

PRODUCTS OF COAL (COKE, TAR, GAS) AND THEIR ANALYSIS

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Abstract - An essential portion of the coal output in the world is carbonized. The main product of the high-temperature carbonization is coke; in addition about 4% of the input coal is converted to tar and crude benzol (light oil); considerable quantities of gas are also produced. Carbonization at low temperatures also yields coke, tars and gases, but of a different composition and in different quantities. There is no doubt that low-temperature carbonization will be of more importance in future as a primary step for the production of formed coke, as well as for the preliminary degasification of power plant coal and coal to be gasified. The gasification of coal and coke to synthesis gas or synthetic natural gas (SNG), will be carried out increasingly and will be further improved. In addition to the production of fuel gases, mixtures of hydrogen and carbon monoxide are used for the synthesis of hydrocarbons, methanol and ammonia. Finally, an investigation has commenced on the direct hydrogenation of coal to test this process in pilot plants. There is also a wide range of products from soluble, but not distillable, extracts (e.g. SRC) via oils with different boiling points up to gases. Thus the processes of coal liquefaction offer the future possibility of producing easily applicable and non-polluting fuels, motor fuels and raw material for the chemical industry. With the aforementioned four processes of coal refining, analytical requirements play an important part. Gases; distillable oils and tars; soluble, but low-volatile extracts; and pitches, as well as cokes must be analyzed. Their optimum production and utilization depends on an exact knowledge of their properties.

The world coal production amounts to more than 2000 million tons yearly, of which the major proportion is used for conversion into electric power or for heat generation. Of the remainder, some 500 million tons are carbonized and used in steel production; thus, generally speaking, providing the basis of modern technology. Coal is utilized to a lesser extent as a raw material for the production of gases which, in turn, are used for heating purposes or for synthesis in ammonia, alcohol, and hydrocarbon manufacturing processes. In this respect, let me at this point stress the outstanding technical achievements of South Africa at Sasol. Finally, in view of the expected reduction in mineral oil supplies, efforts to liquefy coal by direct hydrogenation are being revived.

In all these processes, analyses play a major role; for example, in the combustion of coal for the production of heat or electric power, analyses are necessary to monitor plant operations. During recent years, the requirements of environmental protection have become considerably more rigid in order to reduce emission of sulphur dioxide, nitrogen oxides and other toxic substances. Moreover, power plant operation in itself raises analytical problems, e.g. the composition of coal ashes, their relevant effects on boiler parts and their sedimentation and melting behaviour. These aspects, however, will not be the subject of my paper. I will concentrate instead on cokes, tars, hydrogenation products and useful gases.

Coke production is the main objective of high temperature carbonization carried out on a commercial scale all over the world. Its quality must be adapted for optimum use under blast-furnace conditions or for other specific applications. Valuable by-products of high temperature carbonization are about 3% tar and 1% crude benzol as well as considerable quantities of gas. Low temperature carbonization yields chars, tars and gases of different composition. The

tars obtained as by-products in coal gasification processes, designed for the production of synthesis gas or a natural gas substitute, are rather similar to tars from low temperature carbonization.

Some decades ago, hydrocracking of hard and brown coal was extensively carried out in Germany on a production scale. During world-war II, Germany manufactured some 4 million tons of motor fuel per year by this means. Today, many countries, namely, the United States, the United Kingdom, Japan, India, Poland, South Africa and Germany, are trying to improve these techniques - either by laboratory or pilot plant investigations - and adapt them to modern requirements. The objectives of these efforts are rather diverse and include the manufacture of soluble although not distillable extracts, oils of various boiling ranges including refinery feedstocks, motor fuel and chemical raw materials. By-products of these processes are hydrocarbon gases on the one hand and insoluble residues on the other.

A prerequisite for optimizing these processes and for utilizing the main products and by-products is a precise analysis of the products. Appropriate analytical methods may be subdivided into three categories corresponding to the physical state of the samples, i.e. cokes, oils (including extracts), and gases.

