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Kinetics of the Rapid Degasification of Coals

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1. Introduction

In form of the so-called "LR-Process", developed in team-work by "Lurgi Gesellschaft für Wärmetechnik mbH" in Frankfurt and "Ruhrgas AG" in Essen, the rapid degasification of coal has obtained technical importance.

The basic phenomena of the rapid degasification of coal has been investigated in the laboratory-scale in essential with an equipment shown in figure 1. The most important part of this equipment is the degasification mixing chamber (b). After heating up, the fine-grained heat carriers (coke or sand) are placed into the reactor (b). Immediately behind the inlet of heat carriers, coal of the same granulation is fed into the mixing chamber. Due to the high mixing ratio of heat carriers to coal (about 30 to 6 : 1), each individual coal grain is very rapidly heated and degasified. As the gas development takes place spontaneously and as the mixing chamber is fairly small, the period of sojourn is less than 0.5 sec. After discharge, the products are immediately chilled and partly condensated (f to h). The char coke is transported from the second degasification reactor (d) into the collection reactor (a), from which it is fed, a little overheated, as a heat carrier again to the mixing chamber (b).

The rapid heating and cooling of the products causes a much higher yield of tar. This so-called "rapid degasification effect" is of great interest for the research of coal. It will be the object of this paper to describe the physical-chemical phenomena of this effect. Studying these phenomena, it will be possible not only to describe the reaction kinetics of the rapid degasification, but to draw also some conclusions therefrom on the structure of the substance of coal.

2.1. Heating-up speed of the coal

With the high mixing ratio of heat-carrier:coal, the coal grain, immediately after its entry into the degasification mixing chamber, is surrounded after intensive mixing by hot heat carriers. At the same time it is heated-up presumably very quickly. As it is very difficult to measure the heating-up speed directly, one must fall back on calculations.

The second figure shows the calculated curves at the surface and in the centre of a 1.2 mm \varnothing coal grain with two different heat transmission ratio related to the temperature of the heat carriers. The heat transmission ratio, of course, is of decisive importance. With a slow heat transmission, the difference between the temperature at the surface and in the centre of the coal grain is relatively small but with a rapid heat transmission it is quite high. This fact will play an important part.

Which of the curves plotted on the figure will most approximate the

true state of affairs, can be decided more easily, when the temporal yield of the degasification products is known, as the thermal diffusivity and the heat transmission ratio cannot be measured directly.

Of these investigations, a mixing chamber with a continuous feeding of coal appeared to be unsuitable. Therefore, a pilot equipment (figure 3) was built which corresponded sufficiently exactly to the conditions in the technical degasification mixing chamber.

A cylindrical tube of 80 mm inside diameter constantly heated from the outside is equipped with a stirring rod with pins. Half of the chamber is filled with fine chips of corundum as a heat carrier. For the test, a sample of coal is blown with nitrogen into the chamber and the time is precisely recorded. An ignitor directly at the free outlet of the gas brings the degasification products leaving the chamber to combustion. The size of the flame is an approximate measure for the quantity of the gases and tar fumes. The flames are photographed together with a watch showing the time in short intervals. Figure 4 shows a series of pictures taken of coking coal grains of the size 1 to 1.5 mm, the temperature of the heat carriers amounting to about 1000 °C. The seconds recorded underneath the photos are counted as from the impact of the coal grains to the corundum chips onwards.

