous residue.				CO <sub>2</sub> formed. l.
		g.	% of ash-free dry coal used.	g.	Ash. g.	Organic subst. g.	Solubility in pyridine. %.	
1	300	1.4	8.8	11.2	0.8	10.4	high	4.14
2	350	3.1	19.6	9.2	1.0	8.2	"	3.60
3	375	4.1	25.9	7.7	1.1	6.6	"	7.36
4	400	4.7	29.7	6.3	0.9	5.4	53	7.02

The yield of ether-soluble products increased considerably with the rise of temperature, from 9 per cent. at 300° to 30 per cent. at 400°.

*Influence of the Autoclave Material*

Iron is a powerful catalyst in the conversion of carbon monoxide into carbon dioxide in the water-gas reaction. When this fact is borne in mind, it may be presumed that in the hydrogenation in the autoclave at least part of the active hydrogen will come from the iron wall and another part is generated by the contact of the carbon monoxide with the coal. As far as nascent hydrogen is required by the coal, the first part would be lost. If this assumption be correct, the oil yield should be improved by substituting copper for the iron of the autoclave wall, experiments having demonstrated that by heating carbon monoxide with water for 3 hours to 400° only a little carbon dioxide was formed. Hence the parallel tests in iron and copper vessels were made (Table LXV, A and B), the results of which failed to furnish a definite confirmation of our assumption. At 350°, the copper autoclave gave a notably better yield of ether-soluble products than the iron autoclave, *i.e.*, 24.4 per cent. against 17.1 per cent.; at 400°, however, the relations were reversed, *i.e.*, 23.2 per cent. and 25 per cent.

In two further experiments made with semi-coke from brown coal, the copper autoclave proved less effective. The corresponding experiments with hydrogen gave very small quantities of ether-soluble products in both autoclaves.

To account for the failure of the hoped-for effect, it might be suggested that the carbon monoxide present was so far in excess of the proportion of the coal which could be hydrogenated that a fraction of it was quite sufficient

TABLE LXVII

*Comparative Hydrogenation of Semi-coke from Saxon Brown Coal with Carbon Monoxide and Hydrogen in Copper and Iron Autoclaves at 400°*

Expt. No.	Gas.	Initial pressure.	Auto-clave.	Ash-free dry coal used.	Ether-soluble product.		Carbonaceous residue.		Gas blown off.		
					g.	% of ash-free dry coal.	g.	% of dry coal.	CO <sub>2</sub> in gas.		
		Atm.							g.	l.	%.
1	CO	128	Fe	14.84	3.32	22.37	12.53	66.86	14.80	44.2	6.54
2	CO	126	Cu	14.84	3.12	21.02	12.96	69.16	15.91	43.6	6.94
3	H <sub>2</sub>	90	Fe	14.84	0.22	1.43	16.15	86.18	8.16	11.4	0.93
4	H <sub>2</sub>	90	Cu	14.84	0.30	2.02	15.91	84.90	8.41	15.4	1.30

for the possible hydrogenation. In that case the expected difference between the metals would only show itself by the reduction of the quantity of carbon monoxide to the minimum required. That coal promotes the catalytic oxidation of carbon monoxide very strongly is known by the carbon monoxide experiments made in the copper autoclave, in which the proportion of carbon dioxide, after deducting that derived from the coal, as found in the hydrogen experiment, was always very considerable. For commercial work iron autoclaves would then appear to be quite suitable.

#### *Influence of Water*

Table LXVIII shows that the presence of water causes an increase in the yield of ether-soluble products. This increase was small, yet distinct, in Expts. 1 and 2 of Table LXII, made in the absence of hydrogen or carbon monoxide, and also in the hydrogen Expts. 3 and 4. The effect was very marked in the experiment with carbon monoxide, in which the hydrogenation is closely associated with the chemical interaction between carbon monoxide and water. A small series of experiments was undertaken in order to ascertain the influence of varying quantities of water on the yields of ether-soluble products in the hydrogenation with carbon monoxide. For this purpose

## CONVERSION OF COAL INTO OILS

20 grams of Rhenish brown coal and carbon monoxide were heated under pressure with 10, 20, and 40 c.c. of water for 3 hours to 400°, in a copper autoclave.