Table 1. Processes of coal utilization

Process	Solid	Liquid	Gaseous
Pyrolysis	Coke	Tar	Coke oven gas Low temperature carbonization gas
Hydrogenation and extraction	Residue	Extracts oils	Hydrocarbon gases
Gasification		Tar	Synthesis gas Methane

1. Coke

Coke may be defined as the highly carbonaceous residue from the thermal decomposition of organic substances. The pyrolysis of hard coal at temperatures above 1000°C yields high temperature coke which is mainly used in blast-furnaces as an ore-reducing agent.

Table 2. Comparison of the total analysis of coking coal and coke

	Coking coal	Coke
	% d.a.f.	% d.a.f.
Carbon	87.0 - 90.0	97.5 - 97.8
Hydrogen	5.0 - 4.5	0.2 - 0.5
Oxygen	4.5 - 3.2	0.2 - 0.7
Nitrogen	1.8 - 1.0	1.0 - 1.4
Sulphur	1.8 - 0.6	0.5 - 0.9

From a chemical point of view, pyrolysis is a decomposition during which hydrogen, initially bound to the coal, is evolved as such or in the form of volatile compounds. These volatile compounds (tar, crude benzol, water, and coke oven gas) contain, moreover, the major proportion of oxygen initially bound in the coal and also a proportion of its sulphur and nitrogen.

Table 3. Coking plant output (percentages refer to dry coal and coke)

Coke	79%
Tar and crude benzol	4%
Gas	12%
Water	4%

For use as blast-furnace coke, foundry coke, in the chemical industry (e.g. manufacture of carbide, silicon, phosphorus) and for gas generation, coke has to meet certain quality requirements which are subject to permanent controls. The ash, water and volatile contents of coke are analysed. Water in coke originates from quenching and generally amounts to about 3% to 5%. Ash contents of coke should be as low as possible (the average is 8% to 10%). As a result of thermal treatment in the coke oven, high temperature coke retains hardly any volatiles, on average only about 1%.

TABLE 4. Properties of blast-furnace coke (Germany)

Grain size:	about 40 - 80 mm
Mechanical strength:	
Drum test:	> 78%
Abrasion:	< 10%
Humidity:	3 - 5%
Ash:	8 - 10%
Sulphur:	0.7 - 0.9%
Alkali:	0.2 - 0.3%

Whereas the feed coal generally contains more than 1% sulphur, the corresponding value for high temperature coke is approximately 0.7 to 0.9%. As a result of the high temperature carbonization the sulphur linkages in coke differ from those in coal. Pyrite, initially present in the coal, is decomposed. Most of the sulphur is bound in the carbon structure of the coke but there is also some sulphur present as sulphide compounds.

The ash composition as well as the sulphur content of the coke plays an important part in the reduction of ores.

TABLE 5. Composition of coke ashes (Germany)

Silicon oxide	38 - 48%
Aluminium oxide	27 - 32%
Iron oxide	8 - 18%
Calcium oxide	2 - 8%
Magnesium oxide	1 - 3%
Potassium oxide	1 - 4%
Sodium oxide	1%

The composition of the ash affects both the behaviour of blast-furnace slag and the furnace performance. The alkali content should be low. The phosphorus content should also be low because it affects the quality of the pig-iron; phosphorus accounts for some 0.2 to 0.3% of coke ashes.

Lump size and mechanical strength as well as the bulk density of coke are of specific importance. Grain sizes of blast-furnace cokes are approximately 40 - 80 mm. Mechanical strength is determined by conventional procedures, e.g. by drum test in the Micum drum. After the application of mechanical load the percentage of grain sizes over 40 mm obtained should be as high as possible, whereas the proportion under 10 mm should be as small as possible. Depending on the grain size the bulk density of coke may vary from 400 to 500 kg/m³. Other characteristic features are reactivity, coke structure, and the degree of anisotropy.

Low temperature carbonization within the range of 600 to 800°C yields specific cokes characterized by a higher reactivity and higher volatiles content.

Carbonization of tar pitches from hard coal is also carried out on a commercial scale and yields special cokes of low ash contents suitable for making electrodes. Coal extracts can be carbonized in a similar way by a process which may become important in the future.

