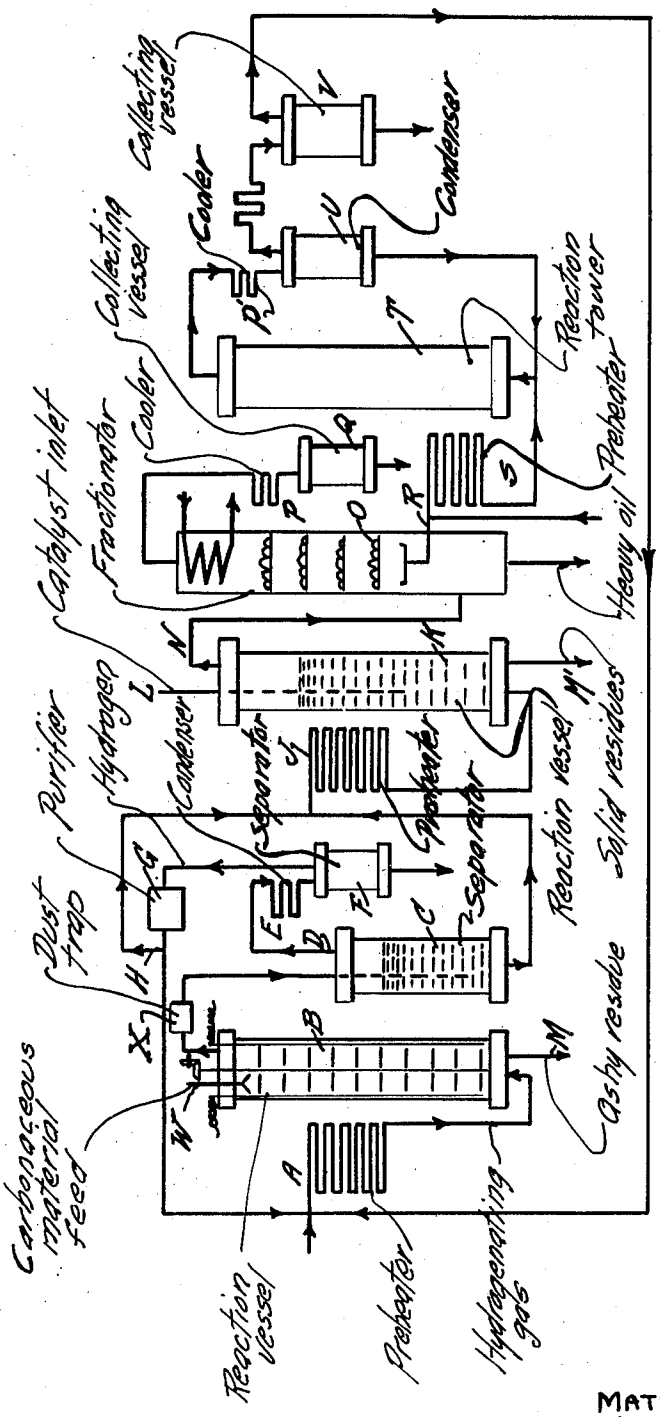
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DESTRUCTIVE HYDROGENATION

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INVENTORS
MATHIAS PIER
WALTER KROENIG.

BY Ranff & Warland.
ATTORNEYS.

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DESTRUCTIVE HYDROGENATION

Mathias Pier, Heidelberg, and Walter Kroenig, Ludwigshafen-on-the-Rhine, Germany, assignors to Standard-I. G. Company, Linden, N. J., a corporation of Delaware

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This invention relates to an improved process for the conversion of solid or liquid distillable carbonaceous materials into valuable liquid hydrocarbon products, especially benzines.

It has already been proposed to treat distillable carbonaceous materials with hydrogen, under pressure and at an elevated temperature, in several stages. It is also known that products of suitable boiling point range obtained by the destructive hydrogenation of solid carbonaceous materials, may be converted in the vaporous state into hydrocarbons of lower boiling point by treatment with catalytically acting materials, namely with metals of groups 2 to 8 of the periodic system, preferably zinc, magnesium, tungsten, molybdenum, vanadium, cobalt or compounds of these metals. It has been found, however, that these vaporous products obtained according to the methods hitherto practiced sometimes contain substances which settle down on the catalyst and impair its activity.

