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PRODUCTION OF VALUABLE LIQUID
HYDROCARBONS

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1 Claim. (Cl. 196—53)

The present invention relates to the production of lower boiling hydrocarbons and contingently of their derivatives, more particularly low boiling motor fuels, as also kerosene and the like by destructive hydrogenation in the presence of catalysts of liquid carbonaceous materials of higher boiling point range, such as mineral oils, tars or their high boiling products of destructive hydrogenation, distillation or cracking or products of the destructive hydrogenation of coal.

Hitherto most high boiling materials of said type could not be converted in a high yield into lower boiling hydrocarbons or contingently their derivatives by destructive hydrogenation in the presence of stationary catalysts.

We have now found that lower boiling hydrocarbons and contingently their derivatives, such as low boiling motor fuels, kerosene and the like can be obtained in a high yield from liquid carbonaceous materials of higher boiling point range, such as mineral oils, tars or their high boiling products of destructive hydrogenation, distillation or cracking or products of the destructive hydrogenation of coal by separating from said initial material a residue mainly consisting of pitch, asphalt, resin, gum and/or similar high molecular substances, which expression for the purpose of the present invention is to include also the products giving rise to the formation of these substances under the conditions of working, which impair the activity of the catalyst by distillation, preferably under reduced pressure, if desired, with scavenging gases or vapors, or by treatment with liquefied, at atmospheric temperature and pressure gaseous hydrocarbons or with solvents for carbon compounds poor in hydrogen and destructively hydrogenating the thus pretreated initial material by passing it together with a gas comprising free hydrogen, i. e., free hydrogen itself or a gas containing sufficient free hydrogen, under pressure, preferably high pressure under splitting conditions over catalysts stationarily arranged in the reaction space, if desired while recycling the higher boiling fractions.

If desired, several of the said pretreatments may be applied in the same process.

More particularly the said process is applicable with advantage to those initial materials having an upper end boiling limit above 350° C. at atmospheric temperature and pressure, for example oils containing large amounts of high boiling constituents.

For carrying out the process the initial materials may, for example, be distilled down to a

pitch-like residue at temperatures at which practically no decomposition yet occurs. The distillation may be carried out in the presence of gases, such as hydrogen, nitrogen, or vapors, such as water vapor. It may be carried out under atmospheric pressure, for example, up to 350° C. and, if desired, subsequently, advantageously under reduced pressure at a temperature which brings about the distillation effected, under ordinary pressure, at a temperature up to 500° C., preferably up to 470° or 445° C. and more particularly up to 425° C. Thus, under reduced pressure, for example 10 to 15 millimeters mercury gauge, the distillation may be carried out at temperatures up to about 350° or 400° C. particular care should be taken that on the one hand no constituents of the pitch-like residue pass over in the distillation, since already small amounts of these substances in the distillate may affect the activity of the catalyst in the subsequent catalytic treatment, and that on the other hand, in order to obtain as large a yield of distillate as possible, the fractions boiling at 10 to 15 millimeters mercury gauge and at temperatures up to 300° C., if desired, up to 350° C., also distil over.

The initial materials can also be freed from pitch and like products impairing the catalytic activity with the aid of solvents dissolving the said pitch and like products, such as phenol, aniline, ketones, nitrobenzene, organic chlorine compounds, as also liquid sulphur dioxide or the like. The amount of the solvent and the working temperature are so chosen that only the substances consisting mainly of pitch, resin, asphalt and similar high molecular substances are removed from the initial material.

Liquefied hydrocarbons which are gaseous at atmospheric temperature and pressure, such as propane, propane-ethane mixtures, butane and the like have proved to be particularly advantageous for the separation of said substances of high molecular weight impairing the activity of the catalyst. In this case the fractions rich in hydrogen dissolve, leaving behind the residue consisting mainly of pitch and the like.

