PROBLEMS IN THE CHEMISTRY OF COAL[1]

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This lecture will deal with the major problems in the chemistry of coal, taking up first its constitution and formation, passing thence to a discussion of other problems in coal chemistry and their bearing upon a chemical industry based upon coal.

From microscopic studies of coal and observations of the processes of decomposition and transformation which occur in decayed organisms in nature, we obtain a clue to the basic substances in the formation of coal. Such studies teach us that coal was formed from the lignified portions of higher plants, pollens, spores and the flora and fauna of plankton, or, chemically speaking, from woody substances, fats, albumins, resins, and waxes. We differentiate these coals as *humus coal* and *sapropel* coal, depending on whether the raw material from which they were produced was wood or a material rich in fats and albumin. Often both forms occur in alternate layers. So-called striated coal is well-known, i.e. a hard coal made up of bright coal, called humus coal; and dull coal called sapropel coal, with a kind of mineral charcoal called mother of coal. Recently Stopes and Wheeler have introduced the nomenclature Clarain for the bright coal, Durain for the dull coal, and Fusain for the mother of coal. According to Thiessen of the Bureau of Mines what was originally called Vitrain by them and was said to have no structure does actually possess structure and is identical with Clarain. Thiessen calls Clarain, which has a predominantly woody structure, anthraxylon, and Durain, which is a mixture of different materials, he calls attritus.

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Little or nothing is known of the chemical structure of sapropel coal; consequently my remarks will be confined chiefly to the humus coals which are much more abundant than the sapropel coals.

According to Fuchs the woody substance of the kinds of coal-forming plants which have been studied show the same composition, qualitatively, at least, i.e. they consist essentially of cellulose and varieties of lignins. This warrants the certain conclusion that the substances in question participated in the formation of coal throughout all geological epochs. Consequently hard coals and brown coals are not, as was assumed for a time, fundamentally different formations conditioned by the difference in their raw materials, but rather represent different stages of a transformation process starting in the decayed plants. Of course it should not be maintained that our hard coals of today were once exactly like the brown coal of today. The degree of similarity existing between them would vary on account of the fact that the raw materials were not quantitatively, but merely qualitatively alike.

The organic material in humus coal consists essentially of the actual humus, forming the substance of the coal, and the bitumen. These two constituents can be separated by various solvents. Benzol and pyridine should be mentioned particularly as useful when the intention is to make a thorough study of the bitumen instead of limiting the study to a determination of the yields of the extraction.

Three characteristic stages are to be distinguished in the humus substance. Peat and the young brown coals have an acid character due to the presence of humic acids and dissolve in cold alkali with a dark coloration. This property is no longer found in the second stage represented by the older brown coals. The brown coal humins however, which are to be conceived of as anhydrides and lactones of humic acids can be dissolved by boiling in lye and so reconverted to humic acids. On the other hand, when heated to 250 degrees, humic acids are converted into the humins which are insoluble in alkali. The humus portion in hard coals, that is to say the third stage, is also insoluble in boiling alkali. However, according to Fischer and Schrader it can be converted into substances resembling humic acids by auto-oxidation at higher temperatures or by oxidation under pressure in the presence of alkali or by moderate oxidation with hydrogen peroxide. This indicates the genetic relation of hard coal humus to the humic acids and humins of brown coal from which the humus substance is formed as a result of a more extensive condensation and polymerization process, with carbon dioxide, and water, and probably methane also, splitting off.

The easy interconvertibility of the three characteristic stages of the humus substance is itself an indication that no fundamental alteration in the chemical structure can have taken place during the transitions of the humic acids first into humins and finally into the substance of hard coal. Fischer and Schrader have now shown that the decomposition of coal by pressure-oxidation with air in the presence of soda solution runs in the same way in all humus coals.

First there are obtained dark solutions of products similar to humic acids which, with progressive oxidation, are then broken down to lighter acids with smaller molecular weights. To be sure, it is not yet possible to isolate individual chemical acids from these but when the decomposition is carried further aromatic carboxylic acids and lower aliphatic acids are formed. Under pressure-oxidation one of the vegetable substances, lignin, behaves like the humus substances while the cellulose reacts quite differently. The conclusions with respect to the formation of coal which Fischer and Schrader have drawn on the basis of these discoveries are yet to be discussed. The fact that at least one-third of the unidentified acid mixture consists of benzol derivatives, can be demonstrated by the fact that it is convertible into aromatic carboxylic acids by heating under pressure, benzoic acid and isophthallic acid in particular being obtained in this way (table A).

Since there is a further destruction of the aromatic carboxylic acids under the conditions of pressure oxidation the yields obtained by Fischer and Schrader are to be considered minimum and there can be no doubt that coal is essentially aromatic in structure.

By the use of alkaline permanganate solution to break down the coal substance which had previously been freed from bitumen by extraction, Bone and Quarendon have reached similar conclusions within the last few years. They also obtained large quantities of acids, probably aromatic, which they were unable to identify. Definite aromatic carboxylic acids, particularly mellitic acid, could however only be obtained in amounts equal to 0.8 to 1.6 per cent of the coal used.

TABLE A

Oxidation under pressure from cellulose, lignin, brown coal and bituminous coal

	VOLATILE ACIDS	NON-VOLATILE ACIDS	RECOGNIZED HITHERTO	
			Quantity	Acid
	per cent	*per cent*	*per cent*	
Cellulose	ca. 28	ca. 14	0.7	Fumaric Succinic
			5.0	Oxalic
Lignin	ca. 11	ca. 34	>0.3	Mellitic
			3.7	Benzene pentacarbon
			7.2	Oxalic
Brown coal	ca. 14	ca. 34		Mellitic
				Benzene pentacarbon
				Pyromellitic
				o-phthalic
				Benzoic
Bituminous coal	Not estimated	ca. 30	0.58	Mellitic Benzene pentacarbon
			0.93	Trimesinic Phthalic
			0.33	i-phthalic
			0.35	Benzoic
			11 after heating under pressure	Benzoic and phthalic

Under pressure-oxidation, cellulose behaves quite differently from coal and lignin. No humic acids are formed as intermediate products and, when oxidation is pushed farther, large quantities of aliphatic acids are obtained. In particular acetic acid, oxalic acid and small quantities of fumaric and succinic acids have been identified. On heating under pressure the non-volatile and unidentified acids yielded furan. It is noteworthy that, under the same conditions, no furan can be obtained from coal and lignin and consequently the old view as to the furan structure of coal has no justification. The detection of furan derivatives among the products of pressure-oxidation of cellulose proves also that the furan ring is fairly stable under this method of decomposition and that, if furan derivatives resulted from the pressure oxidation of coal, they would surely have been observed.