We have now found an improved method, according to which distillable solid or liquid carbonaceous materials are converted, to an extensive degree, into valuable liquid hydrocarbon products, especially benzines by destructively hydrogenating the initial materials under pressure, preferably above 50 atmospheres, if desired, in paste form, and then subjecting the resulting products preferably after the sufficiently converted products have been removed, to a second destructive hydrogenation, in the liquid phase and with a smaller amount of free hydrogen relative to the amount of carbonaceous material present in the reaction chamber, than in the first stage.

The amount of free hydrogen relative to the amount of carbonaceous material present in the reaction chamber is indicated in this specification by cubic meters of hydrogen per kilogram of carbonaceous material, and wherever a volume of hydrogen is referred to in this specification it should be understood that this refers to the volume measured under normal conditions of temperature and pressure. The statement that a smaller amount of hydrogen is employed in the second stage than in the first stage whereever employed in the present specification is intended to indicate that the reduction in the amount of hydrogen in the second stage is greater than that due simply to the consumption of hydrogen in the first stage of the process, and it should be understood that this latter reduction is not a reduction under the terms of the present invention.

For the first stage of the treatment it is preferable to employ a considerable excess of hydrogen, for example 4 to 20 cubic meters per kilogram of solid distillable carbonaceous material and suitable temperatures for the treatment are from 300° C. to 600° C., preferably from 400° to 600° C. If the liquefaction products obtained in this stage are to consist chiefly of heavy oils in which case pasting media may be used or omitted when treating solid carbonaceous materials, it is preferable both to employ a low temperature, such as 450° C., and to operate with a throughput of over 0.5 kilogram of initial carbonaceous material to be converted, such as coal per 1 liter of reaction vessel capacity, per hour. Suitable pressures for carrying out the first reaction stage are for example pressures of 200, 250 or 400 atmospheres or more.

The initial materials which come under consideration comprise coal of all varieties including pit coal and lignite, peat and wood, in the raw state or dried shale or tar sand (and these are preferably granulated or finely ground prior to use), or liquid materials, such as mineral oils or tars or tar oils, or heavy residues. When the solid initial materials are treated without being made into a paste, they are preferably brought into contact with the hydrogen while in a finely divided state, the finely ground carbonaceous material sliding or being mechanically moved over plates, screens, tubes or oblique spiral surfaces, fixed or movably mounted in the reaction vessel.

In case liquid substances are employed as initial materials these are hydrogenated in the first stage to a substantial extent without, however, being split up very far, so that no dehydrogenation of the constituents of very high boiling point which under other conditions is liable to occur takes place and losses in the further stages due to polymerization are substantially avoided. In the further stage these products are then treated with smaller amounts of hydrogen and thereby split up into products of lower boiling point. It is preferable to maintain the same total pressure in the several stages, which is attained by reducing the partial pressure of the hydrogen to the same extent as the partial pressure of the hydrocarbons increases.

Pulverulent catalytic substances such as the metals of groups 5 and 6 of the periodic system or cobalt or their oxides or sulphides, may be added to the initial materials prior to the treatment. Or, the materials may be sprinkled or

impregnated (with or without the application of pressure) with an aqueous solution of a catalytic salt, such as ammonium molybdate.

If desired, the initial carbonaceous material to be destructively hydrogenated is preheated, and in case of the use of a solid material this may be effected with the addition of a liquid pasting medium which may vaporize as soon as the charge enters the reaction chamber, as for example benzine, benzene or other substances or fractions boiling at low temperatures derived from mineral oils or tars, or which may be a medium of high boiling point which does not vaporize to any substantial extent as for example fractions of petroleum, tar or hydrogenating product, boiling above 325° C. Heating up in the said manner may be effected for example in a preheater in which the initial materials are passed through a tube over the outside of which a heating fluid is passed in the same direction, said preheater being provided with means whereby the heat transfer is reduced along the length of the tube beyond the reduction in heat transfer which would occur if no such means were provided.