After 0.37 seconds in phase two, a high flame can be seen which, however, is falsified by the nitrogen which still flows out. After that, the cone of the flame is much reduced. Comparing this observation with the calculated temperatures of the coal in fig. 2, much more can now be said about the heating-up process. When coal is heated, the first combustible degasification products develop at a temperature of about 350 °C. Real degasification becoming visible in phase 2, however, occurs at a temperature of 400 °C at the earliest. That means that, after 0.37 seconds, the coal must have temperatures of above 400 °C at its surface. According to fig. 4, a temperature of 400 °C at the surface, i.e. the value $\delta = 0.4$, is reached with a heat transmission coefficient of $\alpha = 100 \text{ kcal/m}^2 \text{ h}^\circ\text{C}$, in 5 seconds only. In practice, the heat transmission coefficient must be much higher. With $\alpha = 1000 \text{ kcal/h m}^2$, 400 °C at the surface will be reached in 0.28 seconds. It can be assumed, however, that degasification started much earlier so that heat transmission coefficients of at least $\alpha = 1000$ can be reckoned with. The further development of the heating-up curves agrees with the series of pictures, too. This leads to important consequences. With such a high heat transmission coefficient, a steep temperature gradient must be given in the inside of the grain. The reactions of degasification begin at the outside of the grain, when there are still nearly initial temperatures (30 °C) in the inside. The temperature of beginning decomposition in the centre is attained only, when after-coking temperatures have been reached at the surface of the grain already and when the gas yield is already strongly decreasing, as fig. 4 shows.

These rather qualitative statements show clearly that the reactions of degasification and the heating-up are much interdependent. This becomes evident also when lower temperatures of the heat carriers are applied, thus decelerating degasification with the result that more details show up from the diagram. This test can be seen from fig. 5. The phases 2 to 4 give reason to assume, that, during the main phase of degasification, the yield of products is nearly constant. This, however, would again indicate the particular importance of the heat transmission.

2.2. Speed of degasification

The extremely rapid heating of the coal with this process promised interesting results with regard to the structure of the substance of coal. The equipment shown in fig. 3 proved to be suitable for such tests, too. However, different devices for the quantitative recording of the temporal yield of the products of degasification had to be connected to the gas outlet. A difference was made between the products condensated at room temperature and gaseous products which were measured, for experimental reasons, separately in parallel tests. The diagrams in the two following figures show the yield of products as a function of the time of sojourn of the coal in the degasification chamber. For instance, figure 6 shows the tar yield of three different coals and figure 7 the gas yield at different temperatures.

The curves of the gaseous products and the condensate products are added, at last, to the degasification curves plotted in fig. 8 for different temperatures.

All these curves show one and the same characteristic development: a linear start until 60 to 70 % of the products have been released, then a bend and, finally, an asymptotic development into the horizontal. After the main yield of products, relatively more gas is increasingly released than tar and, in the development of the curve behind the bend, practically gases with a low molecular weight only are released. Summing up, it can be stated:

With rapid heating, the so-called "rapid degasification" is a reaction of zero order which ends in a different process of second degasification. This statement may be surprising as the coal pyrolysis is composed of decomposition reactions of first order. That we had to do with quite a different process, is proved by the energy of activation found to amount to 2.5 kcal/Mol (1) which is by 10 to 20 times smaller than the values known so far. This low energy of activation is an argument against the assumption that the reactions of decomposition determine the speed.

Presumably, a mutual dependence of transporting processes is decisive for the rapid degasification. A transmission of heat from the heat carriers to the coal and the endothermal degasification process are joined with each other by the flow-off of the degasification products which hinder the inlet of heat. These two processes give an equilibrium as long as still efficient substance for degasification is available in the coal grain.

As for the dependence of the speed of degasification on the temperature of degasification and the grain size, the following equation for the yield of products M is obtained, considering the fact that we have to do with the reaction of zero order:

$$M = 0,03 (T_a - 330) d^{-0,26} t$$

in which M means the yield of products in % (by weight), T_a the temperature of degasification in °C, d the grain size in mm and t the time of reaction in seconds (1).

The interpretation of the equation is rendered easier by the fact that the drying of coke represents a similar process. Therefore, processes for the drying of coke were carried out in a modified

degasification mixing chamber. Figure 9 shows clearly, how much the two processes are related to each other. In both cases, there is again the initial straight characterising a stationary process of evaporation, a bend in the curve and, at the end, an asymptotic turn into the horizontal.