Not only is the aromatic structure of the humus portion of coal indicated by the results of the break-down by oxidation; it is confirmed also by the character of the products obtained from coal by Bergius and Billwiller on treating it with hydrogen under pressure at temperatures around 450 degrees.

Working with Ter-Nedden, I was able to show that, in addition to 20 per cent phenol, cyclic hydrocarbons were present in the products obtained by Fischer and Frey from the high pressure hydrogenation of lignite semi-coke. Kling and Florentin obtained benzol derivatives almost exclusively in the pressure-hydrogenation of hard coal from lower Silesia.

As we have seen, all decomposition reactions which have been undertaken with the humus substances of lignite and anthracite coal pass through the humic acids. On the other hand these represent a conversion product of plant substances in the process of decay. The humic acids therefore point the way to a better knowledge of the constitution and formation of coal. In many reactions the humic acids possess quite the character of phenol derivatives. Nitrophenol-like substances result on treatment with nitric acid. Schellenberg and I succeeded in isolating a quantity of a well crystallized trinitrodioxybenzol of unknown constitution, equal to 5 per cent of the humic acid used.

In recent years, Francis and Wheeler have likewise obtained nitrophenol-like substances, which they call regenerated ulmins, by the action of nitric acid on humic acids obtained from hard coal by moderate oxidation with hydrogen peroxide. Among these nitrophenol-like substances they identified picric acid in a quantity equal to 2.7 per cent of the coal, a discovery which is somewhat like our own, and indicates that the humic acids regenerated from hard coal also possess a phenol structure. At this point it should be mentioned also that, as early as 1888, Guignet obtained from hard coal with nitric acid, a nitrophenol which he called trinitroresorcin. Many other reactions also indicate the phenolic character of humic acids.

The phenols of crude tar are to be traced back to the humin substances. On dry distillation to be sure, humic acids, isolated with admission of air, yield little or no tar. Erdmann, who isolated humic acids under particularly painstaking conditions, was however able to obtain from them, though only in small quantities, a tar which was very rich in phenol compared with the tar from the other constituents of coal. The products, still resembling humic acids, which are obtained after treatment of humic acids with lye at 300 degrees, also behave in this way.

An attempt was made to draw a conclusion as to the chemical constitution of humic acids from the formation of the artificial humic acids. It has long been known that alkali-soluble substances of the character of humic acids can be formed from various organic compounds. Best known are the artificial humic acids from carbohydrates, particularly from sugar. But humic acids should also be obtained from other classes of organic compounds. Easiest to convert into humic acids however are the higher phenols and phenol derivatives, such as pyrocatechol, hydroquinone, phenolcarboxylic acid, etc. This reaction which had long been known qualitatively was carefully studied by Eller and Koch. They have discovered a convenient way of preparing such synthetic humic acids in the oxidation of the phenols mentioned with alkali persulfate solution. If we examine the reactions which are known to lead to artificial humic acids we find that these run most smoothly from phenols. If we start with non-phenols, as for example from carbohydrates, an intermediate formation of phenols is possible directly; apparently therefore in the formation of the humic acids, it is a question of substances with phenol complexes. Here then we have genetic relations with one of the constituents of the woody substance, lignin, which brings us to the question of the formation of the humic acids and then of coals in nature. Until a short time ago the view was held that cellulose was to be looked upon as the raw material of humic acids. This was even held to be almost an obvious conclusion since cellulose greatly preponderates in the substance of plants. The work of Hoppe-Seyler, Fremy etc., restricted mainly to biological fields, from which important conclusions as to the cellulose derivation of the humic acids can be drawn, were not very highly regarded by the chemists and geologists who worked with coal. In consequence of their discoveries in pressure-oxidation, Fischer and Schrader were the first to go deeply into the question of the plant constituent from which coal is formed and, on the basis of already known facts as well as their own experiments, they became convinced that genetic relations existed only between lignin and the humic acids and that, on account of its chemical and biological behavior, cellulose cannot be considered to take an essential part in the formation of humic acids.

The lignin theory of Fischer and Schrader states that, in the decay of plant residues, the cellulose is altered and consumed by the action of bacteria. It disappears with formation of carbon dioxide, methane, water, and water-soluble organic acids, such as formic acid, acetic acid etc., which are carried away by the water of the soil and may exert a solvent and decomposing action upon the rock beneath the peat. The quantity of aromatic lignin on the other hand increases with increasing age of the peat, going over to humic acids from which there then form the humus substances of brown coal which are insoluble in alkali and, finally, the substance of hard coal. The wax and resin-like materials of the plants remain however when the coal is formed and make up the bitumen.

Fischer and Schrader have adduced a large number of facts in support of their theory.

Though the chemical constitution of lignin cannot yet be cleared up entirely, we can now say with a reasonable degree of assurance that we have to do with a substance the molecule of which possesses an essentially aromatic and even phenolic character. In various ways protocatechuic acid or derivatives of this acid, such as vanillic acid and eugenol can be obtained from lignin. Since aromatic carboxylic acids form from lignin under pressure-oxidation it is possible that unphenolated benzol rings are also present. Recently Fuchs has found an unsaturated sugar complex in the lignin molecule. All in all however, lignin, like the humic acids, may be considered to be of a phenolic character. This is shown for example in vacuum distillation which gives a tar very rich in phenol. The methoxyl content of lignin is important for the characteristic and easily recognizable methoxyl group makes it possible to trace the lignin in the formation of the coal. The genetic relations between lignin and the humic acids arise from their chemical similarity and the possibility of converting lignin into humic acids. This can be accomplished by heating with alkali liquors at 200 degrees or by auto-oxidation in the presence of alkali.