In any one case it is advisable to conduct the heating with such precautions as to ensure the prevention of any coking, since the formation of coke implies a reduction of yield in the subsequent hydrogenation under pressure.

If desired the hydrogenating gas alone may be preheated, or again the carbonaceous material may be preheated in admixture with the hydrogenating gas. Finally the reaction vessel may be heated, for example by heating means arranged therein. Any of the aforesaid heating means may be combined.

The products from the first stage of the reaction vessel are usually in continuous working passed directly to the second stage. In this case the amount of hydrogen relative to the carbonaceous material may be reduced either by a withdrawal of a part of the hydrogen, or by an admixture of additional carbonaceous material or both of these methods combined. The products may also intermediately be passed to storage.

In practice the reaction products from the first stage may be passed into an adjoining high pressure separating vessel, without coming into contact with air. A certain degree of pressure release may occur between the first and the second stage, but occasionally it may also be advantageous to avoid any pressure release between the two reaction stages. Here, the gaseous and low-boiling components, such as benzine (in vapor form), can be wholly or partially drawn off, together with hydrogen, at the upper part of the vessel. According to the extent to which cooling occurs, middle oil constituents can also be withdrawn in the state of vapor.

The liquid or paste present in the said high pressure separating vessel is heated up again to the temperature necessary for attaining that used in the second stage of the reaction, for example, in a preheater, together with fresh hydrogen and/or together with a portion of the gaseous constituents consisting substantially of hydrogen, methane and its homologues, which may still contain low boiling hydrocarbons.

In order to maintain the liquid condition during the second stage of treatment, carbonaceous liquids of high boiling point, such as high temperature tar, may be added, if desired without otherwise reducing the amount of hydrogen after the first stage of the process. A suitable method of procedure consists in mixing, after the first stage and the removal, if desired, of the low boiling constituents, the improved products obtained with the added liquid and an amount of hydrogen of up to 4 cubic meters per kilogram of oil, and, after being passed through a heating apparatus, leading the mixture to the reaction vessel for the further hydrogen treatment, in the liquid phase.

When the hydrogen employed in the first stage has become too far enriched in impurities formed in the first stage, such as methane and its homologues and possibly hydrogen sulphide or carbon dioxide and is to be employed in the second stage, it is advisable to free the hydrogen from the impurities formed in the first stage, before proceeding to the second stage of the treatment, this being effected, for example, by washing it with liquid adsorbents or by passing it over solid adsorbents. The materials are then passed into a second reaction vessel, where they are subjected, in the liquid phase, to catalytic treatment under a high pressure preferably of at least 50 atmospheres. This second stage is carried out at temperatures between 300° C. and 500° C., preferably between 300° and 450° C. The reaction products of the first stage may, however, be passed directly into the adjacent reaction vessel, without the interposition of an intermediate vessel, in which case care must be taken to reduce the volume of hydrogen at a suitable point after the first stage. This may be effected by withdrawing a part of the hydrogen after cooling in a cooler and conducting the vaporous parts to a condenser. In the second stage, the proportion of hydrogen usually amounts to between 1 and 4 cubic meters per kilogram of carbonaceous materials, for example, oil and the high boiling constituents are converted into middle oils.

In the second stage, it is advisable to maintain a certain level of liquid in the reaction vessel, this being accomplished by drawing off the liquid through the side of the reaction vessel, or by means of an upcast pipe, and mixing it again with the liquid reaction product from the first stage, whilst the vaporous products are drawn off at the top. The second reaction vessel, may also be provided with a separate circulation of hydrogen, since the partial pressure of the gas must be lower, in this stage of the treatment, than during the treatment of the initial carbonaceous material. Suitable catalysts are the metals of groups 4 to 8 of the periodic system and zinc and cadmium or compounds of these metals, preferably their oxides, sulphides, phosphides, nitrides or carbonates.

The said second stage may be followed by still further stages of treatments with hydrogen in which the amount of hydrogen may be still further reduced, if desired.

