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PRODUCTION OF VALUABLE HYDROCARBONS OF LOW BOILING POINT

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It is already known that valuable liquid hydrocarbons may be produced from distillable carbonaceous material, such as any kind of coals, tars, mineral oils, their distillation, conversion and extraction products, residues, and the like, by heating, especially in contact with hydrogen or gases giving off hydrogen which are equivalents for the purpose of the present invention, to high temperatures, under pressure and by the use of catalysts.

We have now found that it is particularly advantageous to employ for this process catalysts which are deposited in small quantities on metals or metallic alloys which do not melt under the conditions of working. These metals or alloys as for example aluminium, silver, manganese, chromium, chromium-nickel, silicon and the like, are preferably used in a form presenting a dense and coherent surface, such for example as grains, balls, chips, ribbons, wire, wool and the like. A great variety of substances may be used as catalysts, the amount of which need often be merely fractions of one per cent of the amount of metal or alloy used. Particularly suitable catalysts are the oxids or compounds furnishing the same under the conditions of working of the elements from groups 3 to 7 of the periodic system, such as uranium oxid, vanadium oxid, chromic acid anhydride, manganese oxid, molybdenum oxid, boric acid, and the like, either alone or in admixture with one another or with other substances. Other substances effective as catalysts comprise oxids or compounds furnishing the same of platinum, ruthenium, cobalt, gold, cadmium, and the like. A mixture of iron oxid, copper nitrate and cadmium nitrate may be mentioned as examples of such compounds. The said catalyst may be prepared by treating the metals, such as commercial granular aluminium, preferably after etching, for example, with hydrochloric acid or mercuric chlorid, with, preferably acidified, solutions of salts of catalytic elements, as for example by moistening with solutions of uranyl nitrate, boric acid and the like. The said compounds furnish oxids under the conditions of working. Thus uranyl nitrate is converted into the oxid by splitting off of oxids of nitrogen. The deposition onto the metal may also be effected in any other way, such as by evaporating a salt solution in the presence of the fragments of metal, by electro-chemical means or also by intimately mixing in a ball mill the metal granules, which may be etched beforehand, with small quantities of moistened vanadium oxid and the like. It may also sometimes be of advantage to render catalytic, by activation in the above manner, the metal walls, pipes, stirring or paddle devices and the like situated in the reaction zone in which case it is not necessary that additional catalysts be employed, since the walls themselves serve as catalysts, but additional catalysts may of course be added. This last procedure without the employment of additional catalysts may be of importance, when using initial materials containing ash liable to produce obstructions and the deposition of coke when passed through a catalyst layer. These last drawbacks may also be more or less eliminated by the employment of stirring mechanisms or of a high velocity of flow. A particular advantage of the catalysts according to the present invention is also their high heat-conducting capacity which enables the otherwise readily occurring local superheating within the reaction zone to be more or less completely prevented.

In many instances the metal or alloy not only acts as a carrier, but may also possess catalytic properties or acquire same by reason of the treatment herein described. Many metals, such as aluminium, possess a certain catalytic capacity, especially after being etched with acids and the like. This capacity is considerably increased by the substances applied to the metal and surpasses that of the substance applied when the latter is used alone or on non-metallic carriers such as charcoal, pumice stone and the like. Not only the proportion of substances of low boiling point produced in a single passage is increased thereby but also the output capacity. In the manner herein described it is easy to convert 80 per cent and more of a petroleum fraction of a boiling point above 300° centigrade by

passing it only once with hydrogen over the catalyst under a pressure of the order of pressures employed in destructive hydrogenation and at about 450° centigrade into benzines boiling below 200° centigrade, even when working continuously for weeks with the same catalyst.

The aforesaid catalysts are very well adapted for the production of low-boiling products of the benzine type, and are also very suitable for dehydrogenating hydrocarbons, tars, mineral oils, their distillation, conversion, extraction products and the like, or for converting the same into aromatic hydrocarbons. In such cases, the working temperatures are generally higher for example 550° to 650° centrigrade than those necessary for the production of benzines.

The methods already known for converting coals, tars, mineral oils and the like into valuable hydrocarbons, may also be applied in connection with the present process, for example such as the operation in a cyclic system, prepurifying the gases, purifying the gases in circulation, separating the reaction products by cooling and/or by adsorbent masses or by washing with suitable liquids, means for heating the reaction components and avoiding, in those parts of the apparatus coming into contact with the hot reaction components, the presence of substances which promote the deposition of carbon or the formation of methane this being achieved, for example, by lining the apparatus with aluminium, high-grade steel alloys and the like.

The operations may be conducted in such a way that the hydrocarbons or the like are brought into reaction in the state of vapor wherein the operation is preferably carried out with a large excess of hydrogen, or the hydrocarbons and the like may be brought into reaction, wholly or partially in a liquid condition, in the presence of the above described catalysts.

The reaction components may also be admitted into the reaction chamber in the form of mist or in an atomized condition, or they may be in thin layers, or the gases may be introduced into the substances under treatment through a porous stratum.

The reaction components may also be subjected to repeated treatment by heat, with or without the presence of hydrogen or gases giving off hydrogen.

The following examples will further illustrate the nature of the said invention which however is not limited thereto.

Example 1

A mineral oil fraction boiling above 270° centrigrade is passed with an excess of hydrogen, at a temperature of 450° centigrade, and under a pressure of 200 atmospheres, through an aluminium-lined pressure vessel containing a catalyst consisting of fine granules of aluminium activiated with 1 to 2 per cent of uranyl nitrate with the aid of hydrochloric acid. The nitrate is converted under the conditions of working. In this way an oil is obtained consisting to the extent of 80 per cent and over of benzines boiling up to 200° centigrade. Similar action is exerted by a catalyst prepared by activating aluminium with boric acid.

