

Cl 260

ALIEN PROPERTY CUSTODIAN

PROCESS FOR DIRECTLY OBTAINING BENZENE HYDROCARBONS FROM COAL

Bernard Juettner, Essen (Ruhr), Germany;
vested in the Alien Property Custodian

No Drawing. Application filed October 28, 1940

This invention relates to a process for directly obtaining benzene hydrocarbons from coal, without resorting to the hitherto required roundabout step of applying the coking process, and increasing to a multiple the yield, relative to the coal, of such products.

It is known partly to decompose mineral and brown coal and their transformation products by treating them with oxidizing agents in an alkaline medium. This treatment substantially yields water insoluble humic acids and their decomposition products from which certain amounts of benzene hydrocarbons may be obtained by subjecting them to a corresponding subsequent treatment. The yields thus obtainable are, however, extraordinarily small and amount, as a rule, to less than 3% of the coal, so that it is not possible to obtain benzene by this method in an economically satisfying manner.

It has further been attempted to decompose brown coal by treating it with nitric acid for a short time, whereby nitrohumic acids and nitrophenols besides a very slight quantity of benzene-carboxylic acids were recovered. This process is therefore unsuited for obtaining benzene.

Efforts have also been made to break up mineral coal by treating it with diluted nitric acid, and it was found that in this manner a certain percentage of the coal can be decomposed to form soluble oxidation products. Owing to its low yield, this procedure, too, is not adapted for the economical recovery of benzene.

The invention is based on the knowledge that, by choosing corresponding conditions, it is possible when working in an acid medium to bring not merely a fraction of the coal but the entire quantity thereof into solution and to convert it into a product from which a high yield of benzene hydrocarbons is technically obtainable in economical manner. For this purpose, the coal is decomposed according to the invention in an acid medium with the aid of oxidizing agents in such manner as to produce, above all, water soluble low-molecular cyclic carboxylic acids.

To bring about this effect the treatment with oxidizing agents of suitable concentration is carried out in the heat and so as to withdraw the products that have gradually or continuously passed into solution from any further action of the oxidizing agents and to continue decomposition under these conditions until as large a portion as possible of the initial substances has passed into solution.

This procedure prevents further decomposition of those substances that have passed already into solution by the action of the oxidizing agent and exposes to this action only the residue. The decomposition products are then subjected to a treatment with alkali under pressure, which is similar to the well-known decarboxylation proc-

ess, though in this instance larger molecules are split up also, and are thus in a very simple manner converted into a product which contains benzene hydrocarbons up to 20% of the coal with slight admixtures of other aromatic hydrocarbons besides nitrogen bases like pyridine and chinoline, phenols, etc., while simultaneously gaseous cleavage products, as methane and hydrogen, accrue. Oxidizing agents of any desired kind, as air, oxygen, ozone, peroxide, acids rich in oxygen, etc., may be used in decomposition, though the employment of acids rich in oxygen is particularly advantageous, since they are also remarkably effective oxidizing agents. The oxidizing agent should be chosen as to its nature and degree of concentration with respect to the quality of the coal to be treated and the purpose in view, i.e., to obtain therefrom a decomposition product consisting chiefly of water soluble low molecular carboxylic acids.

A very suitable oxidizing agent is nitric acid having a concentration of between 1 and 15 N.

There is no noteworthy consumption of oxidizing agents, which is particularly due to the fact that an oxidizing agent after its separation from the oxidation product may be regenerated in a very simple manner and then returned to the cycle for further use during decomposition.

The decomposition is preferably performed in two or more stages with the aid of oxidizing agents of different concentration or composition, because the reaction would be too violent if the starting material were to be subjected immediately to the action of an oxidizing agent showing a comparatively high degree of concentration. This arrangement makes it possible, moreover, to influence the composition of the intermediate products, which is particularly advantageous, since it may be necessary or desirable at times to reduce the benzene yield, for instance by the initial employment of weaker oxidizing agents or by carrying out oxidation under more preserving conditions, and to produce a correspondingly higher share of decomposition products which are not so far decomposed or are higher molecular and the treatment of which will yield therefore less benzene and more higher hydrocarbons.

Decomposition may be accelerated, possibly also while reducing the concentration of the acid used, by applying increased pressure.

In further development of the invention it has been found that the yields of benzene resp. generally benzene hydrocarbons obtained in the manner described can be substantially increased by subjecting the coal to a preliminary oxydation in a gaseous or liquid oxydizing medium. Hereby in the final result the chemical oxydation of the coal is obtained in much easier and more perfect manner.

