INTRODUCTION

The generation of power in stationary engines offers no difficulties in coal-producing countries. It is always possible to fire coal under boilers and raise steam for power purposes, or to gasify it and to use the gas as a heating or motive agent.

Limitations in weight and space, both as regards engines and the quantity of fuel required, influence the generation of energy for transport purposes, as on board ship, in motor vehicles or aircraft. So long as electrical energy in large bulk cannot be carried more efficiently than present-day accumulators permit, so long are we restricted to the use of liquid fuels of relatively high potential energy for motor propulsion. High calorific value, low specific gravity, freedom from incombustible constituents, small space occupied and many other advantages render liquid fuels indispensable for motor purposes.

Aircraft, motor cars and small boats call for low-boiling, commercial vehicles and large ships for high-boiling liquid fuels. The choice of fuel is determined by questions of fire hazard, type and speed of engine, the available space and permissible weight in the vehicle and other considerations. Sea-going vessels are not likely to be run on petrol, even at very low petrol prices, but on oils of higher boiling range on account of the smaller fire and explosion risk. In aircraft, on the other hand, motor fuels of very low boiling points and high calorific value must be used, as only these are suitable for light, high-speed engines, if a minimum weight per horsepower-hour is to be carried.

It is therefore not likely that either now or in the future a standard liquid fuel will be used, but different types will be required for different purposes.

The principal sources of liquid fuels are petroleum, and the gasoline frequently, but not invariably, present in natural gas. The latter and the low-boiling fractions of petroleum oil are petrol or benzine, the motor spirit of commerce. To these must be added the " cracked " spirits made by thermal decomposition of higher boiling petroleum fractions, produced particularly in America on a very large scale. The fractions of higher boiling range and the residue of the crude oil, in as far as they are not applied for lubricating purposes, find a use as fuel for oil engines of many types and for steam raising by direct oil firing.

There is a ready demand for the present very considerable production of petroleum. As regards low-boiling fractions, there exists a distinct shortage, which is made good by adapting engines to heavier fuels, by combining low- and high-boiling fractions and by other means.

The rapid development of motor transport makes countries not producing petroleum in more than negligible quantities dependent on its importation from abroad, but the shortage of crude oil, even in the most favourably situated countries such as the United States of America, is becoming more and more acute.

The world's oil production has experienced a tremendous development during the present century. Fig. 1 gives a picture of the magnitude and increase of the production of oil as compared with that of coal.

It shows that oil production has reached during the last few years one-tenth that of the coal mined, amounting to about 120 million tons of oil as compared with 1,200 million tons of coal.

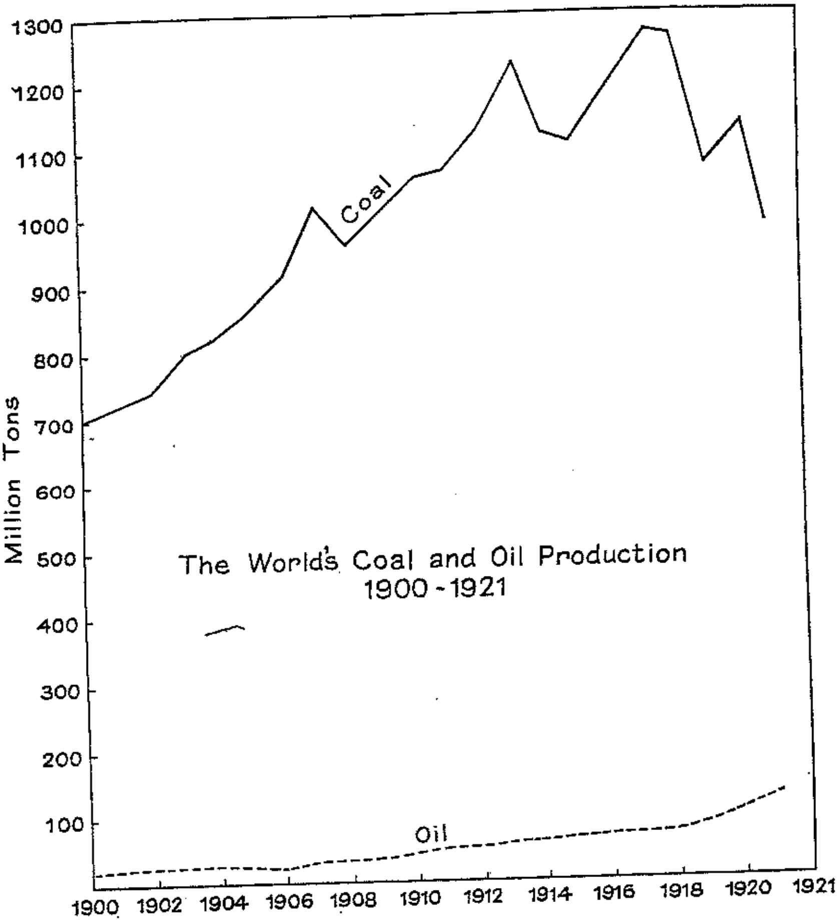


FIG. 1.

