

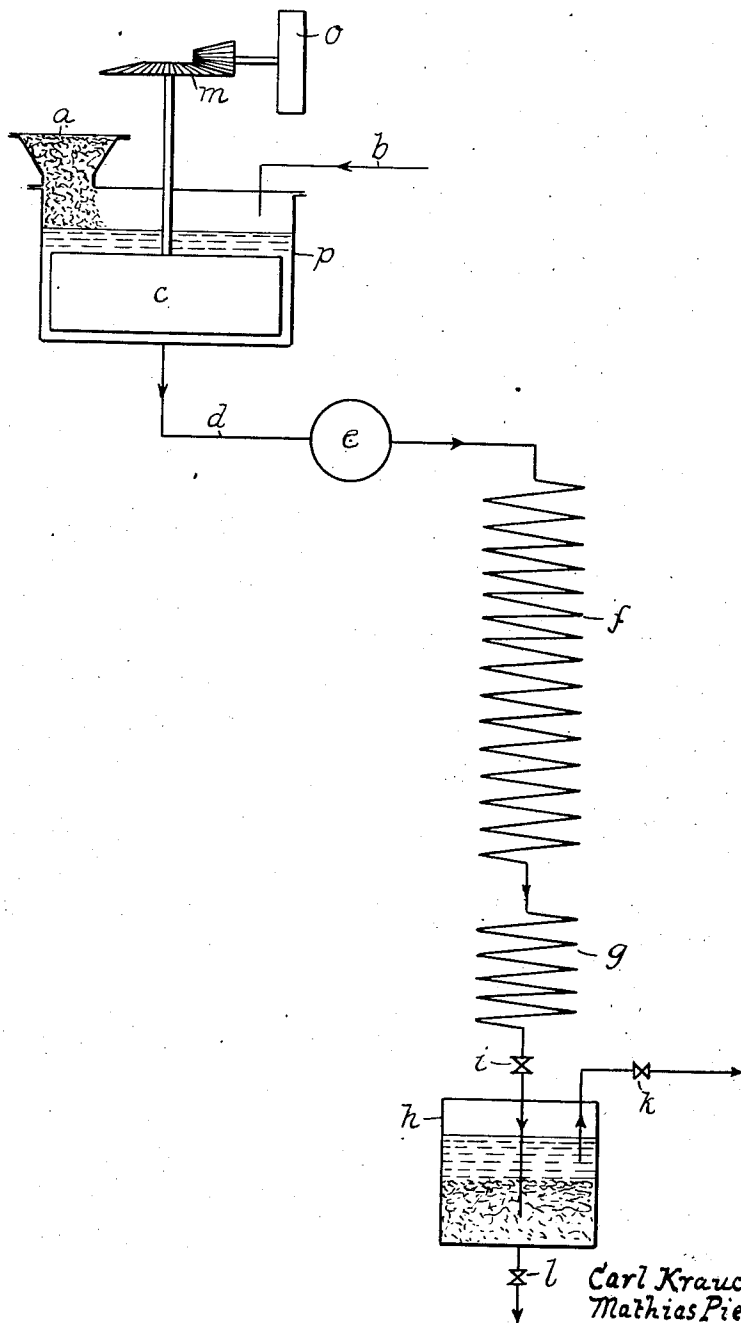
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PRODUCTION OF VALUABLE ORGANIC PRODUCTS

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## UNITED STATES PATENT OFFICE

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## PRODUCTION OF VALUABLE ORGANIC PRODUCTS

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This invention relates to the production of valuable organic products from solid carbonaceous initial materials.

We have found that an excellent yield of liquid products and products which liquefy when heated and which are hereinafter referred to for the sake of brevity as valuable hydrocarbon products, is obtained by treating solid carbonaceous materials with such hydrocarbons as are liquid under the conditions of the reaction, substantially free from components boiling below 100° C. and which mainly boil between 100° and 300° C. under elevated pressures of at least 75 atmospheres, but preferably 100 atmospheres or above, at temperatures below the coking temperature of the added hydrocarbons and in the absence of substantial amounts of hydrogen. By this manner of proceeding the formation of gases and especially such as condense with difficulty is prevented to a large extent.