The yield of water vapour from the drying of coke was calculated in the same way as the yield of gas and tar from the rapid degasification of coal. This led to the formula (1)

$$M = 0.029 (T - 83) d^{-0.65} t.$$

Again, there is an analogy which gives reason to assume that the two processes are still much more similar than can be recognized directly:

Thus, the rapid degasification of coal represents a process of evaporation the same as a drying process.

The above expositions lead to the following summarizing picture of the degasification processes:

Figure 10 shows the development of the degasification curve in time as well as the calculated temperatures of the coal grain. At first, a fresh coal grain is very rapidly heated up under the influence of the hot heat carriers. After about 0.2 seconds, the surface of the grain reaches a temperature of about 350 °C. The primary bitumen which is then formed, begins to evaporate from the surface. With further heating, more primary bitumen is brought to the surface of the coal grains and evaporates there. The released distillation products now hinder the transmission of heat, and there is an equilibrium of the two processes opposed to each other: with a constant boiling temperature the same quantity of heat per time unit thus flows to the surface from which the bitumen evaporates in constant quantities. During this period, temperature does not increase any more as the amount of new heat covers just the demand for evaporation heat, except the negligible amount flowing-off into the inside of the grain for heating up. A balance of temperature in the grain is established only after a good second.

When not enough primary bitumen flows to the surface of the coal grain any more, the front of evaporation is shifted concentrically to the inside of the grain. This does not yet mean a disturbance of the equilibrium, as the good heat conductivity of the coke affords a good transmission of heat. Besides, the coarse pores of the coke do not offer much flow resistance to the vaporous product. When the front of evaporation shifted far enough to the inside, the equilibrium is disturbed and the curve begins to bend, until the yield of products decreases much in the last course of the curve. In the final phase, the outside zones of the grain heat up essentially. During this process, semi-coke is forming, with the release of gaseous products. Finally, the temperature adapts itself everywhere to the temperature of the heat carriers.

3. Yields of degasification

The evaporating substance, called "primary bitumen" in this paper, must not exist necessarily in the coal in the same way. We try to clarify this question by investigation of the degasification products, especially of the tar. In doing so, it was not so much the intention

to identify as many individual substances as possible but rather to obtain a good review of larger complexes of substances.

For the purpose of comparison with products obtained under normal conditions of the pyrolysis of coal, tars were analysed which had been made in the Fischer-retort from the same coal. This was thus a tar which had been formed at a much slower heating-up speed ($12^{\circ}\text{C}/\text{min}$) and a much longer time of sojourn in the reaction room.

The two tars were made at a temperature of 600°C as we obtained at this temperature the highest yield of tar as reported elsewhere (2). Investigations about secondary reactions led us to assume that the decompositions occurring during these reactions at this temperature are much suppressed. But this question, too, can be explained in the following.

The pronounced differences between both methods of degasification become visible already in the next table (fig. 11). Particularly striking is the high yield of tar with the rapid degasification. With the gasification according to Fischer, however, the yield of gas and coke is higher as the longer influence of heat caused, in this case, a cracking and coking of the tar. Very different fractions are obtained from the vacuum distillation of both tars. By virtue of the cracking, the tar according to the Fischer degasification possesses a high fraction of light oil, whereas the tar from the rapid degasification process has the highest yield of pitch. The last column of the table shows the quotient of the different yields from both methods of pyrolysis. According to these figures, the tar products from the rapid degasification process have a much higher molecular weight. This could be determined, however, so far only with regard to the total yield of tar.

3.1. Composition of tar

The tars obtained were not to be treated with the usual methods. Therefore, methods of analysis had to be developed which separated the tar products under most mild and gentle conditions, as the tar, already from its origination, is most sensitive against thermal and chemical influences. It is thus very difficult to elaborate suitable methods.

A scheme for the entire preparation of tar in fig. 12 shows, how many steps were required to obtain fractions which could be assumed for the gas chromatographic analysis (4). It proved to be impossible to separate further the undistillable residues of pitch. Therefore, we carried out, after a further extraction, a structural analysis according to van Krevelen (6).