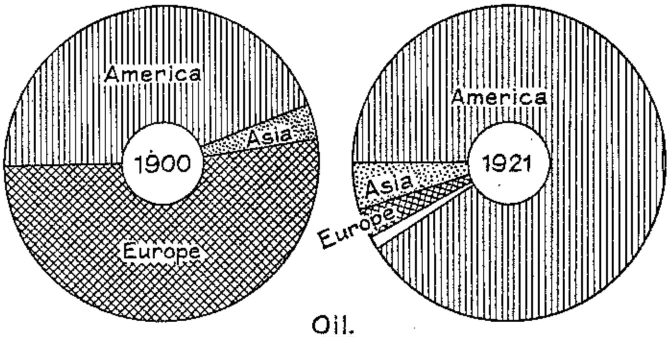
Fig. 2 gives a comparison of the quantities of oil and coal contributed by each continent during recent years.

Since 1900 Europe's participation in the world's oil production has receded to a minute fraction as compared with America. Even in the production of coal, Europe's contribution has considerably diminished and is already overtaken by America.

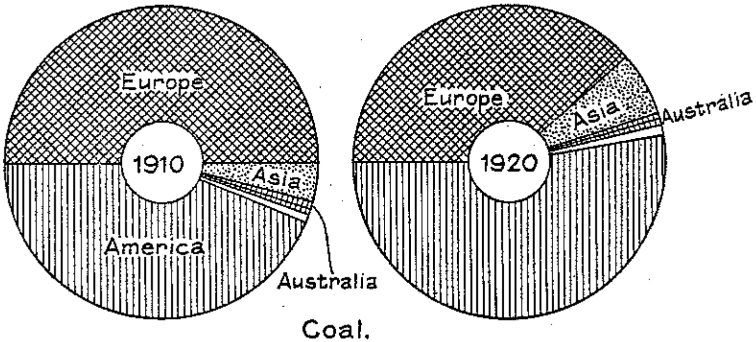
It is difficult to judge the duration of the productivity of oil wells or the additions to the existing production by drilling.

As any estimate of the visible and potential oil deposits must be largely based on guess-work, surprises must be expected in the future.

An estimate of the proved and probable coal deposits, on the other hand, is not quite so uncertain. An approximation of the coal resources of the world [1] is shown in Table I.



Oil.



Coal.

FIG. 2.—DISTRIBUTION OF OIL AND COAL PRODUCTION.[2]

TABLE I

	Total deposits, including proved, probable and possible.	Proved deposits.
	Million tons.	Million tons.
Europe	784,190	274,189
North America	5,073,431	414,804
South America	32,097	2,087
Asia	1,279,586	20,502
Australia	170,410	4,073
Africa	57,839	500

The great advantages inherent in the possession of liquid fuel for the economic and political superiority of any country has led to keen competition for the control of the oil deposits of the world. It is to be expected that the victors in this struggle for oil are not likely to give up to other countries more than the surplus over their own requirements. These other countries are therefore forced to seek means by which substitutes can be found for petroleum, or for its components and products.

For this reason, Science and Industry have begun seriously to study the possibilities of a discovery of new sources and new kinds of liquid fuels, and to work out suitable chemical methods to this end. Disregarding the obvious certainty that new oil-fields will be successfully opened up, the most promising line of investigation seems to be the further development of those technical processes which even to-day yield liquid fuels not derived from petroleum.

The main sources of supply in this respect are gas-works and coke-ovens, the Scottish Shale Industry and the Brown Coal Carbonising (Schwel-) Industry of Central Germany.

An expansion of coking plants can economically take place only at the rate at which the demand for metallurgical coke increases. The same applies to gas undertakings and the increase in gas consumption. The production of tar oils and benzol as by-products of coke-ovens and gas-works is therefore not capable of unlimited expansion. The yield of benzol from existing plants could no doubt be increased by combining with the oil scrubbing plant, auxiliary absorption apparatus charged with activated charcoal or silica gel. Although such an increase in production would be valuable, it is still very small in comparison with the total requirements of low-boiling motor spirits.