TABLE LXVIII

20 grams Union briquettes, increasing quantity of water, CO under 140 atmos. pressure, heated for 3 hours to 400° in copper autoclave of 130 c.c. capacity.

Expt. No.	Ash-free dry coal used. g.	Water used. c.c.	Ether-soluble product.		Carbonaceous residue.			Gas blown off.		
			g.	% of ash-free dry coal.	g.	% of dry coal.	Solubility in pyridine.	l.	CO <sub>2</sub> in gas.	
									%.	l.
1	15.82	10	2.20	13.9	6.92	41.3	about $\frac{1}{3}$	17.5	22.8	3.99
2	15.82	20	4.65	29.4	7.02	41.9	$\frac{1}{3}$	17.5	35.4	6.2
3	15.82	40	5.56	35.1	6.71	40.1	almost completely	11.58	44.4	5.1

With increasing proportions of water the yield of ether-soluble products was observed to improve considerably.

Hydrogenation of coal by means of carbon monoxide and water vapour becomes more complete as the pressure of the carbon monoxide, the quantity of water, and the temperature are increased. The temperature rise should probably be limited to 500°, in view of the instability of the products. Better results could certainly be anticipated if the hydrogenation were performed in an apparatus admitting of a circulation of the gas, and of a continuous removal of the volatile products. Owing probably to the liberation of nascent hydrogen, hydrogenation is, under otherwise equal conditions, more satisfactory with carbon monoxide and water than with molecular hydrogen, but less complete than with the use of an equivalent amount of sodium formate, as Table LXIX shows.

TABLE LXIX

*Ether-soluble Substance formed by Hydrogenation at 400°*

Per cent. of organic substance used.

	With carbon monoxide. %.	With sodium formate. %.
Semi-coke from bituminous coal . . . . .	0.6	10
Gas-flame coal . . . . .	13	39
Semi-coke from brown coal . . . . .	22	32
Rhenish brown coal . . . . .	35	45

As in the experiments with sodium formate, relatively small quantities of oily products are obtained under our conditions of working. The bulk of the



product is soluble in ether, but of pasty consistency at ordinary temperature. The residue of the ether extract is frequently soluble in pyridine.

(e) HYDROGENATION WITH SODIUM CARBONATE AND HYDROGEN

Subsequently to the hydrogenation experiments described, H. Schrader<sup>153</sup> observed that formate is produced when sodium carbonate solutions are heated with hydrogen under pressure. On my suggestion, A. Jaeger\* investigated whether solutions of sodium carbonate and hydrogen under pressure could be substituted for the finished formate or for  $\text{CO} + \text{H}_2\text{O}$ .

The Rhenish brown coal (Union briquettes) used in these experiments contained 1.2 per cent. of ether-soluble constituents. 25 grams of the briquettes were heated with 100 c.c. of *N*-sodium bicarbonate solution for 2 hours to  $400^\circ$ , in a high-pressure autoclave at various hydrogen pressures, with the results given in Table LXX.

TABLE LXX.

Expt. No.	Initial hydrogen pressure.	Ether-soluble product obtained % of ash-free dry coal.
1	20	10
2	60	19
3	100	36

As the initial hydrogen pressure was increased, the percentage of ether-soluble product increased in a marked degree, and hydrogenation became more complete. The coal residue was caked, indicating changes of the ether-soluble portion.

In order to ascertain whether the partial conversion of sodium bicarbonate into formate was really essential for hydrogenation, no bicarbonate was used in the next experiment, 25 grams of powdered brown coal and 100 c.c. of water being heated to  $400^\circ$  for 2 hours at a hydrogen pressure of 100 atm.; the ether-soluble diminished from 36 to 10.8 per cent. The water was then omitted; 25 grams of the powdered coal were carefully ground up with 10 grams of solid bicarbonate and heated for 2 hours to  $400^\circ$  at a hydrogen pressure of 90 atm.; the quantity of ether-soluble constituents then amounted to 8.4 per cent. only, instead of 36 per cent. in the presence of water. Neither the bicarbonate nor the water can therefore be dispensed with. In the last experiment, the mixture of brown coal and bicarbonate was probably not so homogeneous as if an aqueous solution had been used. Whether or not the coal remained at the high temperature of  $400^\circ$  in contact with liquid

\* Unpublished.

water cannot definitely be stated, but it is not impossible, since the critical temperature of the solution is higher than that of pure water.