By the hydrogenating treatment in the second or further stages the products which have a tendency to polymerize when further treated by destructive hydrogenation in the form of vapor, are rendered harmless. They are therefore particularly adapted for a further destructive hydrogenation wholly or partially in the vapor phase, to which they may be subjected with or without intermediate condensation according to circumstances, and therefore the liquid products obtained may be passed, wholly or partially in the state of vapor, over catalysts in the presence of hydrogen under pressure. The last mentioned

reaction may be carried out at temperatures between 300° C. and 600° C. preferably between 300° and 500° C. The pressure may be for example 20, 100, 200, 500 or 1000 atmospheres.

For example the vapors issuing from the second or further reaction stage may be condensed and then passed wholly or partially in the state of vapor over catalysts, in the presence of hydrogen under pressure of for example 50, 100, 200, 500 or 1000 atmospheres and at an elevated temperature ranging between 350° and 550° C., by which means they undergo practically complete conversion into benzine, without any substantial loss and without any deposits being formed on the catalyst or in any other places in the reaction vessel. Suitable catalysts for this third reaction stage are the metals of the groups 3 to 8 of the periodic system of the elements and their oxides and sulphides, for example as described in application Ser. No. 586,948, filed January 15th, 1932.

In the second stage of the process, catalysts must be employed. Generally it is advantageous to employ catalysts also in the first stage. In the first stage preferably amounts of from 0.01 to 2 per cent, reckoned on the weight of the initial solid materials, are employed, while in the second stage amounts of from 10 to 30 per cent reckoned on the amount of carbonaceous material present, are suitable.

The advantage of the process according to the present invention consists in the fact that it furnishes very high yields of valuable, and in particular low-boiling hydrocarbons from solid carbonaceous materials, with a considerable saving of energy and without any working troubles.

The following example will further illustrate the nature of this invention and is given with reference to the accompanying diagrammatic drawing, which illustrates an arrangement of apparatus suitable for carrying out the process according to the invention but the invention is not restricted to this example nor to the particular arrangement shown in the drawing.

Example

Pit coal is finely ground, and impregnated with an aqueous solution of ammonium molybdate, so as to contain 2 grams of ammonium molybdate per 1 kilogram of coal. It is then charged at W into the reaction vessel B, under a pressure of 250 atmospheres, and is passed through the vessel by means of revolving inset members of the plate type. The hydrogenating gas is preheated to 450° C. in a gas heated apparatus A, and passed through the reaction vessel in counterflow. The volume of gas is 12 cubic meters per kilogram of coal. If in the first stage the coal is treated without an addition of paste oil, the ashy residue is removed at M and freed from catalyst and oils. After passing a coal dust trap X, which is omitted, if coal paste is employed in the first stage, the contents of the reaction vessel enter a separator C., in which a constant level of the separated liquid products is maintained. The vaporous products and hydrogen pass off at D and are led, through a condenser E, into a high pressure separating vessel F, in which the benzine and middle oil constituents are condensed. The hydrogen is then passed through a purifier G, for the removal of impurities. A portion of the hydrogen, the amount of which can be ascertained with precision by means of a balance provided in the piping, is then diverted at H and is led, in association with the products coming from the separator C, through a gas heated preheater J, and thence into the reaction vessel K. In this latter, a colloidal catalyst, composed of 80 parts of molybdic acid, zinc oxide and magnesia in molecular proportions based on the molybdenum, and 20 parts of tungsten sulphide, and made into paste with a heavy oil, is introduced through the pipe L, and may remain in the reaction vessel for a considerable period. The quantity of catalyst is selected so that a concentration of 25 per cent reckoned on the liquid present in the reaction vessel, is maintained in the said vessel. The temperature in the latter is 460° C. and the amount of hydrogen 2 cubic meters per 1 kilogram of oil. Solid residues are preferably removed from the reaction vessel K at M'. The vaporous products passing off at N are transferred to a fractionating column O, where they are separated into heavy oil, middle oil and benzine, the latter passing through the cooler P and being collected in the vessel Q. The middle oil drawn off at R is heated, together with hydrogen, to 450° C. by the aid of a preheater S, and is passed, in the condition of vapor, into a reaction tower T, charged with tungsten sulphide in lump form. After passing through the cooler P', the improved effluent products are freed from middle oils in the first condenser U, the said oils being immediately returned to the reaction tower T, for complete conversion into benzine, whilst the resulting benzine is collected in the vessel V. Heavy oil is drawn off at the bottom of the column O, and may be employed for converting fresh amounts of coal, into the state of paste, or passed into the reaction vessel K. A pressure of about 200 atmospheres is maintained in the said reaction tower T, and the amount of hydrogen is reduced as compared with the second stage.