Example 2

A bituminous coal tar oil with a range of boiling points between 300° and 420° centigrade is passed with hydrogen at 480° centigrade and a pressure of 200 atmospheres, over a catalyst consisting of aluminium gauze, which has been activated, by heating it with ammonium vanadate and uranyl nitrate in the presence of hydrochloric acid. A mixture of the oxids of vanadium and uranium is thus produced on the aluminium under the conditions of working. An oil is obtained up to 70 per cent of which passes over up to 200° centigrade.

Example 3

Elwerath oil, boiling at above 300° centigrade, and mixed with an equal amount of an ash-free middle oil, is forced, with the aid of hydrogen, through an aluminium-lined pressure vessel at 450° centigrade. In order to obtain a high velocity of flow, suitable spiral ribbons of aluminium are arranged, so that the oil takes a spiral course. The aluminium parts are previously activated with hydrochloric acid and boric acid. In a single passage, 40 per cent and more of the crude oil is converted into benzine, and further large proportions into middle oil.

If the initial material is forced through the apparatus without the aid of hydrogen, the yield obtained in a single passage is generally somewhat lower, and moreover the resulting product is partially unsaturated.

If a working temperature of about 600° centigrade or higher be employed, the reaction product contains 30 per cent and more of aromatic hydrocarbons.

Example 4

A middle-oil fraction from bituminous coal tar, boiling between 200 and 350° centigrade is passed in a current of hydrogen at 450° centigrade and 200 atmospheres pressure over a catalyst consisting of zinc wool activated by evaporating an aqueous suspension of blue molybdenum oxid containing the zinc wool. Even in a single passage, more than 50 per cent of the initial materials is converted into benzine, and complete conversion into benzine is effected by further treatment in circulation.

The said middle oil may also be replaced by corresponding mineral oils, such as middle

oil from Elwerath crude oil, and the zinc wool containing molybdenum oxid may be replaced by tungstic acid on zinc wool.

Similarly, the zinc wool may be replaced by silver or copper wool or the like or by metals in other forms, such as gauze, or the like, it being advisable, especially when copper is used, to prevent the occurrence of injurious action by freeing the initial materials to a far-going extent from any sulfur present.

Example 5

A brown-coal-tar oil boiling substantially above 250° C. is passed at a temperature of 460° C. and at a pressure of 200 atmospheres together with hydrogen over a catalyst consisting of small compact aluminium granules on which 1 per cent of metallic silicon, and 0.1 per cent of vanadium oxid is deposited in a fine state of division by treatment with a solution of a salt of vanadium oxide. If the oil is passed over the catalyst only once, an oil is obtained 70 per cent of which boils below 250° C.

What we claim is:

1. A process for the production of valuable hydrocarbons of low boiling point from a distillable bituminous material which comprises subjecting said material to a heat treatment at a temperature of between 450 to 650° C. and at a pressure of the order of the pressures employed in destructive hydrogenation, in the presence of a catalyst comprising small quantities of an oxid of a metal of groups 3 to 7 of the periodic system deposited on a metal, which is in a dense coherent state under the conditions of working and which, under said conditions, does not cause deposition of carbon, selected from the class consisting of aluminium, chromium-nickel, silver, manganese and chromium.

2. A process for the production of valuable hydrocarbons of low boiling point from a distillable bituminous material which comprises subjecting said material to a heat treatment with hydrogen at a temperature of between 450 and 650° C. and at a pressure of the order of the pressures employed in destructive hydrogenation, in the presence of a catalyst comprising small quantities of an oxid of a metal of groups 3 to 7 of the periodic system, deposited on a metal, which is in a dense coherent state under the conditions of working and under said conditions does not cause deposition of carbon, selected from the class consisting of aluminium, chromium-nickel, silver, manganese and chromium.

3. A process for the production of valuable hydrocarbons of low boiling point from a distillable bituminous material which comprises subjecting said material to a heat treatment with hydrogen at a temperature between 450 and 650° C. and a pressure of the order of pressures employed in destructive hydrogenation, in the presence of a catalyst comprising small quantities of an oxid of a metal of groups 3 to 7 of the periodic system, deposited on a metal, which is in a dense coherent state under the conditions of working and which, under said conditions, does not cause deposition of carbon, selected from the class consisting of aluminium, chromium-nickel, silver, manganese and chromium, by treating said metal with an acidified solution of a salt of a metal of the 3rd to 7th groups of the periodic system, which salt yields the said oxid under the conditions of working.

4. A process for the production of valuable hydrocarbons of low boiling point from a mineral oil fraction boiling above 270° C. which comprises passing said mineral oil fraction, with an excess of hydrogen, at a temperature of about 450° C. and a pressure of 200 atmospheres, over a catalyst comprising an oxid of uranium deposited on granules of aluminium.

5. A process for the production of valuable hydrocarbons of low boiling point from a distillable bituminous material which comprises subjecting said material to a heat treatment with hydrogen at a temperature between 450 and 650° C. and at a pressure of about 200 atmospheres in the presence of a catalyst comprising small quantities of an oxid of a metal of group 6 of the periodic system deposited on chromium-nickel which is in a dense coherent state, under the conditions of working.

6. The process as defined in claim 3 wherein the conversion is effected in the presence of an excess of hydrogen.

7. A process for the production of valuable hydrocarbons of low boiling point from a heavy hydrocarbon oil, which comprises passing the said oil mixed with hydrogen at about 450° to 480° C. and at a pressure of 200 atmospheres over a catalyst consisting of aluminium in a compact coherent state and small amounts of an oxid of a metal from the group 6 of the periodic system deposited thereon.

In testimony whereof we have hereunto set our hands.

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