Surely, it would lead too far to mention all results of tar investigations in this paper. It is hoped, however, that the following data of analysis will contribute to elucidate the problem. It is sufficiently known that the pyrolysis of coal is composed of several part reactions which take place partly parallel to each other and partly subsequent to each other. The primary products represent large molecular units which are decomposed in the secondary process into fragments of different sizes. In the end, larger units can develop again by polymerisation and condensation. The composition of the final products depends decisively on the pre-set conditions for the secondary reactions. Especially temperature and the time of reaction are of great importance.

Kröger (3) showed in a paper about the structure of coal macerals that the substance of coal is made up of at least three main complexes of groups of material. These are at first the group of waxes and resins, secondly the group of oxyhumic components and, finally, the group of dehydrohumic substances.

Kröger presumes that the coal represents a structure of solid material built up of many cells, into which bituminous coal components are embedded. He proved this by microscopical photos of a vitrinite before and after cauterization with dimethylformamid. A solvent shows clearly the structure of the cells of the otherwise structureless vitrinite after cauterization. During this process, the material inside the cells (waxes, resins, oxyhumines) - which are probably connected to the skeleton of the cells not without any bonding but also through functional groups - , are released.

If such a structure of cells is slowly heated, gaseous products are formed in the individual cells leading to excess pressure and diffusing to the outside through fissures and pore passages. How far there will be secondary reactions, depends on several parameters such as the structure of the cells and of the pore system as well as type and manner of thermal treatment. Due to such factors of influence, there will always be a different composition of the products of degasification,

With a very rapid heating of the coal, the pressure inside a cell increases very quickly. Then, the walls of the cells are torn up at weak points and the contents of the cells are so rapidly distilled that a cracking and reaction of the material is hardly still possible. On the other hand, it can be observed, that certain groups of substances are decomposed into smaller fragments at the prevailing relatively high temperatures already at extremely short times of sojourn. According to this idea of the process of pyrolysis, it can now be concluded from comparison between the yields of tar obtained from the rapid degasification process and of tar obtained from the Fischer process how these two processes act on the composition of such tars.

As the individual chemical compounds are very different indeed, it is preferable to evaluate them separately, viz. in the condition how they were obtained from the primary separation. In doing so, it is practical to limit this evaluation to the neutral components, moreover as this fraction is the largest. Then, the main two groups are obtained within this fraction: the aliphatic and the aromatic components. The values found by the urea method are partly very significant. Figure 13 shows the yield of aliphates. With hydrocarbons with 14 and 20 C-numbers, there are clearly two maxima which are a little higher for the tar obtained by the Fischer analysis. With high C-numbers, the curve of the tar obtained by the rapid degasification process, however, lies essentially above that for the tar obtained by the Fischer analysis. As products would be proved only up to the C-number of 31, it can hardly be assumed that there will be much longer chains in the substance of coal. There must be mainly hydrocarbons with C-numbers of 20 to 25 in the coal assumed for the tests. The maxima at a C-number of 14 indicate reactions of decomposition of the long chains into 2 halves. This does not mean, of course, that the lower hydrocarbons are formed only by reactions of separation. On the contrary, it must be assumed that these aliphates exist already in the substance of coal in form of waxes of vegetable origin.

By thermal treatment, the paraffins are distilled and diffused from the structure of the cells to the outside. With a "slow heating", they distill successively when reaching their boiling temperatures. With "rapid heating", however, the substances are at once exposed to high temperatures, at which they split up. Only the long-chain hydrocarbons, the boiling points of which lie at higher temperatures, are hardly decomposed. With the Fischer analysis, the longer time of sojourn leads to a cracking into smaller fragments. Therefore, the yields of these hydrocarbons with the slower degasification are lower.