The initial material may also before or after said separation be partly or wholly subjected, prior to the destructive hydrogenation to a refining, for example, with sulphuric acid or with aluminium chloride or an adsorption agent, such as bleaching earth and the like or by treatment with hydrogen, which latter treatment is preferably effected in the presence of catalysts having

a hydrogenating action and at temperatures below 300° C.

By the separating process described a substantially maximum yield is obtained from the initial material of fractions free from high molecular compounds of high molecular weight injurious to the activity of the catalyst and from compounds giving rise thereto, which fractions have a lower specific gravity than the crude initial material, and which are rich in hydrogen. The said fractions can be subjected to destructive hydrogenation under pressure without interruptions over stationary catalysts.

For the destructive hydrogenation the initial material pretreated as hereinbefore described may, for example, be heated with hydrogen under pressure, for example, to the reaction temperature or a temperature which allows of attaining the reaction temperature and led, while at least in part in vaporous condition, through the reaction space containing the stationarily arranged catalyst.

For obtaining high yields of low boiling products it is advantageous to work as far as possible and preferably entirely in the vapor phase.

As catalysts may be used metals, more especially the heavy metals, of the 2nd to the 8th group, particularly of the 4th to the 8th group, such as molybdenum, chromium, tungsten, vanadium, in particular, their compounds such as oxides, sulphides, halides and the like. The catalytic substances can also be supported by carriers, such as active carbon, active silica, alumina, deashed brown coal small coke or brown coal small coke pretreated with acids or acid substances. The catalyst is advantageously applied in a shaped form, for example, in the form of pellets, cubes and the like.

The destructive hydrogenation in accordance with the present invention is usually carried out under pressures of at least 20 atmospheres and as a rule preferably in excess of 50 atmospheres. Generally however pressures of about 100, 200, 300, 500 and in some cases even 1000 atmospheres come into question.

The amount of hydrogen maintained in the reaction space and parts connected therewith, if any, varies greatly with the nature of the particular initial materials treated or according to the result in view. In general 300, 600, 1000, 2000 cubic meters or more of hydrogen, measured under normal conditions of temperature and pressure, per ton of carbonaceous material treated may be used. The smallest amount of hydrogen employed per ton of carbonaceous material will be about 100 cubic meters of hydrogen and amounts of up to about 3000, 4000, 6000 cubic meters or more may be employed in many cases.

In the destructive hydrogenation temperatures of 350° to 550° C., especially of 380° to 450° C. are advantageously used as reaction temperatures, particularly under the usual working pressures and with pressures of say 300 to 1000 atmospheres temperatures up to 500° C. may be employed with advantage.

The time of sojourn in the reaction space of the material to be treated is so chosen that considerable splitting takes place. According to the product to be obtained the fractions lying above the boiling range of the desired final products are advantageously returned to the reaction space for further conversion.

It is particularly advantageous to operate by continuously introducing fresh carbonaceous material into the reaction vessel and to con-

tinuously remove products therefrom. If desired several reaction vessels may be employed in which different conditions of temperature and/or pressure, may, if necessary, be maintained and in which different catalysts may also be employed. Sufficiently converted reaction products may be removed behind any of the reaction vessels. Materials which have not been sufficiently reacted on may be recycled or treated in a further reaction vessel.

The single figure of the drawing represents the apparatus employed to carry out the process.

The gases for use in the reaction may consist of hydrogen alone or of mixtures containing hydrogen, for example a mixture of hydrogen with nitrogen, or water gas, or of hydrogen mixed with carbon dioxide, sulphuretted hydrogen or methane or other hydrocarbons.

The advantage of the process consists in that from the initial material a high yield of low boiling fractions is obtained with slight gasification and that the reaction process can be carried out at relatively low temperature. A high yield of desired products per liter reaction space per hour is obtained in consequence of the high concentration of catalyst in the reaction vessel arising from the fact that the process is carried out with stationary catalyst.

The following examples will further illustrate how the invention may be carried out in practice, but it should be understood that the invention is not limited to the said examples.