Interesting work, strongly supporting the Fischer-Schrader lignin theory, has been done in America. In 1917 Rose and Lisse, in an investigation of the decomposition of wood, showed that it goes hand in hand with a considerable decomposition of the cellulose, the lignin proving more resistant. Their figures for fresh, half decayed, and entirely decayed wood show that during the process of decay the relative content of methoxyl doubled, a proof of the increase in the store of lignin; the cellulose on the contrary disappeared. The studies of Rose and Lisse gave only relative values for lignin, cellulose etc. A new investigation by Bray and Andrews at the Forest Products Laboratory of Madison Wisconsin follows the decomposition of wood quantitatively.

Bray and Andrews started from weighed samples and made a systematic study of the biological decomposition. By a determination of the loss of weight they were able to establish not only the relative alteration but the absolute alteration of the individual constituents of the wood during the process of decay. The quantity of lignin, as indicated by the constituents insoluble in 72 per cent sulfuric acid, remains practically constant. In course of decay however the lignin becomes completely soluble in alkali and loses a part of its methoxyl content. On the other hand it can be seen from the figures of Bray and Andrews (table B) that alkali-soluble and, to some extent water-soluble substances are formed from the cellulose which again disappears during the process of decay. The loss of weight suffered by the entirely decayed wood corresponds to the quantity of cellulose originally present. A splitting off of methoxyl occurs in the transition of the lignin into humic acids so that, in contrast to the lignin which in its most frequently occurring forms contains about 16 per cent of methoxyl, the humic acids show only a few per cent. The farther the carbonization goes the more the methoxyl content shrinks so that, in hard coal, it is possible to detect no more than traces of methoxyl. Since however the decomposition of the cellulose generally runs more quickly than the splitting off of the methoxyl from the lignin we see an increase in the methoxyl content in decaying wood. This is clearly shown by the experiments of Bray and Andrews; but Fischer's and Schrader's studies of samples of peat from various depths of a deposit show that, with progressive humification, the increase first observed in the methoxyl content is followed by a decrease as shown in table 1.

TABLE B

Chemical changes of wood during decay (Bray and Andrews)

STORAGE TIME	LOSS DUE TO DECAY	HOT WATER SOLUBLE	1 PER CENT ALKALI SOLUBLE	LIGNIN	CELLULOSE	PENTOSAN	METHOXYL
		Based on equal weights of sample analyzed (figures in per cent)					
months							
0	0	1.2	10.1	29.7	60.0	12.0	5.5
6	27.12	17.95	54.9	38.0	36.7		
12	49.5	22.2	66.8	53.4	21.8		
36	62.4	16.5	70.0	71.0	16.1	6.8	7.2
		Based on equal weights of original sample (figures in per cent)					
		1.2	10.1	29.7	60.0	12.0	5.5
		13.1	40.0	27.7	26.8		
		11.1	33.4	26.7	10.9		
		6.2	26.3	26.7	6.05	2.56	2.7

As early as forty years ago Hoppe-Seyler made extensive studies of the decomposition of cellulose by bacteria. He was convinced that this process takes place in nature on a tremendous scale. He was not, however, able to establish a relation between the fermentation of cellulose and the process of formation of humin substances, peat, and brown coals. He knew that plants contain substances which are extremely resistant to bacterial influences but he was unable to satisfy himself as to their nature. Today we know that this substance is lignin. Omelianski too carried out very painstaking and thorough studies on cellulose fermentation. He obtained, in addition to gaseous decomposition products such as hydrogen or methane, considerable quantities of acetic acid and butyric acid. Fischer and Schrader were able to determine, by means of experiments with bacteria from garden soil, that fungus cultures established themselves only upon cellulose, lignin remaining free from them. Recently Wehmer tried to cultivate bacteria which would have the ability to attack lignin. These experiments were undertaken because of data from other sources indicating the existence of such lignin consumers. These experiments by Wehmer were fruitless, however, surely a proof that if there are lignin consumers they are extremely hard to cultivate whereas the cellulose bacteria can be obtained easily from any garden soil.

TABLE 1

Content of methoxyl of peat from different depths (Fischer and Schrader)

	DEPTH	ASH	METHOXYL
	m.	*per cent*	*per cent*
Peat (Velen) 1	0	1.8	0.49
Peat (Velen) 2	0.9	1.7	1.22
Peat (Velen) 3	1.8	1.8	1.67
Peat (Lauchhammer) 3	Increasing depth	7.1	2.97
Peat (Lauchhammer) 4		6.8	2.73
Peat (Lauchhammer) 5		6.6	1.66

I have already mentioned that pressure-oxidation furnished the proof of the aromatic structure of hard coals. Fischer and Schrader therefore subjected all compounds which have any relation to the formation of coal, that is to say sugar, cellulose, lignin, humic acids, and lignites, to pressure-oxidation and were thus enabled to arrange the substances named into two groups, those which yield furan derivatives, like cellulose and sugar, and those which give benzol derivatives, namely lignin, natural humic acids, brown coals, bituminous and anthracite coals. The results of pressure-oxidation are the best proof of the derivation of humus coal from lignin. Cellulose can still be detected in the lignitic brown coals in which the wood structure is completely retained. The lignites are not looked upon by Fischer and Schrader as normal brown coals but as a wood petrified in consequence of special conditions. The question may be raised whether the Fusain present in many hard coals may not be traceable to such cellulose residues.

If the formation of the humic acids is essentially conditioned by biological processes it must be assumed that physical factors played a part in the conversion of the humic acids and their anhydrides which form the humus of the brown coals into the humus substance of the hard coals.