The expansion of brown coal carbonisation is equally dependent on the ease and certainty with which the solid residue (Grude Coke) can be disposed of. The shale oil industry is hampered by the necessity of dealing with a large amount of incombustible solid residue, and the attempts at establishing it outside Scotland have hardly yet led to any success. No doubt in the two latter industries the yields of low-boiling spirit could be increased by improvements in the absorption plants. Moreover, the progress of oil shale distillation and brown coal carbonisation will depend on their capacity to compete with the petroleum industry in regard to cost of production, and finally on the supply of raw materials worth distilling.

In this connection it must be considered that as the result of technical progress certain deposits will be commercially workable which to-day cannot be treated at a profit.

One of the new possibilities for the production of liquid fuel on a large scale is low-temperature carbonisation, particularly of bituminous coal, a process which stands in close relation to shale oil distillation and brown coal carbonisation. The consideration of this process will form a large portion of this book.

Apart from coal as raw material for liquid fuel, some other possible sources must be mentioned. The use of alcohol as motor spirit is being widely investigated at the moment, in spite of its relatively low calorific value. Its production by fermentation from sugars, its recovery from the sulphite liquors of the paper industry, and its more or less direct production from wood are the most promising forms in which the solution of this problem is attempted. Its production is dependent on a liberal supply of vegetable materials, and one of the difficulties to be encountered is the collection of this material from vast tracts of land at costs which are not prohibitive. Calcium carbide is also suggested as raw material for alcohol.

Tropical countries are now considering the growing of oleiferous plants with a view to using the vegetable oils as liquid fuel, or to produce motor spirits from them by destructive distillation. Such processes may satisfy the local requirements of tropical countries to a limited extent, but are not likely to influence the larger problem of world supply to any considerable degree. Much more favourable are the possibilities for the production of liquid fuels in countries which possess sufficient coals, since Science has demonstrated the possibility of preparing all kinds of liquid fuels, and even the complete conversion of coal into oils.

The purpose of the present book is to consider this problem in detail, and particularly the following five methods :—

1. Extraction by solvents.
2. Production of primary tar.
3. Hydrogenation of coal.
4. Synthol process.
5. Hydrocarbons from carbides.

The second and fourth methods seem to be the most promising, particularly as they supplement each other and make possible the complete conversion of coal into heavy and light liquid fuels.

CHAPTER I

EXTRACTION BY SOLVENTS

(a) THE YIELD OF OIL BY EXTRACTION

IF bituminous coal, brown coal, peat or oil shale are examined for pre-formed oil in the free state, in general only bituminous coal gives a positive result, and the recoverable quantity of oil is very small. The first solvent to be considered is anhydrous liquid sulphur dioxide.[3] It is advisable to dry the coal completely beforehand. During the extraction process, the coal swells somewhat and loses its cohesion. The extracted pieces of coal, after evaporation of the sulphur dioxide, fall to dust under slight pressure. The sulphur dioxide in contact with coal is quickly coloured yellow to orange. When concentrated, the solution is of dark claret colour without showing any fluorescence. After the removal of sulphur dioxide a dark red, heavy but limpid oil remains, from which a slightly fluorescent oil of agreeable petroleum-like odour can be recovered by steam distillation. The residue, not volatile with steam, contains other deep yellow compounds, boiling from 200° to 350°,* which can be kept for years in air without visible alteration. A quantity of oil of not more than 0·5 per cent. of the weight of coal is recovered, and this extraction is therefore of no importance for the industrial production of fuel oil. It might assume some practical importance if these oils should be found to possess particularly valuable properties. In any case, liquid sulphur dioxide seems the only practicable solvent † for the purpose since it is cheap, and the requisite plant and technique have already been worked out by the Petroleum Industry for the Edeleanu process of oil refining. The oils which can be extracted from bituminous coal by sulphur dioxide are mainly hydrocarbons of wide boiling range, from benzine to lubricating oils and paraffin wax.