It was much more difficult to determine the aromatic components as shown by a gas chromatogram of a fraction (fig. 14). Both tars contained nearly the same substances, of course, with different concentrations. A clear representation of the percentages of substances is given in the following picture (15), where the percentages of the individual ring systems of both tars have been plotted. Under the conditions of the "rapid degasification", the 3-ring-system arises preferably, whereas mostly 4 rings occur with the "slow" degasification. Besides, the percentage of substituted components of more than 50 % with the rapid degasification process is much higher than the percentage of only about 27 % with compounds obtained from the Fischer analysis.

It has been proved elsewhere (4) that these substances come from the resin in the coal. During the thermal treatment, this component is subject to reactions of decomposition and condensation. As mainly 3- and 4-ring-system could be found in these reactions which can be assigned to the base molecules of resins, the effects of secondary reactions can be small only. Due to the longer time of sojourn in the hot reaction chamber, the reactions of condensation of the tar obtained from the Fischer analysis are more progressed than for the tar obtained from the rapid degasification process. Therefore, the maximum of the ring distribution is with the 4-ring-system. Apart from the reaction of condensation, the low yield of alkylated aromates gives reason to assume stronger reactions of decomposition.

In order to investigate also the high amount of pitch in the tar obtained from the rapid degasification process, a structural analysis of the fractions obtained according to van Krevelen (6) was carried out. The median ring size calculated by this method has been plotted in fig. 16 in percentages. The maximum at the 10-ring-system shows that this is a much higher condensed system. This is indicated also by the median molecular weights between 140 and 554 found by experiment.

As such high molecular units, surely, are not released unchanged from the substance of coal, it can be assumed that the composition of the pitch is much more determined by secondary reactions than the composition of the liquid tar. This is due, above all, to the above mentioned reactions of condensation which, at a sufficiently long time of sojourn, progress to an extent that macromolecules develop which can no more be distilled and coked in the course of the degasification process even if temperature would be further increased. This can be easily derived from the following table (fig. 17). According to this table, 122.9 g of the pitch formed by the rapid degasification of 1 kg coal, has been changed with the degasification according to Fischer secondarily into 98.9 g of coke and 24 g of gaseous products.

The longer period of heat influence with the degasification process according to Fischer thus led to an intensified condensation and decomposition. The macromolecules developed during this process were coked. During the rapid degasification process, however, the reactions of condensation could be interrupted at an early stage by a quick discharge of the degasification products.

These results of investigation are in accordance with the assumption that tar is principally formed by the wax-resin-component of the coal. According to a calculation described by Kröger (5), it could be shown that this complex of substances is being obtained, with the rapid degasification process, nearly entirely in the form of tar, whereas the yield of products obtained by the Fischer analysis is far below the calculated values.

Thus, it is possible by means of the rapid degasification process to obtain this basic complex of the coal completely in the form of tar. It is true, that the degasification products are not portions of the original substances of coal but represent the primary bitumen developed during the primary decomposition of the coal. The primary bitumen is only a little changed by secondary reactions as they are tied up at an early stage by the quick discharge of the degasification products.

4. Summary

By virtue of these results of investigation, the reactions during the rapid degasification of coal can be explained as follows:

Under the conditions of rapid degasification, notably the heating speed at the coal grain and the quick discharge of degasification products, primary bitumen is obtained which developed from the coal during the primary decomposition. During this process, the same regularities prevail as with any process of evaporation.

The substance, most of which are to be assigned to the wax-resin-component of the coal, can be completely evaporated by this process. To which extent the primary bitumen is being changed by secondary reactions, depends especially on the pre-set temperature of the heat carriers. The tests showed that the maximum of the tar yield is obtained at a temperature of about 600 °C.

After numerous analyses of the degasification products evaporated at this temperatures, it can be stated that the substances obtained are hardly decomposed by secondary reactions.