The formation of hard coals (bituminous and anthracite) cannot be explained exclusively through the influence of the time factor; there must also have been some heat effect, due for example to the fact that the brown coals reached great geothermal depths because of their covering layers. Consequently coals in which such a heat effect did not occur because of a thinner layer above them have remained in the brown coal stage although from their geological strata they should really have been converted to hard coals. An example of this may be seen in certain Russian coals from the lower carbon layer.

To test this assumption Erdmann carried out the following experiments: He heated lignitic brown coals in an autoclave with half their weight of water for one hundred hours at 280 degrees, brown lignite containing 64 per cent carbon yielded a black coal with 91 per cent carbon; and the bitumen, which had been wax-like in the brown coal, went over into a viscous, fluorescent, paraffin-containing oil exhibiting the characteristics of hard-coal bitumen (table 2). As a result of this experiment Erdmann came to the conclusion that a minimum temperature of about 300 degrees must have been necessary for the formation of hard coal. Under these conditions, the humic acids and humins of the brown coals were converted into the substances of hard coal.

Bitumen, the second essential constituent of humus coals, which, to be sure, only makes up a small percentage of the total mass of the organic substance of coal can be separated from the humus substance by different solvents.

TABLE 2

150 grams lignite with 75 grams water during 100 hours heated to 280°

		PURE COAL			PURE COAL
Before heating	C	64.4	After heating	C	91.3
	H	6.56		H	5.7
	O (N)	29.0		O (N)	3.0
	color	brown		color	black
3.6%	Benzene extract solid, brown, montan wax		0.48%	Benzene extract viscous, fluorescing with paraffin wax 0.48%	

TABLE 3

Extraction of coal by benzene

KIND OF COAL	EXTRACT	
	Without pressure	Under pressure
	per cent	*per cent*
Saxon high bituminous brown coal	15.0	23.0
Rhenish brown coal	3.3	7.1
Bohemian brown coal	2.3	7.1
American lignite (North Dakota)	1.3	
Bituminous coal	0.1	6.6
German Cannel coal	1.1	4.0

The bitumen hitherto studied was extracted from the various brown coals with boiling benzol. The substances called bitumen B, extracted with benzol at about 270 degrees in the autoclave, are similar to the bitumens obtained at atmospheric pressure, but have no more precise information about them. The bitumen content of the brown coals varies widely as can be seen from the data in table 3.

Today we have very complete information as to the composition of brown coal bitumen. Broadly speaking we may say that it consists of wax and resin-like substances, present in the individual coals in very variable proportions. A good idea of the distribution of wax and resin-like substances in the bitumen of brown coals from different sources can be obtained from the data of Graefe, given in table 4.

The wax-like constituents of brown coal bitumen were studied as early as 1852 by Brückner who isolated an acid of the formula $C_{28}H_{56}O_2$ from a brown coal from the brown coal fields of middle Germany and called it geocerinic acid. The work of Brückner was apparently forgotten at that time for it was only through the investigation, carried out by Hell in 1901 of the so-called refined montan wax of Von Boyen that attention was drawn to this acid.

TABLE 4

Resin content of bitumen of brown coal

ORIGIN OF BITUMEN	RESINS
	per cent
Pyropissite	6.6
Saxon brown coal	16.5
Bohemian brown coal	31.5
Silesian brown coal	67.9
Rhenish brown coal	17.6
American lignite (North Dakota)	74.0

It was sometimes given the formula C_{28} and sometimes C_{29} by various workers and consequently I made a painstaking study of it with Kreutzer as a result of which I was able to show that the acid constituents of the bitumen of brown coal consist, not of a single acid but of an acid mixture which can be separated by fractional distillation of the methyl ester followed by fractional precipitation of the free acids with magnesium acetate. We were able to establish the presence of the acids C_{25}, C_{27}, and C_{29}, in the bitumens of the brown coals of central Germany and the presence of acids of still higher molecular weights appeared probable.

Of the two acids, C_{27} and C_{29}, we named the first carbocerinic acid and for the second we retained the designation montan acid. These two made up the greater part of the fatty acids of the bitumen in the brown coal from central Germany. A later study with Dilthey of the bitumen in Rhenish brown coal confirmed these findings and showed that the same acids occurred in the bitumen of other brown coals as in those of middle Germany.

The acids of the bitumen of brown coal can be looked upon as normal fatty acids for their melting points indicate that they connect smoothly with the already known normal fatty acids having an odd number of carbon atoms.

The alcohols esterified with the acids in the bitumen of brown coals from middle Germany were distinguished by Pschorr and Pfaff as tetrakosanol $C_{24}H_{50}O$; cerylalcohol $C_{26}H_{54}O$ and myricylalcohol $C_{30}H_{60}O$. In the bitumen of Rhenish brown coals Dilthey and I discovered, in addition to myricylalcohol, another unknown alcohol $C_{32}C_{64}O$ which we called bituminol. From the acid and saponification numbers, as well as from the quantitative preparative working up of brown coal bitumen, it appears that, in montan wax, we have to do with a mixture which contains about 25 per cent free fatty acid and 75 per cent real wax consisting of the esters of the fatty acids mentioned with aliphatic alcohols.

Our knowledge of the resin-like portion of brown coal bitumen is less extensive. It is only recently that Steinbrecher studied the resin-like constituent of the bitumen of brown coal from central Germany and came to the conclusion that we have to do with resinolic acid resins which are comparable with amber and therefore consist of free resinic acid, and resinic acids, esterified with resin alcohols. The strongly acid portions are very much like colophonic and colophenic acids, that is to say typical resinic acids. Between the composition of resin from montan wax and real earth resin there are of course quantitative, but no qualitative, differences.

The bitumen of hard coal, as it is extracted for example by benzol under pressure or by pyridine, can be split up by petroleum ether into a soluble oily portion and an insoluble solid portion. The oil bitumen consists of hydrocarbons while the solid bitumen contains oxygen-containing substances.