(b) IDENTIFICATION OF CHEMICAL COMPOUNDS IN THE EXTRACTS

The composition of these petroleum-like oils, which are contained in bituminous coal to the extent of about 0·5 per cent., has been studied by Pictet and his collaborators,[4] and later by F. Hofmann and Damm.[5] These workers used, however, other solvents and different coals. Fischer and Gluud in their experiments with sulphur dioxide used a fat coal from the Ruhr District. Pictet extracted Loire and Saar coals with benzol, whilst Hofmann and Damm extracted an Upper Silesian coal with pyridine. On account of the difference in the coals, the hydrocarbons obtained have probably different composition. Pictet identified the following hydro-aromatic hydrocarbons: dihydrotoluene, dihydroxylene, dihydromesitylene, dihydroprehnitol and dihydrofluorene, with a number of naphthenes from C_8H_{16} to $C_{13}H_{26}$, hexahydrofluorene and

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* Unless otherwise indicated, all temperatures are in degrees Centigrade.

† Tetrahydronaphthalene being, under pressure in the autoclave at 250°, a powerful solvent, possibly hydrogenates coal, forming dihydronaphthalene or naphthalene.

melene, a solid paraffin wax-like hydrocarbon of m. p. 62° to 63°, to which he ascribes the formula $C_{30}H_{60}$. The boiling points of the hydrocarbons examined by Pictet range from 100° to 300° and many of them are identical with those found by Mabery in Canadian petroleum. F. Hofmann and Damm [6] also found several complete series of unsaturated and saturated hydrocarbons in their coal extracts.*

The low-boiling members are missing; the unsaturated series begins at 154°, whilst no saturated hydrocarbons boiling below 200° were found. The unsaturated series runs from C_8H_{12} to $C_{21}H_{26}$; the saturated, from $C_{11}H_{20}$ to $C_{24}H_{40}$. Paraffins were found from $C_{21}H_{44}$ to $C_{27}H_{56}$. Pictet found in the saturated oils only compounds of series C_nH_{2n}, but Hofmann and Damm observed higher derivatives, indicating the presence of polycyclic hydrocarbons in their oils. The densities of their unsaturated hydrocarbons differ also from those of Pictet's products.

A comparison of Pictet's results with those of Hofmann and Damm shows that many coals are impregnated with small quantities of petroleum-like hydrocarbons which differ in kind according to the type of coal investigated. It should be pointed out that Pictet, by establishing their optical activity, made the relationship of the hydrocarbons extracted from coal with those in petroleum still more probable.

It has already been stated that oil is not extracted by solvents at ordinary temperature from brown coal, peat and oil shale. They need therefore not be considered for the production of oil by extraction. The bulk of the bitumen in coal, and particularly that in brown coal (Montan Wax), peat, and oil shale, yield oil only by thermal decomposition at about 400°. The oil is, therefore, not a component, but a decomposition product of the bitumen,† and is only formed by destructive distillation.

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* Hofmann found phenolic constituents in the extracts, but "the data so far obtained are not sufficient to admit of definite formulæ with any degree of certainty."

† By bitumen is understood resin-, wax- and asphalt-like constituents which are extracted with organic solvents or decomposed on heating to 400° with the formation of oil (tar) and gas.

CHAPTER II

PRODUCTION AND WORKING-UP OF PRIMARY TAR

(a) METHODS OF DESTRUCTIVE DISTILLATION OF FUELS

DESTRUCTIVE distillation consists in heating the fuel to temperatures of several hundred degrees, when a few of the constituents pass over undecomposed, whilst the bulk of the material undergoes thermal decomposition, the gaseous and liquid products of which are to be found in the form of gas and tar. It will be understood that by the application of a considerable reduction of pressure a larger portion of the less volatile constituents can be recovered unchanged in the distillate. It is likewise evident that too rapid a distillation at ordinary pressure will, by superheating of the walls of the carbonising vessel, lead to a secondary and unnecessary decomposition of the products which have already passed into the gaseous state.

The vacuum distillation of coal has been studied by Pictet [7] in Switzerland. and by Wheeler [8] in England, almost at the same time. It was found that by the use of a vacuum some of the petroleum-like hydrocarbons present in coal, which Pictet had isolated by extraction, could be obtained as distillates. For commercial purposes vacuum distillation will hardly come into question, firstly on account of the cumbrous apparatus required, and secondly because the same product can apparently be obtained by distillation at ordinary pressure with the aid of superheated steam.

My collaborators, W. Schneider and H. Tropsch,[9] have investigated the vacuum distillation of lignite. They have found that, as against the liquid vacuum-tar of coal, a solid tar of as high a solidifying point as 53° is obtained, which consists of partly decomposed montan wax and a good deal of viscous oil. As regards the vacuum distillation of peat, little is known, but results similar to those from lignite are to be expected.