What we claim is:—

1. A process for the conversion of distillable solid or liquid carbonaceous material into lower boiling liquid hydrocarbon products which comprises destructively hydrogenating said material under a high partial pressure of hydrogen and at a temperature between 300 and 600° C., and for such a period of time such as to effect a substantial saturation of said material without a material conversion into hydrocarbons of the boiling point range of benzine and middle oil, separating from the resulting products any benzine and middle oil formed, subjecting the remainder to a further destructive hydrogenation at a temperature between 300 and 500° C. in the liquid phase in the presence of free hydrogen the ratio between which and the carbonaceous material is materially smaller than the ratio between these materials resulting from the first stage, for such a time as to effect splitting of said material to lower boiling hydrocarbons without coke formation and then destructively hydrogenating in the vapor phase at least part of the lower boiling products obtained in the second stage treatment.

2. A process for the conversion of distillable solid or liquid carbonaceous material into lower boiling liquid hydrocarbon products which comprises destructively hydrogenating said material under a high partial pressure of hydrogen and at a temperature between 300° and 600° C. and for such a period of time as to effect a substantial saturation of said material without a material conversion into hydrocarbons of the boiling point range of benzine and middle oil,

separating from the resulting products any benzine and middle oil formed, subjecting the remainder to a further destructive hydrogenation at a temperature between 300° and 500° C. in the liquid phase in the presence of a materially smaller amount of free hydrogen relative to the amount of carbonaceous material present in the reacting chamber than in the first stage for such a time as to effect splitting of said material to lower boiling hydrocarbons with absorption of less hydrogen than in the first stage and then destructively hydrogenating in the vapor phase, at a higher temperature, at least part of the lower boiling products obtained in the second stage treatment under a similar low partial pressure of hydrogen.

3. A process according to the preceding claim in which 4 to 20 cubic meters of hydrogen per kilogram of distillable carbonaceous material are employed in the first stage.

4. A process according to claim 2 in which from 4 to 20 cubic meters of hydrogen per kilogram of distillable carbonaceous material are employed in the first stage and 1 to 4 cubic meters of hydrogen per kilogram of distillable carbonaceous material are employed in the second destructive hydrogenation.

5. A process according to claim 2 in which in the first stage the temperature employed is between 400 and 600° C., the pressure is at least 50 atmospheres and from 4 to 20 cubic meters of hydrogen per kilogram of distillable carbonaceous material are employed and in which the temperature of the second destructive hydrogenation is between 300° and 400° C.

6. A process according to claim 1 in which the smaller ratio of hydrogen to carbonaceous material employed in the second destructive hydrogenation is effected by withdrawing part of the hydrogen from the reaction mixture issuing from the first destructive hydrogenation.

7. A process according to claim 1 in which the smaller ratio of hydrogen to carbonaceous material employed in the second destructive hydrogenation is effected by adding a carbonaceous liquid of high boiling point to the mixture of hydrogen and carbonaceous material resulting from the first destructive hydrogenation.

8. A process according to claim 1 in which a destructive hydrogenation catalyst immune to sulphur poisoning is used in the first stage in an amount of from 0.01 to 2 per cent of the weight of the initial material and a destructive hydrogenation catalyst immune to sulphur poisoning is employed in the second destructive hydrogenation in an amount of 10 to 30 per cent of the weight of the carbonaceous material subjected to that step.

9. A process according to claim 2 in which a destructive hydrogenation catalyst immune to sulphur poisoning is used in the first stage in an amount of from 0.01 to 2 per cent of the weight of the initial material and a destructive hydrogenation catalyst immune to sulphur poisoning is employed in the second destructive hydrogenation in an amount of 10 to 30 per cent of the weight of the carbonaceous material subjected to that step.

MATHIAS PIER.
WALTER KROENIG.