As early as 1913 Pictet extracted hydrocarbons from hard coal with boiling benzol and studied them. Later Hofmann and Damm subjected a large amount of hard coal from Upper Silesia to pyridine extraction, split up the products, and identi-

TABLE 5

Extraction of Saar bituminous coal by benzene (Pictet)

Benzene extract, per cent from the coal

UNSATURATED HYDROCARBONS	SATURATED HYDROCARBONS
Dihydrotoluene: C_7H_{10}	C_8H_{16}
Dihydro-m-Xylene: C_8H_{12}	C_9H_{18}
Dihydromesitylene: C_9H_{14}	$C_{10}H_{20}$
Dihydroprehnitene: $C_{10}H_6$	$C_{11}H_{22}$
$C_{11}H_{16}$	$C_{12}H_{24}$
$C_{14}H_{16}$	$C_{13}H_{26}$
Dihydrofluorine: $C_{13}H_{12}$	
$C_{13}H_{16}$	
$C_{17}H_{20}$	
Melene: $C_{30}H_{60}$; F.P. 62–63°	

TABLE 6

Extraction of Upper Silesian bituminous coal by pyridine (Hofmann and Damm)

	PER CENT FROM THE COAL
Total extract	10–19
Neutral substances	1.6
Phenols	0.25
Paraffin wax	0.02

PARAFFIN HYDROCARBONS	OTHER SATURATED HYDROCARBONS				UNSATURATED HYDROCARBONS
$C_{21}H_{44}$	$C_{11}H_{20}$	$C_{17}H_{30}$	$C_{17}H_{28}$	$C_{22}H_{34}$	$C_{15}H_{20}$
$C_{22}H_{46}$	$C_{13}H_{24}$			$C_{23}H_{36}$	$C_{16}H_{20}$
$C_{23}H_{48}$	$C_{14}H_{26}$				$C_{17}H_{22}$
$C_{24}H_{50}$	$C_{15}H_{28}$				$C_{18}H_{22}$
$C_{25}H_{52}$	$C_{16}H_{30}$				$C_{19}H_{24}$
$C_{26}H_{54}$					$C_{21}H_{26}$
$C_{27}H_{56}$					
Methylanthracene $C_{15}H_{12}$					

fied the hydrocarbons which they contained. Tables 5 and 6 give a summary of the most important results of the studies of Pictet and Hofmann and Damm. The hydrocarbons found in the two cases were not identical to be sure but broadly speaking they could be placed in the same class. One interesting hydrocarbon should be mentioned particularly, the saturated melene found in the coal by Pictet to which the formula $C_{30}H_{60}$ was assigned. According to the studies by Pictet and also by Fuchs this hydrocarbon can also be obtained from lignin.

Fischer, Broche and Strauch have shown that the oil bitumen causes the caking of the hard coal. There must however be a certain minimum quantity present to cause a sufficient softening and melting of the coal during the coking to produce a caked coke. The tendency to coking on the part of the coal is thus traceable to the solid bitumen while the force of the tendency is determined by the point at which the solid bitumen decomposes. The higher this point the greater the tendency.

In general the formation of the bitumen of coal is assumed to be traceable to a wax and resin content in the coal-forming plants. It is noteworthy that in his recent studies of beeswax Gascard has encountered the same acids as are found in brown coal bitumen. Cerotinic acid and melissinic acid to which Gascard gave the formulas C_{25} and C_{31} had already been known to be constituents of beeswax but this was not the case with carbocerinic acid, C_{27} and montan acid C_{29}. Though it would be premature to draw any conclusions from this discovery nevertheless it is noteworthy that the typical acids of brown bitumen, namely carbocerinic acid and montan acid occur, in a recently formed-substance concerning the formation of which we have definite knowledge.

The beeswax acids with odd numbers of carbon atoms are the typical constituents of other waxes also but not of the animal and vegetable fats in which the glycerides of the much lower fatty acids with an even number of carbons predominate. It is worthy of remark that the latter acids are not found in fossil material, and this permits us to draw some conclusions as to differences in the stability of acids with odd and even numbers of carbon atoms. This is indicated also by the findings of Fischer and Schneider who obtained only odd-numbered fatty acids from the pressure-oxidation of paraffin. In cracking individual hydrocarbons Skraup found similar differences in the stability of compounds with odd and even numbers of carbon atoms.

The conversion of the wax of the brown coal bitumen into the hydrocarbons of bituminous coal bitumen can be explained by a kind of pressure distillation as has been shown by the experiments of Erdmann.

Briefly we may now consider ourselves relatively familiar with the smaller part of coal bitumen. Of the chemical constitution of the real body of the coal on the contrary our knowledge is very sketchy although great progress has assuredly been made within recent years. It is doubtful whether a perfectly satisfactory explanation of the constitution is possible with the methods of classical organic chemistry. With these complicated mixtures of insoluble organic substances it will be necessary to follow the suggestions of Fischer in other fields of work that is to say we shall have to treat not single individuals but groups of related bodies by new methods and possibly success will be achieved, as in albumin and tanning chemistry, by the synthesis of similar substances.

Up to this point my remarks have only dealt with chemical alterations of the coal in so far as these reactions came into play in the problem of structure. The present endeavor of chemistry is to make a chemical raw material of coal which has hitherto been used almost exclusively as fuel.

Essentially we can arrange the chemical changes to which coal can be subjected into three groups;

1. Alteration through the action of heat alone.
2. The breaking up of the larger coal molecules into smaller chemically valuable ones by the action of oxidizing agents.
3. The splitting up of the large, non-melting infusible and insoluble coal molecule by the action of reducing and hydrogenizing agents, to soluble and oily substances—a process which is called popularly the liquefaction of coal.

The heating of coal in the absence of air for obtaining metallurgical coke or illuminating gas has, to be sure, been used for many decades, but the processes which occur thereby, particularly the reactions by which the aromatic anthracite coal tar results have only been explained very recently. If heated gradually from the temperature required for dryness to 325 degrees brown coals give off abundant quantities of gas which consist mainly of carbon dioxide and hydrogen sulfide. Bituminous coal on the contrary evolves no gas up to this temperature. Use is made of this behavior of brown coal in so-called Bertination, a kind of artificial carbonization which leads to a diminution in the oxygen content consequently to an increase in the heating value of the fuel.