The distillation of fuels at ordinary pressure has been practised commercially for decades, on a very large scale, in gas-works, coke-ovens, shale and brown coal carbonising plants, not for the production, however, of a primary low-temperature tar ("Urteer"), but for other purposes. In all cases the desire for a rapid throughput, in view of the poor thermal conductivity of the fuel itself, is likely to lead to excessive heating of the walls of the carbonising vessel. There are also other reasons for this. In coking, the main object is to produce a firm and well-baked coke such as is required in the metallurgical industry. In gas-works the use of high temperature is dictated by the aim at the highest possible yield of gas. In the brown coal distilleries, again, which have hitherto mainly been worked for paraffin wax, there was no inducement to aim at a tar containing undecomposed montan wax, the parent substance of paraffin. Börnstein [10] has shown that distillation at very low temperatures yields tars which differ in their character from those obtained in the above-mentioned commercial processes. Together with my collaborators I

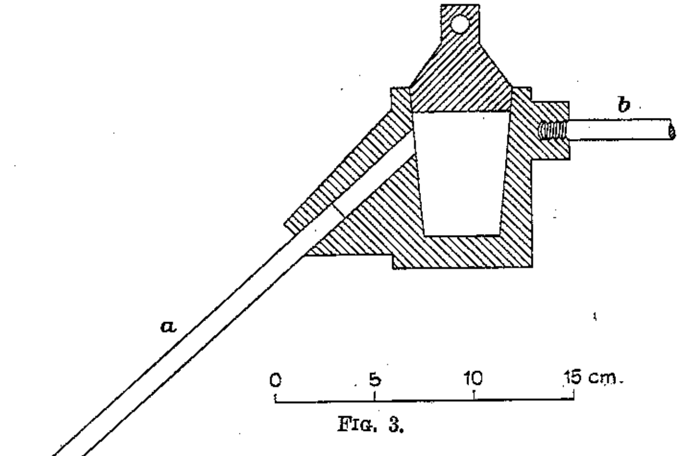

FIG. 3.

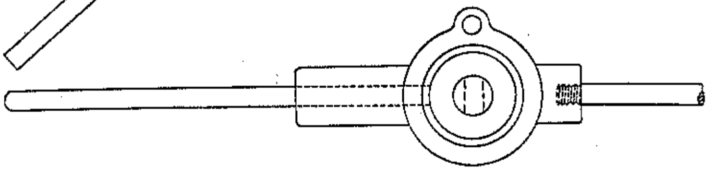

FIG. 4.

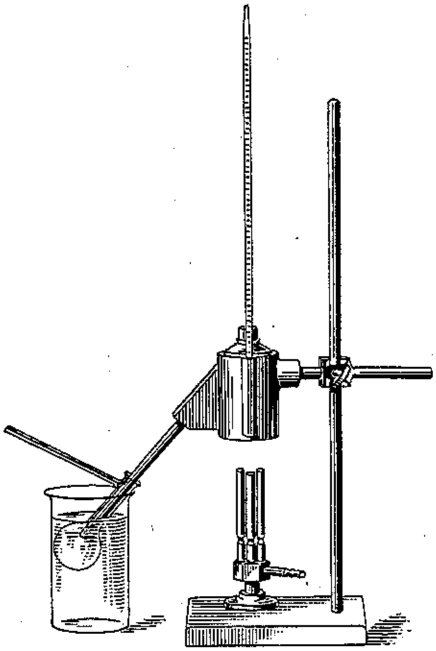

FIG. 5.

have resumed these little-noticed investigations, and have developed them in various directions. I shall revert later to the carbonisation of fuel at high temperatures.

(*b*) SPECIAL LABORATORY METHODS FOR THE PRODUCTION OF PRIMARY TAR

In order to produce oil by the carbonisation of coal, peat, or oil shale, it is necessary to reach the decomposition temperature (400° to 500°) of all the constituents capable of forming oils. It is advantageous not to raise the temperature beyond that absolutely required, so as to avoid any secondary superheating of the oil vapours, and even to cool the vapours as rapidly as possible to temperatures below 300°. Prolonged heating to higher temperatures would lead to the decomposition of valuable constituents with formation of gas and a consequent diminution of the oil yield.

For this reason methods of low-temperature carbonisation have been developed for the production of oil. The crude product of distillation containing the oil is called primary tar ("Urteer"). The gas which is always formed in the process contains the highly volatile oils (benzine).