2. Liquid products from coal(a) Crude benzol

As shown in Table 3, crude benzol and tar (accounting for about 4% of the coal) are obtained as by-products of coke production. The respective proportions are three parts of tar to one of crude benzol. The latter may be defined as the light oil which due to its partial vapour pressure is not condensed and separated from the cooled coke oven gas. Crude benzol must therefore be obtained by secondary measures, such as oil scrubbing, adsorption on activated cokes or by cooling the gas down to very low temperatures. Only a small percentage is condensed with the tar. The crude benzol has a boiling point below 180°C and consists mainly of monocyclic aromatic hydrocarbons. German coking plants mostly resort to scrubbing with certain tar fractions from which the crude benzol is subsequently separated by distillation. Its composition is given in Table 6.

TABLE 6. Composition of a semi-finished benzol

Non aromatic substances	3.9%
Benzene	61.7%
Thiophene and derivatives	0.5%
Toluene	16.9%
Ethyl benzene and xylenes	7.5%
Trimethyl benzene, methylethyl benzene, styrene, dicyclopentadiene and methyl styrenes	4.2%
n-butyl benzene	0.2%
Indane, indene and coumarone	3.2%
Benzonitrile	0.2%
Naphthalene and methyl naphthalene	1.5%

This crude benzol is pressure-refined over a catalyst, whereby the unsaturated compounds are converted into saturated ones and most of the oxygen, nitrogen, and sulphur are removed in the form of water, ammonia, and hydrogen sulphide respectively. A product obtained by pressure refining may have the following composition:

TABLE 7. Composition of the product obtained by pressure refining

Non aromatic substances	1.5%
Benzene	72.4%
Toluene	16.6%
Ethyl benzene and xylenes	7.2%
Other alkyl benzenes	0.8%
Indane	1 %
Tetralin	0.2%

Benzene, which is much in demand as a raw material for the chemical industry, is the main product obtained by this pressure refining. The remainder serves as an additive for motor fuels or is further treated to yield refined products. These products are characterized by their boiling point range. Identification of the constituent compounds, however, necessitates the use of gas chromatography by methods similar to those used in the mineral oil industry.

(b) Tar

The tar yield is about 3% of the feed coal carbonized, and consists of a mixture of polycyclic aromatic hydrocarbons mostly boiling above 180°C, which separate by condensation from the cooled gases leaving the coke ovens. Uses for these high temperature tars differ greatly among the various countries. In the highly industrialized regions of Europe, tars from coking plants are collected and treated centrally in big tar distillation plants. They yield pure products

which are required by the chemical industry as raw material primarily for paints. One may even say that more than a century ago the development of the chemical industry was started by the utilization of these products. Some tar fractions serve as special solvents; others as primary material for the manufacture of carbon black, electrode coke, impregnating agents, roofing materials, adhesives, etc.

The analysis of tars still follows classical methods, e.g. determination of density, water content, and boiling point curve. Extraction, crystallization, polymerization, solvent fractionation, carbonization and elemental analysis yield additional data. Most coking plant tars are of high density, i.e. above 1.14. On distillation, tar is fractionated as follows:

up to 180°C	light oil
180 - 230°C	medium oil
230 - 270°C	heavy oil
beyond 270°C	anthracene oil
distillation residue	pitch

Successive extraction of the various fractions with aqueous sodium hydroxide and sulphuric acid gives respectively the content of acid compounds (most phenols) and of basic compounds (pyridine, quinoline and their derivatives).

In tar analysis, gas chromatography nowadays plays a major role. By this method the distillable part can be characterized. Gas chromatography has also been highly developed for identifying the acidic and basic components of the tar. Paper chromatography and thin layer chromatography are also still in use. Likewise ultraviolet spectroscopy plays an important role since these are aromatic compounds; fluorescence spectroscopy and phosphorimetry are also useful.

As far as the distillable fractions of high temperature tars are concerned, their composition is relatively simple due to their purely aromatic nature. Thus, one third of the total tar consists merely of 12 compounds, each of which represents more than 1% in the tar.