On heating coal further from 350 degrees to 500 degrees decomposition sets in, crude tar and fixed gas being given off. In 1906 Börnstein first proved that crude tar is essentially different from the tar obtained at high temperatures in the coke ovens and in illuminating gas retorts. More intensive investigations of the coking of crude tars have been carried out by Franz Fischer and his co-workers. Crude tar consists essentially of hydrocarbons and phenols. The lowest boiling portions have the character of Caucasan gasoline. Benzol, naphthalene and carbolic acid, the typical constituents of the tar from cokeries, are not present or only in quite small quantities in crude tar which has not been superheated. We must assume that the crude tar hydrocarbons form from the bitumen of coal while the phenols are produced from the actual body of the coal. Schneider and Erdmann, who divided brown coal into bitumen, humic acids and residual coal insoluble in alkali, showed that the bitumen yields a large quantity of a tar poor in phenol, but rich in paraffin, while the humic acids yield only a small quantity of tar rich in paraffin with almost no solid paraffin wax. If we take into consideration the fact that the humic acids have an aromatic structure, the considerable formation of phenols, that is to say of benzol derivatives, is easy to understand.

In table 7 are given the average yields of primary tars obtained for various kinds of coal with their contents of phenols and solid paraffin wax.

Of the brown coals the "Schwel" coal from middle Germany, which is rich in bitumen, yields large quantities of primary tar containing much paraffin and little phenol, whereas we obtain a small quantity of tar rich in phenols from the Rhenish brown coals which are poor in bitumen. Of the brown coals, lignite furnishes the tar richest in phenols.

Of the hard coals the geologically or genetically youngest give the highest yields of primary tar. Since these coals are also richer in oxygen than those which are geologically older, the primary tar contains a large quantity of phenol which runs parallel with the oxygen content of the coals and in the case of the gas flame coals makes up half of the primary tar. From the older coals, we obtain less and less primary tar with a diminishing content of phenol. The lean coals yield almost no primary tar.

TABLE 7

Tar, phenols and paraffin obtainable from various coals

KIND OF COAL	YIELD OF CRUDE TAR	CONTENT OF SOLID PARAFFIN IN THE CRUDE TAR	CONTENT OF PHENOLS IN THE CRUDE TAR
	per cent	*per cent*	*per cent*
Schwel coal (Central Germany)*	24	29	15
Rhenish brown coal	7.6	13	37
Westerwald lignite	2.7		57
American brown coal (N. D.)	5.6		45
Gas flame coal	10–14	1–2	40–45
Gas coal	5–8	1–2	25–35
Fat coal	3–4	1–2	15–25
Lean coal	1.5		0
Cannel coal	29		5–10

* A kind of lignite rich in volatile matter.

The cannel coals yield a great deal of primary tar with a low phenol content, although they contain almost no substances soluble in benzol. We see here an essential difference between the sapropel and humus coals.

The residue from the distillation for primary tars, the semicoke, still contains about 15 per cent of volatile constituents which, on further heating to 1000 degrees, are largely given off in the form of hydrogen accompanied by small quantities of methane hydrocarbons.

The gas evolved in the distillation of primary tars contains a large amount of hydrocarbons but only a little hydrogen. It has a heating value of about 900 B. t. u. per cubic foot which is much greater than that of coke oven gas.

The study of the distillation of primary tars and its products has finally cleared up the question as to the formation of aromatic hard coal tar. After Berthelot succeeded in converting acetylene into benzol the view was held for a long time that acetylene played an important rôle in the formation of the tar of coke ovens. The behavior of primary tar and its constituents, on heating to a high temperature, showed plainly however that the aromatic hard coal tar represents the thermal decomposition product of primary tar. The primary tar phenols are most important in the formation of coke-oven tar. As Fischer and Schrader have shown, they are reduced at 800 degrees with a good yield of aromatic hydrocarbons. At the same time, there occurs a splitting off of alkyl groups so that for example not only toluol, but benzol also forms from cresols. The behavior of the primary tar hydrocarbons in the coke oven differs with their constitutions. The aliphatic hydrocarbons split into smaller fractions and go off as gases like methane and hydrogen with deposition of soot. The napthene hydrocarbons, which have a ring structure, suffer the same fate as the aliphatic to some extent, but in so far as they contain six-membered rings they are converted into aromatic hydrocarbons by the splitting off of hydrogen. The knowledge of this relationship explains also a fact which has long been known experimentally, that is to say that the yield of coke-oven tar increases with the oxygen content of the hard coal. As we have seen, these coals also give the highest yields of primary tar phenols which we must consider to contain the most important elements in the formation of the aromatic tars.

The serious attempts which have been made in Europe, particularly in Germany and England, in the field of low temperature distillation of hard coal are well known. The numberless types of furnaces which have been proposed are built essentially on the two following principles. The coal, which is introduced into either horizontal or vertical stationary or rotating furnaces, receives the heat from the outside, through the wall of the furnace, or by direct transfer from hot gases serving as heat carriers. This method of operating can also be used successfully in furnaces which are built on principles similar to those of the externally heated furnaces.

Until the present time none of the numerous processes for lignites rich in volatile material have yielded entirely satisfactory economic results with hard coal although there can be no doubt, in view of the importance of the problem and the intensity with which it has been worked on, that a positive success is yet to be expected. With hard coal it is important for the economic success of the distillation that the semi-coke, the principal product of the process, be obtained in dense lumps suitable for transporting and storing. A distillation of hard coal for the sake of the oil alone has little prospect of being economically successful.

The purely thermal decomposition of coal at low or high temperatures does, to be sure, yield a series of chemically valuable liquid substances, but their quantities are generally small in comparison with the amount of coal used and in this connection, we speak with justice of by-products. In their production we are limited first of all by the possibility of marketing the principal product, in this case coke. For economic reasons, therefore, the quantities of the by-products which are valuable in and for themselves can not be increased at will.