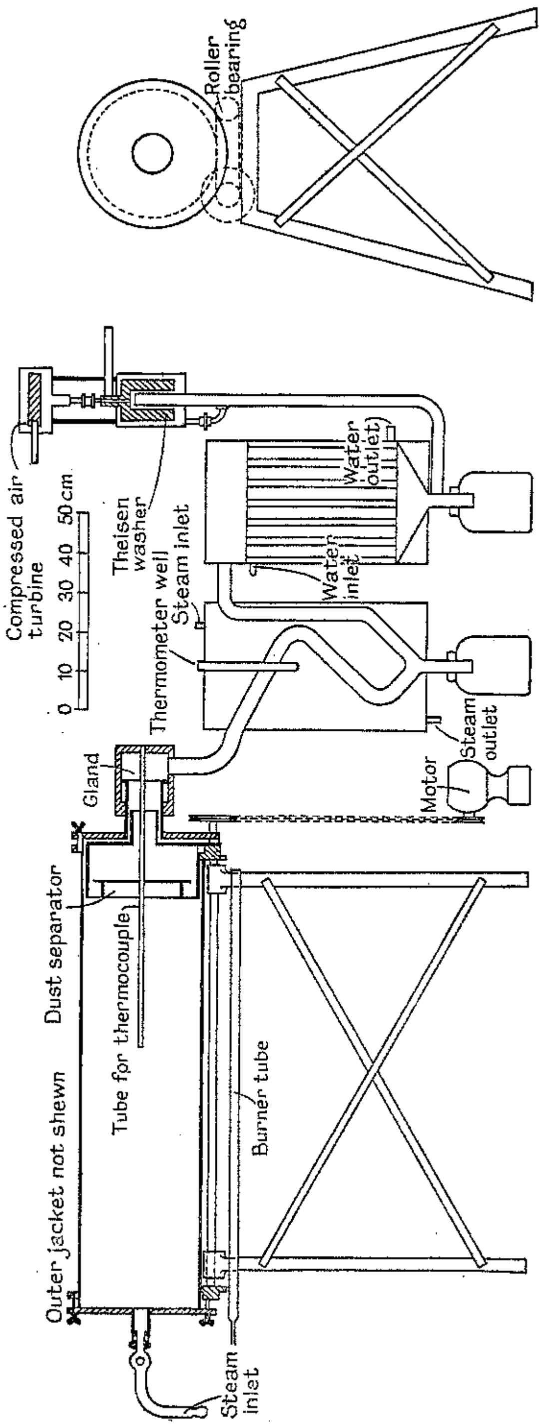

FIG. 6.

These can be recovered by various means, such as washing with oil, compressing, cooling to low temperatures, or by treatment with activated charcoal.

For testing the suitability of fuels for oil production by distillation, the aluminium retort, illustrated in Figs. 3 to 5, is now frequently used.[11]

The apparatus consists of a cast, thick-walled aluminium crucible provided with a ground-in cover and outlet tube of special shape. The crucible is fitted with a lateral bore for the insertion of a thermometer or a thermo-couple. The high thermal conductivity of the aluminium and the thickness of the walls ensure uniform heating of the coal, avoid superheating, and permit an exact temperature control. The apparatus is made in different sizes, for 20, 50, and 100 grams of coal.

For the production of larger quantities of tar it is preferable to use the rotating drum, illustrated in Fig. 6.[12] It admits of performing the distillation without decomposition and in a current of steam.*

The rotating drum consists of a cylindrical vessel made of sheet metal. It turns on rollers, is closed at one end by a screw cover, and takes a charge of from 10 to 20 kg. of coal. At the other end the cylinder is provided with a dust separator and a stuffing-box through which the gas and tar vapours pass to a condenser. The drum is heated by gas, and the temperature is measured with the aid of a thermo-couple. With a charge of 15 kg. of gas flame coal, the drum yields 1·5 kg. of tar in two hours. We have been working with a furnace of this type since 1916, and have examined by its aid nearly all German coals and many coals from other countries. We have also applied this apparatus to the study of brown coal, peat, and oil shales.

(c) YIELDS OF PRIMARY TAR FROM COAL AND PEAT

The distillation of coal at the lowest possible temperatures, with a maximum of 450° to 500°, leaves a coke which contains practically the total nitrogen of the coal and about 10 per cent. volatile matter, *i.e.*, it still contains hydrogen compounds decomposable at higher temperatures with evolution of hydrogen. The tar and gas differ considerably from the corresponding high-temperature products. Tar is formed in much greater quantity and does not contain any aromatic compounds such as benzene, toluene, naphthalene or anthracene. The hydrocarbons of primary tar from all fuels resemble certain kinds of crude petroleum and are more or less rich in paraffin wax. Beside hydrocarbons, primary tars contain large quantities of phenols, which, with some kinds of coal, amount to more than 50 per cent.