Example 1

From asphalt base mineral oil 9 per cent of benzene is removed by distillation. The distillation is continued under ordinary pressure to 350° C. and is carried on further, whilst adding water vapor in vacuo until a pitch-like residue of about 20 per cent is left. The distillate, obtained with a yield of 71 per cent, is heated to 410° C. together with hydrogen under a pressure of 250 atmospheres in a gas-heated tube preheater and led through a reaction vessel filled with lumps of tungsten disulphide, whereby a temperature of 425° C. is maintained. The reaction conditions are so chosen, that there are 2 to 4 cubic meters of hydrogen per liter of oil and the throughput amounts to 1.1 kilograms per liter of catalyst volume per hour. The gases and vapors leaving the reaction vessel are fractionally condensed. The fractions boiling above 200° C. are returned to the apparatus together with fresh initial material. 90 per cent of benzene is obtained calculated on the initial material. This is washed with dilute caustic soda before it comes into contact with air.

The residue remaining in the distillation is mixed with 2 per cent of neutralized, that is acid-treated brown coal small coke containing 2 per cent of molybdic acid, and treated in liquid phase with hydrogen under a pressure of 250 atmospheres at 470° C. A product is obtained containing 10 per cent of constituents boiling up to 180° C. and 48 per cent boiling up to 325° C. This product is subjected to the above described distillation together with the above mentioned mineral oil and further worked up as indicated.

The same results are obtained if the mineral oil freed from benzene is treated with five times its volume of liquefied propane at 40° to 60° C.

Example 2

Finely ground bituminous coal is made up to a paste with an equal amount of a heavy oil obtained from the same coal by destructive hydrogenation and converted in known manner by cat-

alytic destructive hydrogenation into a liquid product, which boils for 15 per cent up to 200° C. and for 55 per cent up to 325° C. The constituents boiling above 180° C. are distilled in a vacuum of 13 millimeters mercury gauge up to an end boiling point of 310° C., which corresponds with an end boiling point under atmospheric pressure of about 410° C. The distillate is introduced together with hydrogen under a pressure of 200 atmospheres at a temperature of 340° C., through a reaction vessel in which tungsten sulphide in the form of lumps is stationarily arranged. The reaction products are passed without preliminary condensation together with hydrogen through a second reaction vessel, which is packed with tungsten disulphide in the form of lumps and heated up to 425° C. After cooling the reaction product a condensate is obtained which consists for 40 per cent of benzine. The remainder of the product is introduced again with fresh distillates boiling above 180° C. to the first reaction vessel, that is to the hydrogenation stage.

Instead of the above mentioned destructive hydrogenation products containing asphalt of bituminous coal other initial materials rich in asphalt, such as, for example, Venezuelan oil may be applied.

Example 3

A vacuum distillate of bituminous coal tar-oil, with an initial boiling point of 236° C. (at ordinary pressure), of which 47 per cent distills up to 325° C. and the end boiling point of which lies at about 400° C. is treated in the same manner as the destructive hydrogenation product of Exam-

ple 2. A product is obtained with 60 per cent of benzine; the remaining 40 per cent may be used as gas oil or may be returned to the reaction vessel for further conversion into benzine.

What we claim is:

The process of producing a liquid hydrocarbon product of substantially lower boiling point from an unhydrogenated liquid carbonaceous material containing high molecular substances of the nature of pitch, asphalt, resins and similar substances which impair the activity of a destructive hydrogenation catalyst which comprises subjecting said unhydrogenated material to distillation under atmospheric pressure to the extent that this is possible without decomposition of the material and completing the distillation under reduced pressure, said distillation effecting a separation of the material into an overhead fraction free from said high molecular substances and a pitchy residue, destructively hydrogenating said overhead fraction by passing it in the vaporized state together with a gas comprising free hydrogen under elevated pressure over a destructive hydrogenation catalyst under conditions leading to a substantial splitting of higher boiling hydrocarbons in said overhead fraction into hydrocarbons boiling within the gasoline range, subjecting the pitchy residue to catalytic destructive hydrogenation and returning the product obtained in the last mentioned hydrogenation to the initial distillation step.

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