TABLE 8. Main components of high temperature tar

Compound	Average contents in crude tar
Naphthalene	10 %
Phenanthrene	5 %
Fluoranthene	3.3%
Pyrene	2.1%
Acenaphthylene	2.0%
Fluorene	2.0%
Chrysene	2.0%
Anthracene	1.8%
Carbazole	1.5%
2-methyl naphthalene	1.5%
Diphenylene oxide	1.0%
Indene	1.0%

Other important hard coal tar compounds are: phenol, cresols, quinoline, indole, dimethyl phenols, pyridine, picoline, etc. Pitch, which accounts for about 50% in the tar, contains thousands of chemical components, only some of which have been identified.

(c) Extracts and oils

Whereas pyrolysis of hard and brown coal yields only limited quantities of liquids, coal extraction and direct coal hydrogenation, give high yields of soluble, fusible and liquid products. Coal is almost insoluble in most solvents. Only by extraction with hydrogenating solvents (e.g. Pott-Broche process) does it yield soluble products which are, however, still of relatively high molecular weight and are solid at room temperatures. Hydrogenation with limited quantities of molecular hydrogen at high temperatures and pressures can decompose the coal to a somewhat greater extent. Finally, hydrogenation with greater quantities of hydrogen (as practised in the "slurry phase" of the Bergius-Pier process) yields directly a mixture of oils having a wide boiling range. This process was applied on a large scale in the UK and Germany more than 30 years ago. The oils thus obtained were then further decomposed by a second hydrogenation step, the so-called gaseous phase, and refined to yield motor fuel.

Coal hydrogenation at high temperature involves a multitude of hydrogenating and cracking reactions whereby, with increasing severity of hydrogenation conditions (pressure and temperature), products with progressively lower boiling point and lower sulphur content are obtained. As shown in Figure 1 coal becomes soluble by reaction with about 1% hydrogen; but in order to render more than half of the solubilized coal distillable, reaction with over 4% hydrogen is required. On reacting with more than 8% hydrogen, most of the coal is converted into medium distillates, light oil and gases.

In many countries today pilot plants are being run with various objectives. In some, the aim is to manufacture fuel oils low in sulphur and ash, in others to manufacture motor fuel - as we did earlier in Germany. Others are attempting to provide further sources of material for the chemical industry, particularly the production of aromatic hydrocarbons.

I do not wish to discuss in detail the analysis of the hydrogenation products, the more so as none of the techniques has taken precedence over the others. Moreover, the hydrogenation products depend on such factors as the feed coal, pressure, temperature, catalysts, times of residence and other parameters, all of which can differ from one process to another. A common feature of all the analytical developments, however, is that the products are analysed by methods derived from those used for petroleum analysis.

3. Gas from coal

Whereas in pyrolytic and hydrogenation processes gases are obtained only as by-products, gases are the main objective of coal gasification.

Commercial high temperature carbonization of hard coal yields, besides 4% water, some 12% gas with the following analysis:

TABLE 9. Coke oven gas

	% by volume
Carbon dioxide	1.5 to 2.5
Carbon monoxide	4.6 to 5.8
Hydrogen	55 to 64
Methane	25 to 27
C_nH_m	2 to 4
Hydrogen sulphide	0.3 to 3.0
Carbon bisulphide	0.016
Sulphide of carbon monoxide	0.009
Mercaptans	0.003
Ammonia	~ 1.1
Hydrocyanic acid	0.1 to 0.25
Nitrogen oxide	0.0001

As can be seen, coke oven gas consists mainly of hydrogen and methane. Numerous sulphur and nitrogen containing impurities must be removed. Before the hydrogen from coke oven gas can be utilized for chemical purposes, e.g. for

ammonia production or for hydrogenation with sulphur-sensitive catalysts, further expensive purification steps are required. There are excellent methods available for gas analysis for the determination of even minor impurities; these methods are chemical procedures, such as precipitation methods, and physical methods like gas chromatography and mass spectrometry.