In order to make a chemical raw material of coal, it must never be subjected to such chemical effects as convert the principal body of the organic substance of the coal into chemically valuable products. In the discussion of its chemical constitution, the oxidative break-down of the coal by pressure-oxidation, has already been mentioned, leading to aromatic carboxylic acids. It is not possible to predict today the future significance of this gentle combustion of coal. We have here, at any rate, a way of obtaining chemically valuable substances from coal.

Another possibility of getting from the complicated coal molecule to simple soluble and liquid substances consists in allowing hydrogen, or reagents which give off hydrogen to act upon coal. This splitting up of the coal molecule was first achieved by Berthelot in 1869 by means of his classic hydriodic acid method. In addition to hard coal he hydrogenized artificial humic acids, charcoals, etc. and he says that in every case he obtained saturated hydrocarbons, particularly hexane and hydrocarbons with a number of carbon atoms divisible by six. Ten years ago we repeated the experiments but could obtain no such degree of liquefaction under the conditions cited by Berthelot. It was only when we used higher temperatures that we were able to confirm the Berthelot experiments. Nevertheless we made the interesting observation that the younger they are the more easily hard coals are hydrogenized by hydriodic acid. The chloroform-soluble constituents formed by the hydrogenation were taken as the measure of this (table C).

TABLE C

Comparative hydrogenation of different coals with hydriodic acid

KIND OF COAL	COKE YIELD	SOLUBLE IN CHLOROFORM	
		Before hydrogenation	After hydrogenation
	per cent	*per cent*	*per cent*
Gas flame coal	64	1.5	70
Fat coal	78	0.7	55
Semi-bituminous coal	85	0.6	18
Anthracite	89	0.5	12

The first experiments in the hydrogenation of coal by a method which could be transferred to large-scale operation were carried out in 1913 by Bergius and Billwiller who allowed molecular hydrogen to act upon finely pulverized coal at temperatures of about 450 degrees and pressures of several hundred atmospheres. Even in their first patent they state that they can convert 85 per cent of the coal to liquid, soluble, or gaseous compounds. Bergius expressly stated his process to be non-catalytic and as proof of it stated that he had also observed the formation of liquid products in an apparatus with a glass lining, that is to say under exclusion of any possible catalytic effect of the iron autoclave wall. On the other hand it may be said with respect to this experiment that Bergius surely did not use an ash-free coal and that consequently the ash might have affected the reaction catalytically. As a matter of fact, in his process Bergius added iron oxide equal to about 5 per cent of the weight of the coal as he says to fix the sulfur which otherwise would favor the polymerization of the heavy oils. There are numerous publications by Bergius himself, as well as by other investigators, concerning tne treatment of coal with hydrogen under pressure. The various experiments may be summarized as follows. In this case also the younger, and, to be sure, non-coking, coals are most suitable. They are most easily hydrogenized and give the highest yields of oil. In the Bergius process the consumption of hydrogen amounts to about 5 per cent of the weight of the coal or 625 cu. m. per ton of coal. In spite of this the total liquid reaction products contain no more hydrogen by weight than was originally present in the coal, for the hydrogen entering into reaction is later found again in the form of gaseous reaction products, methane and lower homologues which make up from 25 to 30 per cent of the coal. In order to obtain a clear picture of how the coal substance, which has been freed from tar, behaves on hydrogenation and, in particular, to get an idea of the composition of the oils formed, Fischer and Frey subjected brown coal semi-coke, obtained by careful distillation of Rhenish brown coal, to pressure hydrogenation. Forty per cent of oil which could be distilled was obtained from the semi-coke by this means. A study of this oil, undertaken by Ter-Nedden and myself, yielded the values shown in table 8.

TABLE 8

Hydrogenation of semi-coke from brown coal under pressure

Semi-coke	14% water			
	40% oil	65–280° 63%	22% phenols 3% bases 75% neutral oils	B.P. 180–215° 60% B.P. 180–260° 80%
		Above 280° 20%		
		Residue 17%	87%	

We see that over 20 per cent of phenols are contained in the main body of the oil. They consist half of carbolic acid and cresols, that is to say o- and m-cresol were found but no p-cresol was found. Noteworthy is the high content of basic constituents in the oil. They were very high-boiling and had an odor of the higher pyridine bases and quinoline. There were no lower boiling bases. The hydrocarbons obtained in the hydrogenation of brown coal semi-coke gave off an odor of gasoline or petroleum. Table 9 gives the atomic proportions of C:H and the boiling limits and densities of single fractions.

TABLE 9

Hydrogenation of semi-coke from brown coal

Boiling limits, ratio of C:H and density of different fractions

FRACTION	BOILING LIMITS	C:H	DENSITY
	°C.		
1	60–85	1:1.9	0.739
3	95–115	1:1.7	
6	135–145	1:1.5	0.850
12	100–115 b. 35 m/m	1:1.2	0.933
16	155–168	1:1.2	0.972

TABLE 10

Reduction of cresols with hydrogen under pressure

KIND OF SUBSTANCE USED	TEMPERATURE	TIME	HIGHEST H_2 PRESSURE	STILL SOLUBLE IN ALKALI	FORMED HYDROCARBONS AND GASIFIED SUBSTANCE
	°C.	*hours*	*atm.*	*per cent*	*per cent*
m-Cresol	460	1½	245	92.6	7.4
p-Cresol	460	1¼	240	93.7	6.3
o-Cresol	460	7	240	86.8	13.2

Since only small quantities of unsaturated hydrocarbons could be detected there must be some of cyclic nature and the densities obtained are in agreement with this. The occurrence of the phenols is to be explained by their great stability under the conditions of pressure hydrogenation. Experiments with pure cresols showed that, at 460 degrees and 240 atmospheres hydrogen-pressure, for an experimental period of one to seven hours, not even 10 per cent can be reduced to hydrocarbons or converted into gaseous products (table 10).