The most simple and probably optimal kind of

performing this preliminary oxydation consists in heating the coal in the presence of air or other oxydizing gases such as oxygen or nitrogen oxydes.

The effect of this preliminary treatment is the better the higher the temperature of heating is so that it is recommendable to perform this heating under conditions which besides lower the danger of ignition of the coal i.e. to work in a thin layer preferably even in suspension or f.e. in a rotating drum.

Instead in a gaseous medium the preliminary oxydation can also be performed in a liquid oxydizing medium by a treatment f.e. with sulphuric acid under heat f.e. at a temperature of 180° C one hour. Thereafter the sulphuric acid is washed out and the coal dried and further treated in the manner described above.

Certain, however, generally not equal good results are also obtained if the preliminary heating is performed in the absence of air resp. oxygen. Also by such a treatment a certain composition is obtained which facilitates the further treatment according to the new process.

Besides it is possible and recommendable to apply the oxydation resp. preliminary treatment described to the residues of the single steps of the general process to prepare them for a further treatment in the next stage. Such an intermediate oxydation in a gaseous or liquid medium ameliorates in the same way the conditions for the next stage.

Besides giving a very high benzene yield, the process according to the invention affords the added economic advantage of yielding on a large scale valuable solid, liquid and gaseous by-products, particularly phenols, pyridine, chinoline, hydrogen and methane.

If the decomposition is performed in different stages and at different concentrations of the oxydizing agent or with oxydizing agents having a different composition in the various stages, fractions of different composition will result which under certain circumstances may be separately subjected to further treatment so as to increase or vary the share of other aromatic hydrocarbons obtainable besides benzene under the new process by the decomposition of these intermediate products.

Higher molecular oxydation products developed during single- or multi-stage decomposition are converted into valuable products, when splitting up under pressure occurs, by the application of an excess of alkali.

The following examples are intended merely to illustrate the application of the new process and are not limitative in character.

Example 1

100 g. mineral coal ground to 400-mesh fineness and containing 75 g. carbon are boiled for 24 hours with 8 times the amount of 2 n nitric acid, whereupon the solution is separated and the residue is boiled for several days with 5 times the

quantity of 5 n nitric acid and the dissolved portions are repeatedly removed until almost everything has passed into solution. The solutions obtained at the various steps are combined, thickened by evaporation and dried, and yield 91 g. residue chiefly consisting of polycyclic carboxylic acids. The 91 g. dried acids are then subjected to pressure for 3 hours at 450° C. and 300 metric atmospheres above atmospheric pressure in the presence of 135 g. sodium hydroxide and 120 g. water. The contents of the hot autoclave are then blown off into a receiver with cooled diluted sulfuric acid, whence the volatile matter is driven by superheated water vapor into a burette. In this way 21 g. benzene hydrocarbons are obtained which chiefly comprise benzene, toluene and xylene and slight amounts of diphenyl. The water vapor distillate contains 2 g. volatile phenols and the residue from distillation 2 g. difficultly volatile hydrocarbons and phenols besides 1.2 g. pyridine. The total yield amounts therefore to 26.2 g. aromatic substances to which must be added a certain quantity of volatile fatty acids previously produced during oxydation.

Example 2

100 g. mineral coal, as specified in Example 1, are filled with 800 cu.cm. water containing 20 cu.cm. hydrochloric acid in an acid-proof pressure vessel. At a temperature of 250° C. air enriched by oxygen is blown through, the pressure being kept below 100 atmospheres above atmospheric pressure by blowing. The solution is continually drawn off through an immersion filter and water replaced accordingly. After a period of 80 hours almost all the coal has passed into solution. 80 g. oxydation products were obtained after boiling down and treated under pressure with alkali. The yield comprised 18 g. benzene hydrocarbons and 4 g. phenols and difficultly volatile hydrocarbons.

Example 3

100 g. mineral coal as specified above were filled with 500 cu.cm. water in an autoclave, whereupon nitrous gases diluted with air were pumped through and the reaction temperature was gradually raised to 150°C and a pressure of 20 atmospheres excess pressure was maintained by reduction. The outgoing gas mixture was freed from carbonic acid and returned to the autoclave. As in Example 2, the solution was continually discharged through an immersion filter and the water replaced. After 48 hours the coal was fully dissolved. Boiling down yielded 90 g. oxydation products which on being subjected to pressure gave 20 g. benzene hydrocarbons, 4 g. phenols and difficultly volatile hydrocarbons and 1.5 g. pyridine.

In the case of all these examples it is preferable to make use of the preliminary resp. intermediate oxydation by heating in an oxydizing medium or an acid treatment.

BERNARD JUETTNER.