As regards the influence of temperature, a repetition of Expt. 3, of Table LXX, at 350° instead of 400°, yielded only 20 per cent. of ether-soluble products instead of 36 per cent. A continuation of the experiment for two more hours at 350°, with a fresh charge of hydrogen, did not give more than 26 per cent., nor was a temperature of 450° more favourable; at 450° the yield was 21.6 per cent. These results agree well with the observations made by Franz Fischer and H. Schrader, who, as in other experiments described in this section, found 400° the most suitable temperature for the hydrogenation of Rhenish brown coal. It has been pointed out that the coal was found to have caked considerably in the autoclave. The action of the hydrogen would then have been more impeded as the coal surface was reduced. Some further experiments were therefore made in a shaking autoclave.<sup>154</sup> This autoclave admitted of maximum pressures of 150 atm. only, and the temperature could not, therefore, be raised to 400° in the presence of water. When the *N*-sodium bicarbonate solution was shaken with hydrogen at 60 atm., and at temperatures of 200° and 300°, some formic acid (formate) was always found to have been produced. Small quantities of formate were obtained even when starting with solid bicarbonate.

The formation of formic acid having been established, the experiments of Table LXXI were made.

TABLE LXXI

*Hydrogenation of Brown Coal with Hydrogen and Sodium Bicarbonate Solution in a shaking autoclave at 300°*

Used: 10 grams powdered brown coal, 50 c.c. *N*-NaHCO<sub>3</sub> solution, 30 atmos. hydrogen.

Expt. No.	Initial hydrogen pressure.	Duration of expt. hours.	Ether-soluble obtained % of ash-free dry coal.
1	30	2	8.4
2	60	4	12.6

These experiments demonstrate that hydrogenation takes place at 300°, and at relatively low hydrogen pressure. The hydrogenation would no doubt be much improved if shaking apparatus could be designed to work at 400° and higher hydrogen pressures.

The use of solutions of sodium bicarbonate in the presence of compressed hydrogen offers a decided advantage over that of sodium formate, or of CO + H<sub>2</sub>O, as practically nothing but hydrogen is consumed, the bicarbonate or the formate produced during the reaction acting merely as carrier

or catalyst. The use of hydrogen alone (Bergius process) without catalyst gave much poorer results (11 per cent.) instead of 36 per cent. of ether-soluble products. Since  $\text{CO} + \text{H}_2\text{O}$  by itself, as well as  $\text{H}_2 + \text{NaHCO}_3$  solution, are suitable for hydrogenation, it may be supposed that the cheaper water-gas might be substituted for hydrogen when sodium bicarbonate is applied.

It may finally be assumed that hydrogenation with compressed hydrogen without bicarbonate solution might be improved by mixing the hydrogen (or the water gas) with carbon dioxide, which together with hydrogen will form the reactive formic acid as an intermediate product. This supposition should be put to the experimental tests, and the hydrogenation experiments outlined in this section should be carried further for the purpose of ascertaining whether the bulk of coal can be really converted into oil by any of these methods.

The Bergius hydrogenation experiments, which will be further discussed below, are made with molecular hydrogen. The material (gas flame coal) is very finely ground and stirred with half its weight of middle oil from coal tar. Middle oil being a good solvent, it is quite possible that products soluble in ether and in pyridine are also formed in the Bergius treatment, but that they remain dissolved in the oil from which they might be recovered on distillation. The publications concerning the Bergius coal liquefaction do not mention a test of this kind. If the supposition is correct, his results would not prove complete liquefaction of coal any more than ours do; his liquefaction would be apparent, and of the nature of a solution process.