Now since, according to Bergius, the coal should have passed through the hydrogenation apparatus in ten minutes no essential alteration of the phenols would take place once they had formed from the coal.

The hydrogenation of solid fuels can also be carried out with substances which give off hydrogen, for Fischer and Schrader have carried out this process with sodium formate. They made a determination of the ether-soluble constituents in the product of hydrogenation and obtained the figures shown in table D.

TABLE D

Hydrogenation of coal with sodium formate

ETHER-SOLUBLE PRODUCTS OF HYDROGENATION IN PER CENT OF COAL USED			
Bituminous coal		Brown coal	
Anthracite	1.6		
Fat coal	9.2		
Semi-coke	9.8		
Lean coal	10.7		
Fat coal (liable to spontignation)	26.3	Lignite	26.8
		Semi-coke	32.4
		Brown coal (soluble in alkali)	36.3
		Ulmic acids	37.1
Gas flame coal	39.2		
		Saxon "Schwel" coal	43.4
		Rhenish brown coal	45.0

The youngest coals give the highest yields. A mixture of carbon monoxide and steam acts like sodium formate. Comparative experiments by Fischer and Schrader show that this mixture hydrogenizes even better than pure hydrogen, a fact which is probably explained by the fact that in this case we have the hydrogen in the nascent state (table 11).

The hydrogenation of coal consists not only in a reduction of oxygen-containing compounds and an attachment of hydrogen to unsaturated substances but we must imagine that a loosening of the tight bonds of the molecule occurs and that in the moment of dissociation hydrogen then attaches itself to these fractions. Kling and Florentin have found that these temperatures of decomposition are at different points for different substances and they were able to prove that they generally correspond to the temperatures at which the individual substances can be hydrogenized.

The Bergius process has already been tried for many years, in a large experimental plant in Rheinau near Mannheim, but has not yet found practical application. The Gesellschaft für Teerverwertung of Duisburg-Meiderich has recently erected a plant for the Bergius process.

TABLE 11

Hydrogenation of rhenish brown coal with $CO + H_2O$ *(Fischer and Schrader)*

(Comparison with efficiency of H_2)

MEDIUM OF HYDROGENATION	PRESSURE	ETHER-SOLUBLE PRODUCTS OBTAINED (PER CENT OF COAL)
	atm.	
		5
H_2	90	12
CO (dry)	90	12
$CO + H_2O$	90	36

For many years the Badische Anilin-and Sodafabrik, now a part of the I.-G. Farbenindustrie has been occupied with the problem of the hydrogenation of coal and of course they wish particularly to use crude brown coal for obtaining oil. Their method has been briefly described in a lecture by Director Krauch of this company. According to him the process is very similar to that of Bergius in so far as hydrogen is made to act upon coal at those temperatures at which it breaks up into certain fractions. By varying the hydrogen pressure, the velocity of flow, and particularly by the use of certain catalysts, it is said to be possible to obtain the predominance of certain reaction products, particularly low-boiling hydrocarbons, in distinction from the Bergius process in which no, or at least no specific, catalysts are used and only certain products can be obtained for each coal. Now it is possible, by the choice of certain catalysts, to direct the reaction along definite paths so as to get aliphatic or aromatic hydrocarbons or mixtures of both and thus obtain anti-knock motor fuel directly.

The most essential factor in the economical hydrogenation of coal is the obtaining of cheap hydrogen. Now the I.-G. Farbenindustrie has constructed a producer in which finely granular fuel, like coal dust, semi-coke, hard coal of poorer quality, containing a relatively large amount of ash, can be kept in suspension by an ascending current of air or steam. The sensible heat of the gas on leaving is used for preheating the fuel of the charge. I am told that an extraordinarily high performance is achieved with this producer. It is possible to pass 750 tons of crude brown coal through a producer having a cross-section of 12 sq. m. in twenty-four hours, and it is said that the thermal efficiency of the producer is unusually favorable. The cost of the water gas is lowered as a result of the fact that the producer can be charged with the cheaper crude brown coal.

The direct conversion of the organic substance of coal, consisting of complicated compounds, into simple carbon compounds is the one way of utilizing coal chemically. It can however serve as chemical raw material in another way, that is to say if we start from the coke or practically elementary carbon remaining after the thermal decomposition. A great deal of it is used as a reducing agent in the blast furnace and in the Haber-Bosch ammonia synthesis. It has already found application as a chemical raw material in the manufacture of calcium carbide and the related lime-nitrogen, acetic acid manufacture etc.

There are unsuspected possibilities in the chemical conversion of the water gas obtainable from coke. Work done within the last few years has shown that the most various organic compounds can be manufactured in this way, including methanol, synthol, hydrocarbons etc., but a detailed description of these problems must await another lecture.

It should be stated too that we are not restricted to any definite coal for these syntheses but that it is also possible to employ other carbonaceous substances as raw materials, providing water gas can be obtained from them. Thus for example, it is possible to use poorer grades of fuel, anthracitic coal, and even crude petroleum and natural gas. These remarks will show that there are well-founded prospects for making coal the basic material of chemical industry. In particular the obtaining of liquid motor fuels, whether directly, by the high pressure hydrogenation of coal, or through water gas by catalysis, will surely play a very important part in those lands which have no deposits of oil. The question will now be raised as to what quantities of coal will be required for the building of such an industry based upon coal. The coal mine owners, who do not themselves work up the coal, are of course interested in the greatest possible demand and good sales. But a quite incidental calculation indicates that the quantities of coal which are used for the processes described are relatively small in comparison with the quantities which are used at present for fuels and in the iron industry. The coal miner therefore, in so far as he does not work up the coal himself, will not be too optimistic about the process. If however we consider the case from a general economic standpoint and from the standpoint of the most economical utilization of the mineral deposits of a country, a chemical utilization of the coal is only to be welcomed for it heightens its intrinsic value and so has a direct relation to the enrichment of the common wealth of the nation.