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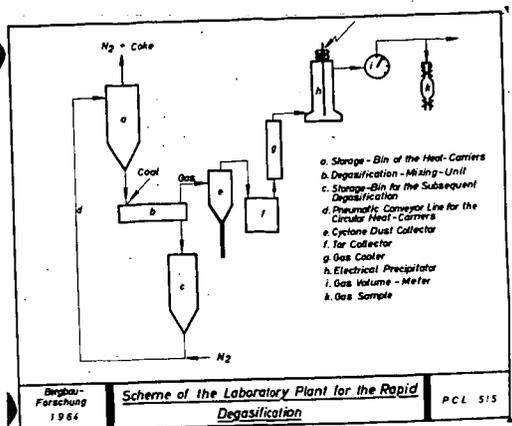


Figure 1

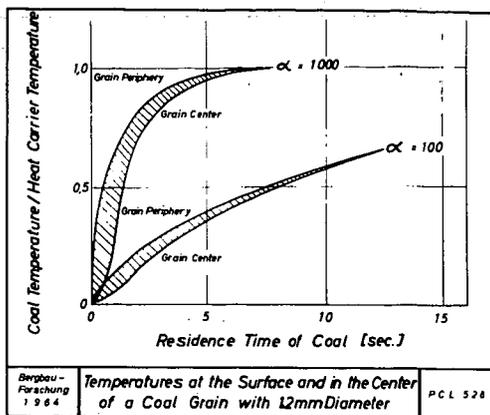


Figure 2

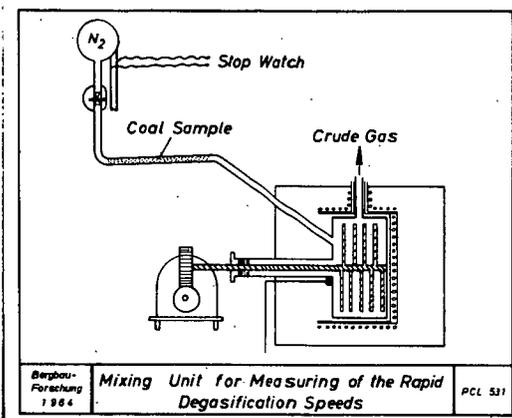


Figure 3

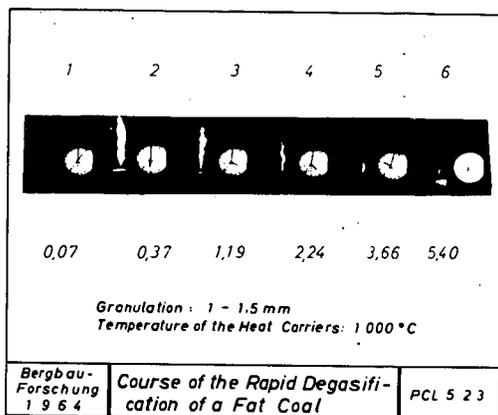


Figure 4

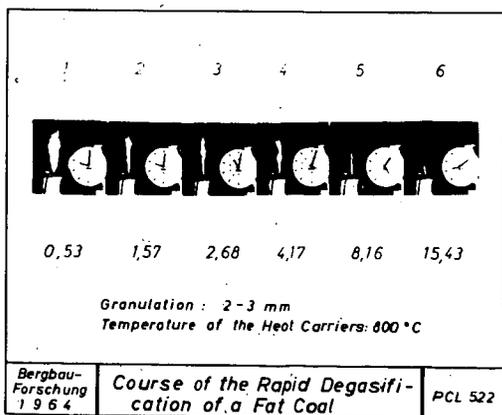


Figure 5

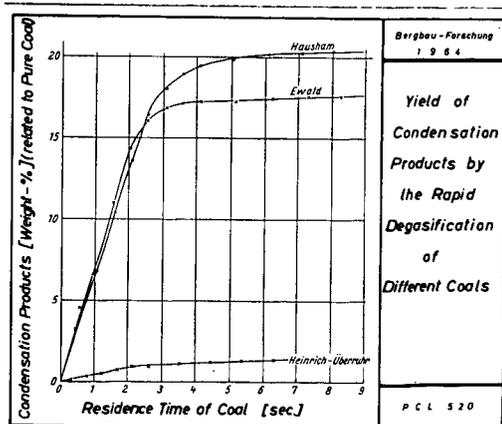


Figure 6

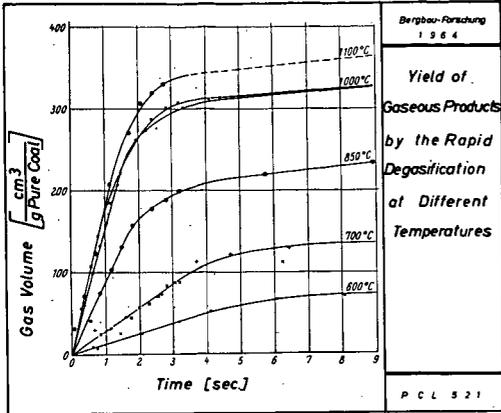


Figure 7

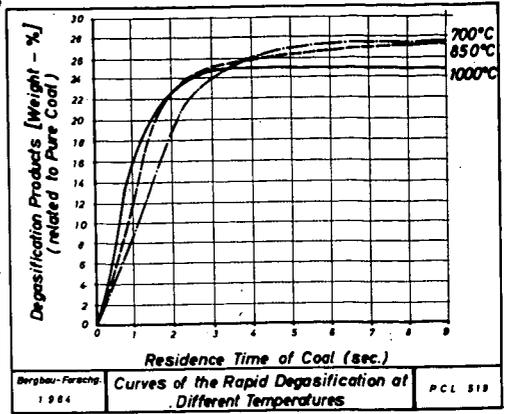