Whilst the gas liquor in high-temperature carbonisation reacts alkaline owing to its ammonia content, the low-temperature liquor has an acid reaction,

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* The aluminium retort and rotary drum are supplied by Andreas Hofer, Mülheim-Ruhr, the mechanic of the Institute.

as most of the nitrogen remains chemically bound in the semi-coke, from which it can, however, subsequently be recovered in the form of ammonia by further heating or by gasification. The gas from low-temperature carbonisation is rich in hydrocarbons, especially methane, and reaches a calorific value of 9000 calories per cb.m. (1000 B.Th.U. per cub. ft.).

TABLE II

Yield of Primary Tar from various Bituminous Coals

Type of coal.	% Primary tar (dry).	Primary tar contains	
		Paraffin wax.	Phenols.
Lean coal	abt. 1·5	?	0
Fat coal	,, 3·5	1–2	15–20
Gas coal	,, 8	1–2	abt. 30
Gas flame coal	,, 12	1–2	,, 45
Cannel coal	,, 29	?	5–10

Table II shows the yields of low-temperature tars from different coals. The figures refer to low-temperature tar free of water, and to dry coal. Percentages of paraffin wax and phenol are also recorded.

It will be seen that bituminous coals proper, from lean coal to gas flame coal yield more primary tar the younger and hence the richer in oxygen they are, and that the primary tars contain more phenols the younger the coal from which they were prepared. The content of paraffin wax in the tar from bituminous coals ranges from 1 to 2 per cent. Cannel coal, essentially of sapropelic and not ulmic character, stands in a class by itself. It is comparatively rare in Germany, but more frequent in England. High-grade cannel coals yield up to 30 per cent. of primary tar, which, as regards its paraffin and low phenol percentage, differs from the tar from bituminous coals and resembles somewhat that from lignites.

TABLE III

Yield of Primary Tar from different Brown Coals

Kind of Coal.	Primary tar calc. for coal dried at 105°. %.	Primary tar contains		
		Paraffin wax. %.	Phenols. %.	Viscous neutral oils. %.
Saxon carbonising coal	24	29	15	17
Rhenish brown coal	7·6	13	36	15
Lignite	2·7	?	57	?

Table III relates to brown coals. Their higher paraffin wax and lower liquid phenol content is manifest from their pasty consistency at ordinary temperature. Unlike bituminous coal, brown coals give tars poorer in phenols and richer in paraffins as their total yield increases. This is clearly seen in Table III by comparing the Saxon carbonising coal with lignite.

In Table IV the yields of primary tars of different kinds of peat are recorded. The figures here vary as they do in the case of the lignites. The Lauchhammer peat, in particular, shows extraordinarily high tar yields.

TABLE IV

Yield of Primary Tar from different Peats

Kind of peat.	Primary tar calc. for peat dried at 105°. %.	Primary tar contains	
		Crude paraffin wax. %.	Phenols. %.
I. Fuel Peat from Velen (Westphalia)	12	—	—
II. Lauchhammer Peat :			
(*a*) Top Layer	18	14	14
(*b*) Middle Layer	17	13	13
(*c*) Bottom Layer	27	17	15

(*d*) PROXIMATE COMPOSITION OF PRIMARY TARS

Fig. 7 gives the composition of the primary tar of gas flame coal in diagrammatic form.[13] It shows at a glance that approximately half the tar consists of constituents soluble in alkali, mainly higher phenols and acid resins. The other half consists of neutral compounds and only about 1 per cent. of bases. On distillation at ordinary pressure, the constituents boiling above 300°, *i.e.*, more than half the tar, would undergo a far-reaching decomposition. It is therefore advisable to distil in vacuo or with superheated steam. The first fraction of about 10 per cent. is tar benzine boiling below 200°. The phenols, having been previously separated, there follow limpid oils, viscous neutral oils and

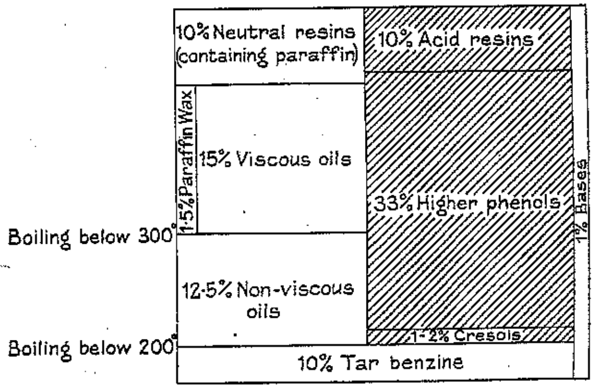

FIG. 7.

neutral paraffinoid resins in three nearly equal portions. The viscous oils deposit, on standing, scales of paraffin wax amounting to about 1·5 per cent. of the total tar. The detailed composition of the hydrocarbons, phenols and bases will be discussed later on.