A great variety of solid carbonaceous initial materials may be employed according to the process as for example different kinds of coal, such as pit coal or brown coal of varied origin and character, as well as bituminous shales, peat, wood and the like.

If desired, gases substantially free from hydrogen such for example as nitrogen, carbon dioxide, carbon monoxid, or gas mixtures containing the same may also be employed, and an addition of catalytic substances which may have a decomposing action on coal, such for example as iodine or other metalloids or substances with an alkaline reaction, in particular the sulfids of the alkali metals and alkaline earth metals, also proves useful.

It may also be advantageous to carry out the operation in several stages at different pressures; for example, the initial material may be pretreated first at a pressure which may be below 75 atmospheres and then the product thus obtained treated at higher pressures according to the process above described. We may, however, also commence with higher pressures and then vary the pressure within wide limits during the process. Pressures of 200 atmospheres and more, for example of 1000 atmospheres may be employed.

The temperature may also vary and, as a rule, higher temperatures give higher yields of liquid products. Temperatures of between 300° and 400° C. are preferably employed. An upper temperature limit is set by the critical temperature of the added liquid hydrocarbons and the like, but the temperatures must not be so high that the added oils are changed in such a manner that they lose their properties as triturating agents for the coal and the like.

The heat may be supplied in different ways:—For example, the mixture of coal and triturating agents, which if desired, may be preheated, is heated externally during the process in tubes, for example coils. Superheating is preferably avoided, for example by the employment of a bath (for instance a salt bath or a metallic melt) or of hot gases as heating medium. The heat may also be produced electrically, for example by heating the tubes or coils themselves electrically or by arranging fixed or movable electric resistances in the tubes. Stirrers may also be employed, and if desired, these may also be constructed as electric resistance heating devices.

We may also work in such a manner that the pasty mass is preheated up to about the reaction temperature and that the heat necessary to carry out the process is introduced by means of heat conveying media, for example a gas or a liquid, which may be allowed to circulate round the reaction vessel or may be introduced into the reaction chamber at a suitable point. The process may also be carried out in such a manner that part of the added hydrocarbons for instance are heated above the temperature of the reaction and are employed as heat-conveying media. The method of heat supply may also be combined with one of the aforementioned methods.

The reaction products are cooled down behind the reaction space so far that part thereof is obtained in a solid form. The liquid oils may be employed for any desired purposes, for example as Diesel oils, lubricating oils, insulating oils and the like or part thereof may be employed afresh for the treatment of fresh coal or the like; or

they may be subjected after the extraction has been carried as far as possible to a treatment with hydrogen with or without the application of pressure and if desired with catalysts, before the solid components have been separated off and in this way substances of the nature of middle oils, benzines and the like are obtained. Also the solid residue may, for example by treatment with hydrogen under pressure, be employed for the production of valuable hydrocarbons and the like. Under certain circumstances it may also be advantageous to release the pressure while the products are still hot and then to cool under normal pressure. After being subjected if required to a preliminary mechanical treatment such as centrifuging and the like the liquid products are separated from the solid residues in any known and convenient manner as for example by low temperature carbonization, if desired in the presence of steam or other gases and vapors, or by extraction or both, or by other means with or without the application of pressure.

The reaction product or components of the same may also be subjected to cracking in the presence or absence of water vapor or carbon dioxide or other gases.

As substances which may be added, mixtures boiling within a rather wide range of temperatures come into question. They may be obtained in various ways, for example by the distillation or low temperature carbonization of lignite or coal or from mineral oils or by the destructive hydrogenation of substances of the nature of coal, tars, mineral oils and the like or by the catalytic reduction of oxides of carbon with hydrogen under pressure. Fractions of oils which are produced in the present process itself and boil above the boiling point range of benzine, namely above about 180° C. are very suitable. Mixtures of such oils with oils boiling above 300° C. may also be employed with advantage, but also homogeneous substances or groups of substances may be employed, for example xylene, cresol, hydrogenated naphthalenes, aniline and the like.