In addition to unreacted hydrogen, the by-product gases of coal hydrogenation contain methane in particular and other hydrocarbon gases, water, hydrogen sulphide, and ammonia. As previously mentioned, the gas yields increase with increasing severity of hydrogenation.

Many processes are available for gasifying coals or coke. As gasification with steam is endothermic the heat required is obtained by burning part of the fuel in air or oxygen. Due to the high nitrogen content, gasification with air yields lean gases of low calorific value. Synthesis gases serving as a feedstock for chemical processes (e.g. for ammonia, methanol, hydrocarbons, or methane production) require oxygen as gasifying agent. A recent suggestion has been to gasify the coal oils by an allothermic process, i.e. with heat from a heat exchanger for which purpose heat from high temperature nuclear power plants is ideally suited. Pressure gasification normally results in higher methane contents, apart from the primarily produced hydrogen/carbon monoxide mixture. The following table shows two examples of gas composition for different gasification conditions.

TABLE 10. Gasification of coal and coke

	CO ₂	C _n H _m	CO	CH ₄	H ₂	N ₂
Revolving grate producer with coke + air	3.6	-	27.8	0.2	12.4	56.0
Lurgi pressure gasifier with high volatile bituminous coal + oxygen	29.2	0.5	18.5	10.0	41.1	0.7

In South Africa gasification in the Lurgi pressure gasifier is carried out on a large scale as a preliminary step of the hydrocarbon synthesis. The Koppers-Totzek dust gasification process also has technical merits. Other processes are currently under trial.

Gases similar to natural gas may be obtained either from synthesis gas or by gasification with hydrogen. They contain, as does coke oven gas, sulphur and nitrogen compounds as impurities which must be removed to an extent depending on the utilization of the gas.

For all gasification processes, analytical methods are of essential importance both for controlling and monitoring these processes and for the further utilization of the gases.

4. Conclusion

I have tried to give you a brief summary of the technologies used to produce cokes, extracts, tars, oils and gases from coals. Coals are naturally occurring substances which have developed from vegetable matter over millions of years in an evolution we are unable to reproduce and which has remained largely unknown. Difficulties arise immediately with any attempt to define the structures of the original vegetable matter. The structure of the evolved products, which we call "coals", are even more complex.

The products formed in the processes I have described and which generally are or will be of technical relevance, need varying efforts to analyse them. Coke, whose main constituent is carbon, as well as the gases, which consist mainly of hydrogen, carbon monoxide and some light hydrocarbons, are relatively easy to analyse. Extracts, tars and oils, however, whose composition is nearly as complex as that of the original coals, present the toughest analytical problems.

For operative monitoring or control of the processes it may often be decisive to obtain analyses either continuously or at short intervals. In this field, essential progress has been achieved quite recently, particularly with physical methods. Many problems remain, however, to be solved by the analyst, in respect of process control, monitoring and structural analysis.

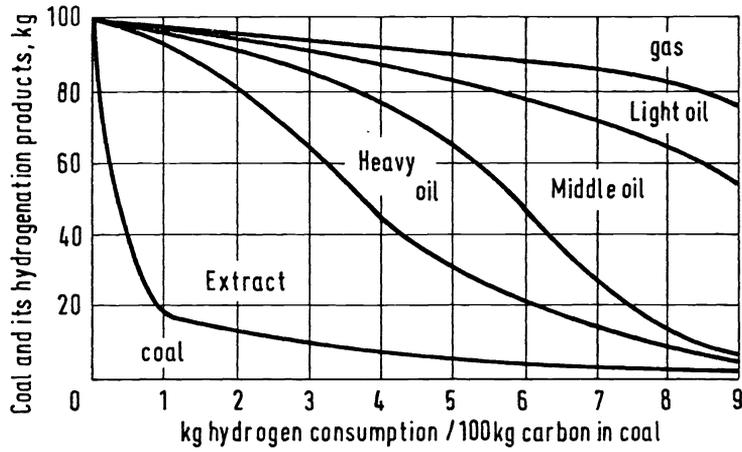


Figure 1. Sump phase hydrogenation of coal (output and hydrogen consumption)