Figure 8

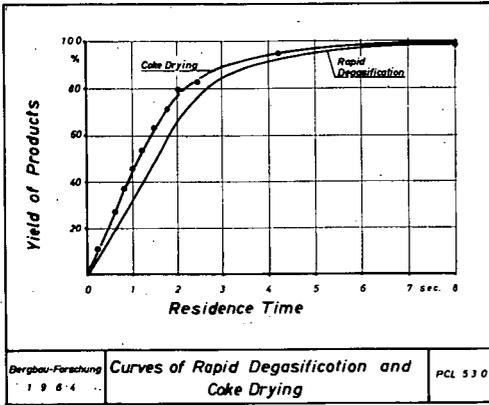


Figure 9

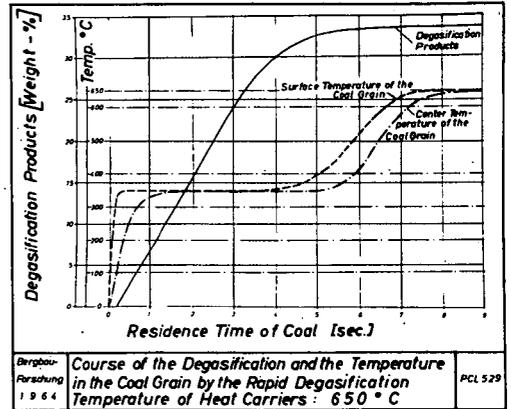


Figure 10

Product	Rapid Degasification	Carbonisation by Fischer	Ratio rapid/slow
Gas	7,25	8,44	0,86
Carbonisation Water	4,10	4,60	0,89
Tar + Carbonisation Benzine	26,40	14,82	1,78
Fraction I up to 140°C/1mmHg	6,50	8,02	0,81
Fraction II up to 140°C/1mmHg	2,87	2,71	1,06
Pitch	17,05	4,11	4,15
Carbonisation Coke	62,25	72,14	0,86