The invention will be further illustrated with reference to the accompanying drawing in which a plant for carrying out the process according to the present invention is illustrated diagrammatically, partly in vertical cross section, although the invention is not limited thereto. *a* is a hopper through which finely divided solid carbonaceous materials can be introduced into a mixing vessel *p*; *b* is a pipe for the introduction of solvent hydrocarbons into the said vessel *p*. *c* is a stirrer which is actuated by rotation of the wheel *o* the rotation being transferred by means of the tooth gear *m* to the shaft *n*. *d* is a pipe for the transference of the liquid mixtures prepared in the vessel *p* to the pressure resistant coil *f* which is constructed of

alloy steel. *e* is a pump assisting the said transference. *g* is a cooler for cooling the products issuing from the coil *f*. *i* is a pressure release valve for releasing the pressure on the said products. *h* is a settling tank from which the liquid products can be removed by means of the pipe *k*, whereas the solid mixtures are removed by means of the pipe *l*.

Referring to the accompanying drawing finely divided coal rich in gas is mixed in the vessel *p*, which is fitted with the stirrer *c* with the fractions boiling between 100° and 300° C. of a crude mineral oil, both constituents of the mixture being continuously introduced. The paste thus obtained is continuously passed to the compression pump *e* and is forced under a pressure of 200 atmospheres into a pressure-resistant coil *f* constructed of alloy steels which is maintained at a temperature of about 320° C. The products issuing from the said coil are cooled down by means of the cooler *g*. The pressure on the said products is released by means of the valve *i* and they are passed into the separating vessel *h*. The solid materials settling down in the said vessel are drawn off at *l* and the supernatant oil is drawn off through a valve *k*.

The following examples will further illustrate the nature of our present invention which, however, is not limited to these examples.

#### Example 1

Brown coal containing about 3 per cent of bitumen (that is to say substances which can be extracted by means of benzene) and 5 to 10 per cent of water is treated at about 350° C. with those fractions of oils boiling between 190° and 250° C. derived from the destructive hydrogenation of carbonaceous substances at a pressure of 200 atmospheres. 60 to 70 per cent of the coal is converted in a rapid process, without an appreciable amount of gas being formed, into liquid oils, whereas at a pressure of 50 atmospheres under otherwise like conditions only about half that amount would be obtained.

#### Example 2

Brown coal triturated with xylene is passed through a high pressure coil heated to about between 320° and 340° C. at a pressure of 200 atmospheres. On releasing the pressure, over 50 per cent of the coal is obtained as liquid oils by means of centrifuging followed by extraction or steam distillation.

What we claim is:

1. The process of extracting oils of about the viscosity of lubricating oils from solid non-asphaltic pyrobituminous materials by passing said solid materials through a reaction zone, while treating said materials with a substance of the nature of tar oils, the major

portion of the constituents of which boil between 100° C. and 300° C. and a sulphide selected from the class consisting of the alkali metal and alkaline earth metal sulphides at a temperature of from 300 to 400° C. and  
5 a pressure of at least 75 atmospheres, so rapidly that no low boiling hydrocarbons are produced, then directly cooling the reaction mixture to separate out solid materials from the liquids having a viscosity of about that of  
10 lubricating oils.

2. A process as defined in claim 1 wherein the pyrobituminous material is brown coal and the substance of the nature of tar oils is  
15 xylene.

3. The process of extracting oils of about the viscosity of lubricating oils from solid, non-asphaltic, pyro-bituminous materials by passing said solid materials through a reaction zone while treating them with a hydrocarbon liquid, the major constituents of which  
20 boil between 100° and 300° C., at a temperature of from 300° to 400° C. and under a pressure of at least 75 atmospheres, until at least 50% of the oil contained in said initial material is extracted therefrom but for only  
25 so long that substantially no low boiling hydrocarbons are produced, said hydrocarbon liquid being maintained in the liquid state throughout the process, and then separating  
30 the liquid extraction from the residual solid materials.

In testimony whereof we have hereunto set our hands.

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