#### (f) DESTRUCTIVE DISTILLATION OF BITUMINOUS COAL AT HIGHER HYDROGEN PRESSURES

The experiments of Franz Fischer and H. Schrader were preceded by those of Franz Fischer and Konrad Keller<sup>155</sup> towards the end of 1914. They were made in a high-pressure furnace,<sup>156</sup> suitable for temperatures of  $1000^\circ$  and pressures of 200 atm. The coal used was a fat coal (with 79 per cent. coke yield), geologically older, and hence, as the subsequent researches established, not particularly suitable for hydrogenation. These experiments, which must now be considered for various reasons as superseded, brought out two facts: First, that the tar or oil yields at high hydrogen pressure are several times greater than those obtained at ordinary pressure; and secondly, that, even at  $500^\circ$ , the amount of coke residue is inversely proportional to the hydrogen pressure, so that with rising hydrogen pressure the formation of volatile constituents, and mainly of methane, increases. This is in agreement with the experiments of Pring and Fairlie,<sup>157</sup> who showed that at high hydrogen pressure and high temperature carbon is volatilised as methane. In a prolonged experiment the coke obtained represented only 33 per cent. of the coal, and the tar and ammonia liquor, 30 per cent. The small quantities

experimented with did not permit of an accurate separation of tar and liquor; but the water was estimated as one-third of the mixture, making the tar yield about 20 per cent. as against 3 or 4 per cent. in ordinary distillation of the same coal. The experiments were arranged so as to allow the products formed by the action of hydrogen to distil at once from the hot zone of the furnace into the coldest portions and to escape further decomposition. The temperature measurements were not exact, and the results were of little more than preliminary character. Yet they establish qualitatively the possibility of a hydrogenation of coal to oils.

These experiments were not continued, as they did not seem to promise the possibility of the production of oil from coal on a large scale.

#### (g) HYDROGENATION OF COAL ACCORDING TO BERGIUS AT HIGH HYDROGEN PRESSURE

Nearly a year after the conclusion of Keller's experiments, the patents of Bergius and Billwiller were published. Although application for these had preceded Keller's work, their substance had, of course, remained unknown. An extract of these specifications is given below.

*Bergius' Brit. Pat. No. 18,232 of 1st August, 1914 (date of application in Germany, 8th August, 1914).*

"This invention relates to the treatment of coal and other solid carbonaceous material of vegetable origin formed by natural or artificial carbonisation to produce directly by chemical conversion of the carbonaceous material liquid hydrocarbons or hydrocarbons of a low melting point, and consists in subjecting the coal or the like to the action of hydrogen at pressures above 10 atmospheres, and preferably exceeding 100 atmospheres, and at an elevated temperature less than 600°. In these conditions the hydrogen reacts directly with the coal, which is transformed without destructive distillation and substantially without formation of uncondensable gases into valuable hydrocarbons which are either liquid at ordinary temperatures and pressures or which have a low melting point. The working temperature is preferably between 300° and 500° C. In place of hydrogen, gases containing free hydrogen, such as water gas, could of course also be used, or substances or mixtures which give off hydrogen, such as calcium hydride,  $\text{CaH}_2$ , the hydrogen in all cases, however, coming from a source other than the carbonaceous matter under treatment. . . .

"It is advisable to work in the presence of a solvent for the products formed during reaction, a suitable diluting medium being for instance petroleum distillates. The nitrogen of the coal is obtained in the form of ammonia in the reaction vessel.

"This hydrogenation may be combined with a carbonisation process by subjecting wood or peat or other vegetable matter to heat treatment in a hydrogen-containing atmosphere at high pressure; the hydrogen being supplied from a source different from the wood, peat, etc., under treatment, the working conditions being such that not more than very small quantities of hydrogen which are absolutely insufficient for the hydrogenation aimed at could be formed from the wood, peat, etc., under reaction.

"The products produced in the hydrogenation process consist mainly of hydrocarbons having different boiling points and which resemble chemically the mineral-oil hydrocarbons. By far the greater part of these substances is liquid at an ordinary temperature. The ash of the coal remains in the vessel as solid residues. The nitrogen of the coal escapes as ammonia with the hydrocarbons which have been distilled. The separation of the resulting condensed products can be effected in the usual manner by fractional distillation.

*Example*

"The process could be carried out for instance in the following manner: coal powder is introduced into a vessel capable of withstanding pressure, such as a steel cylinder, hydrogen at 200 atmospheres pressure is forced into it, and the whole is heated to 400° by a suitable furnace. After 15 hours, the vessel is opened, and the products generated condensed. The result is that more than half the coal is converted into a liquid substance. The unused hydrogen is recovered and used again, and the solid residues may be treated again in a similar way.

"Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

"1. A process for manufacturing liquid or easily fusible hydrocarbon compounds from coal or other solid substances produced by natural or artificial carbonisation of vegetable matter, consisting in subjecting the said substances to the action of hydrogen at a pressure of more than 10 atmospheres and at an elevated temperature not exceeding 600° C.

"2. A process as set forth in Claim 1 in which the reaction is carried out at a temperature of from 300° to 500° C. and at a pressure of more than 100 atmospheres.

"3. A process as set forth in Claims 1 and 2, in which the reaction with hydrogen is allowed to take place during the carbonising of vegetable substances.

"4. A process as set forth in Claims 1 to 3, in which the reaction is carried out in the presence of a solvent, such as petroleum distillates, for reaction products formed by the process.

"5. The process of treating coal and other products of carbonisation of vegetable matter substantially as described."

The following description of a hydrogenation experiment made in the Bergin Works at Rheinau, near Mannheim, is given by Bruylants<sup>134</sup>:— 200 grams of gas coal were mixed with 100 grams of middle oil and 200 grams of pebbles as agitating elements, in an autoclave-agitator at a hydrogen pressure of 100 atm., and slowly heated to 434°; the pressure rose to 232 atm. The temperature was kept constant at 434° for 2 hours, during which time the pressure dropped to 177 atm. After cooling, the pressure was 65 atm.

For a second experiment, the hydrogen was put under a pressure of 80 atm.; the temperature was again raised to 434° within 1 hour, during which the pressure rose to 205 atm. After maintaining the temperature at 434° for 2 hours, the pressure had dropped to 101 atm.; after cooling, the gauge indicated 68 atm. The loss of pressure in the first experiment was 35 atm., that in the second, 12 atm.; total 47 atm. The capacity of the autoclave being 5 litres, this would represent a reduction of gas volume by about 2.5 cb.m. at ordinary pressure, which may be caused by the formation of solid, liquid and gaseous compounds at the expense of the coal. The composition of the gas after the first reaction was: hydrogen 68.4 per cent., saturated gaseous hydrocarbons 13.5 per cent.; further details are not given. The composition of the gas after the second reaction was 75.2 per cent. and 11.7 per cent. respectively. On opening the autoclave, a perfectly homogeneous black tarry fluid of syrup consistency was found; it was free from solid particles, apart from the mineral constituents suspended in it.

As to the conclusion drawn, that the coal tar had been completely converted into a liquid fuel, reference should be made to the comment made at the end of the section on hydrogenation of coal by means of carbon monoxide. The fact that, in spite of the addition to the coal of 50 per cent. of thin middle oil, the product was of syrup consistency, indicates decidedly that in this experiment as in the other case the whole of the coal had by no means been transformed into a liquid fuel; but that it had been sufficiently modified, though remaining solid at the ordinary temperature, to become soluble in the oil. This interpretation might be tested by examining the residue remaining after distilling the middle oil off, when probably a pitch-like substance would be obtained. If that is so, the result of the experiment would be in accord with those obtained by hydrogenation with hydriodic acid, with sodium formate, and with carbon monoxide plus steam.

Summing up, hydrogenation of coal yields a small portion of oily products and a large portion of solid products which are soluble in certain solvents. If these solvents are added to the coal beforehand, it appears to be liquefied, though in reality it is only rendered soluble to a large extent. The fine grinding of the coal and its suspension in oil is mainly intended to facilitate charging into the autoclave by pumps. If after every charge, so as to save the supply of fresh oil, one-third were distilled off and used as

medium for suspending a new lot of coal, the total distillation residues would represent a pitch- or asphalt-like product rather than an oil. Nevertheless, the possibility of converting these products by continued hydrogenation into oily materials is not excluded. Whether this can be effected on economical lines is another question which does not come within the scope of this book. Even so, hydrogenation can at best produce high-boiling oils and only minor proportions of low-boiling ones. The size of the molecules which go to build up the coal substance must be very large in all the various types, as is evidenced by its insolubility in most solvents. For that reason, the products of the addition of hydrogen to these molecules will, on the whole, be high-boiling oils, even if a partial scission of molecules takes place.