Values are given in Weight-Percent of the Pure Coal

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1964

Yields of the Carbonisation Products

PCL 518

Figure 11

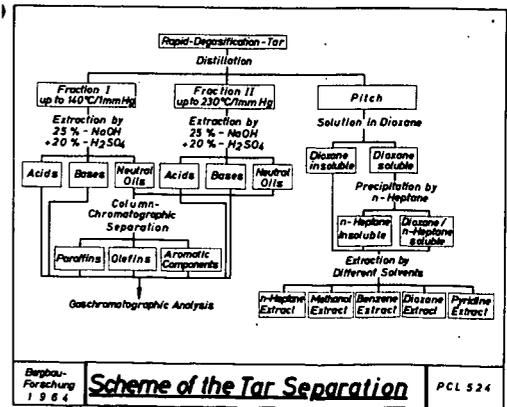


Figure 12

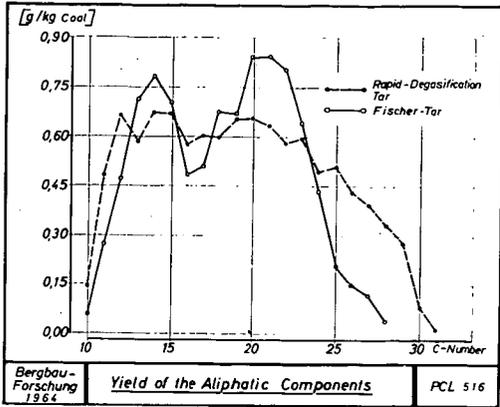


Figure 13

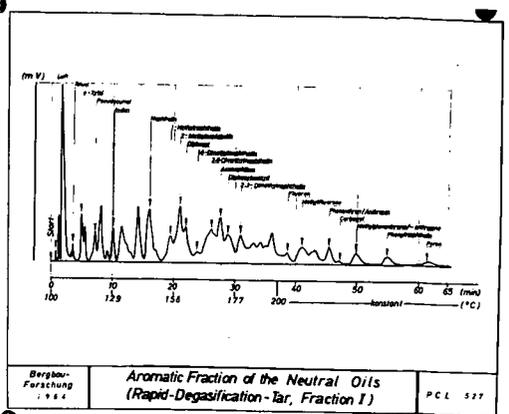


Figure 14

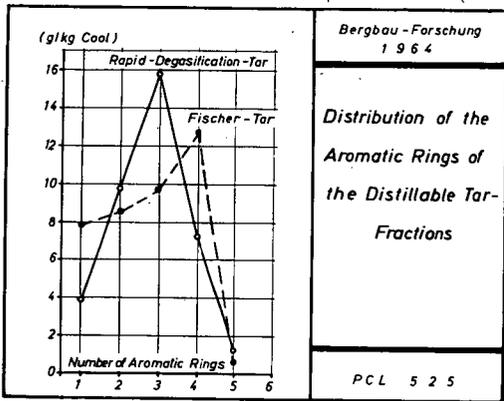


Figure 15

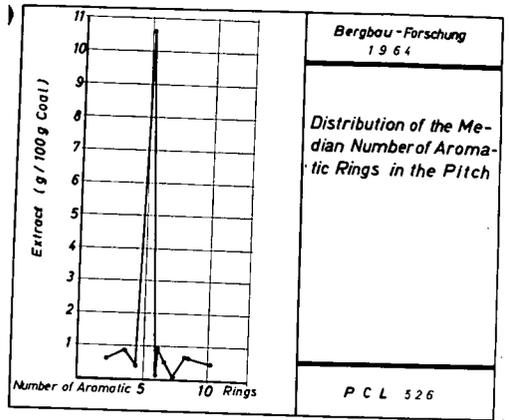


Figure 16

	Pitch	Coke	Sum
Rapid-Degasification-Tar	164,0	+ 622,5	= 788,5 g/kg Coal
Fischer-Tar	41,1	+ 721,4	= 762,5 g/kg Coal
Difference	122,9	98,9	24,0 g/kg Coal

Bergbau-Forschung 1964

Yields of Pitch and Coke

PCL 517

Figure 17