In primary tar from a Saxon carbonising coal, as shown in Fig. 8,[14] crude paraffin wax amounts to about 32 per cent. instead of 1·5 per cent. in the case of gas flame coal. On the other hand, the phenols amount to only about a quarter or one-fifth of those from gas flame coal. The proportion of the limpid neutral oils is roughly doubled; that of the viscous neutral oils is approximately the same. The percentage of bases is in both cases equally small.

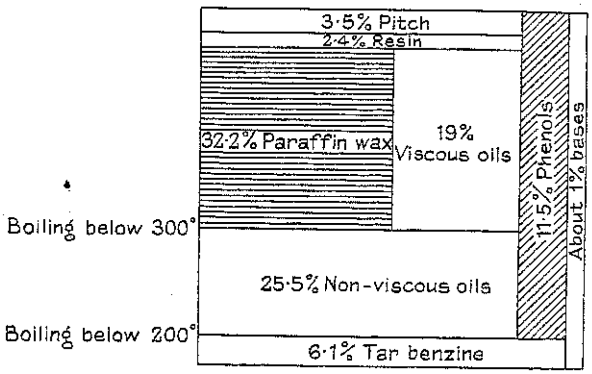

FIG. 8.

(e) THE TEMPERATURES REQUIRED FOR THE PRODUCTION OF PRIMARY TAR

Various statements have been made on the behaviour of coal when gradually heated. Börnstein[15] describes the behaviour of gas flame coal from the Graf Bismarck Colliery as follows :—

About 200°	Water first split off
200–225°	First oily distillate
300°	Copious evolution of water
310°	First evolution of volatile sulphur compounds
390–400°	Main distillation commences
410°	First combustible gas
420°	Strong evolution of gas.

Fritsche[16] reports on the yield of primary tar at different minimum temperatures. He heated the aluminium retort (Figs. 3 to 5) charged with 20 grams of coal at a constant rate of 10° per minute to the desired temperature, maintaining it until the evolution of gas ceased. Table V shows his results with Lohberg gas flame coal.

TABLE V

Lohberg Gas Flame Coal H_2O 2·9%, *Ash* 11·0%; *Used* 20 *grams*; *Rate of Heating* 10° *per min.*

Final temp. ° C.:	425	450	475	500	525	550	575	
Total yield of tar .	1·15	1·94	2·10	2·42	2·40	2·45	2·43	g.
Water of decomp. .	0·2	0·3	0·4	0·6	0·7	0·85	0·95	c.c.
Semi-coke . . .	17·62	16·48	16·11	16·46	15·20	14·83	14·65	g.
Primary gas (air-free), dry at N.T.P.	210	300	580	815	1060	1340	1440	c.c.

The bulk of the tar has come over at 450°, and the maximum yield is reached at 500°. Broche,[17] experimenting recently with a coal of the same origin, but less rich in tar, determined the periods required for securing the maximum tar yield at different temperatures. He heated the coal in the aluminium retort to a definite temperature and maintained it for a definite time. The experiment was then interrupted, and the tar yield determined. The figures of Table VI were thus obtained.

TABLE VI.

Tar Yields at different Temperatures according to Time

Temp. ° C.	%. After 20	%. 45	%. 60	%. 90	%. 180	%. 240	%. 300 minutes.
410	—	—	—	3·4	6·9	7·7	7·7
430	—	—	—	7·5	9·7	9·7	—
450	—	—	8·75	10·0	—	—	—
480	9·6	10·5	10·5	—	—	—	—
500	10·9	10·9	—	—	—	—	—

The table shows that down to 430° nearly the full tar yield is obtained, although the time required is ten times longer than at 500°. Nothing is known of the quality of these low-temperature tars, especially as regards their content of lubricating oils. Owing to the protracted heating they are not necessarily better than those obtained at 500°.

It should be pointed out that the heating periods at different temperatures relate only to the particular coal used, and that temperatures and duration of heating will vary for other coals, lignites and peats, according to their chemical composition. The examples show, at any rate, the course of tar formation at rising temperature and the minimum temperatures required for the highest