

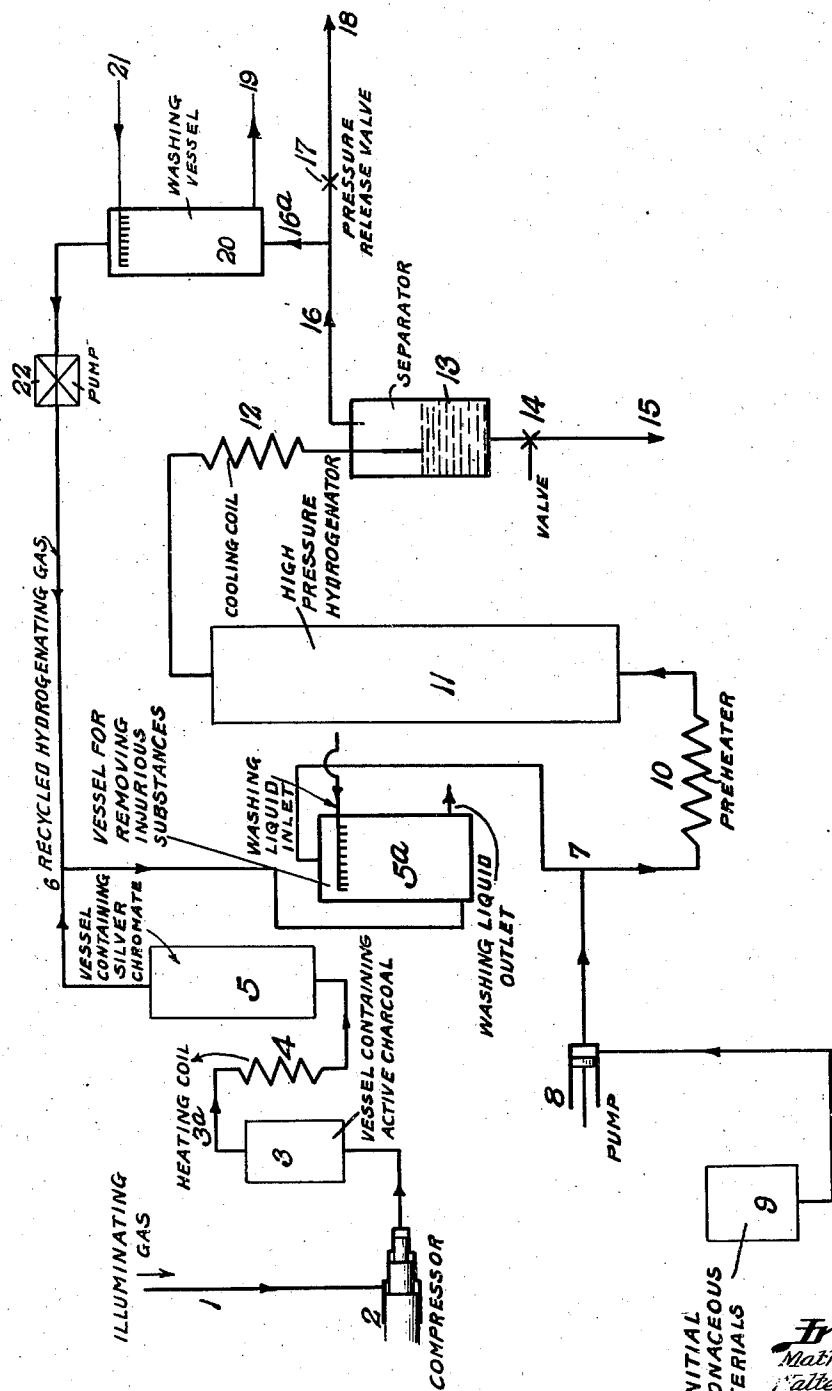
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PRODUCTION OF VALUABLE HYDROCARBONS

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PRODUCTION OF VALUABLE
HYDROCARBONS

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This invention relates to improvements in the production of valuable hydrocarbons.

It has already been proposed to use gases containing hydrogen, preferably in the presence of catalysts, in the preparation of valuable hydrocarbons from distillable carbonaceous materials, such as coals, tars, mineral oils, their distillation and conversion products, by destructive hydrogenation at temperatures between 300° and 700° C., preferably between 400° and 550° C., and under elevated pressures of at least 20 atmospheres, which hydrogenation may also be carried out under such mild conditions, that a refining of liquid mixtures of hydrocarbons from impurities, in particular from sulphur compounds without substantial splitting of the hydrocarbons is effected. It has been found, however, that not all gases containing hydrogen obtained in industrial processes are directly employable for destructive hydrogenations; for example, when employing the gases containing hydrogen, obtained by the degasification of solid fuels, under pressure and at elevated temperature, considerable difficulties, such as deposition of carbon or of solid or semi-solid high molecular carbon compounds, and a reduction in the hydrogenating effect, are liable to occur.

We have now found that these difficulties are due to the fact that gases obtained by the degasification of solid bituminous materials, such as by the low temperature carbonization of brown and mineral coals, by the distillation of oil shales or by the preparation of coke from mineral coal as coke oven gas or illuminating gas, when exposed to temperatures above 300° C. under increased pressure deposit carbonaceous substances, by reason of the occurrence of polymerizations or condensations of certain constituents, peculiar to the said gases and these deposits lead to clogging up of the apparatus after operating for long periods of time.

On the basis of this knowledge, the difficulties encountered when employing the gases obtained by the degasification of solid fuels as the hydrogenating gas are obviated according to the present invention by removing from the said gases before their employment those constituents which when heated under pressure as such or together with the initial materials to be treated undergo changes which give rise to injurious reactions,

such as depositions or reduction of the hydrogenating action.

The said gases usually contain about 0.05 to 1 per cent of oxygen, from 0.1 to 0.5 gram of organically combined sulphur per cubic meter of gas, the sulphur being mainly present as carbon disulphide and mercaptanes, and oxides of nitrogen in an amount of about 0.0001 per cent.

It has been found that in particular the unsaturated hydrocarbons, mainly those of strongly unsaturated nature, further free oxygen, the sulphur compounds and the oxides of nitrogen present in the said gases give rise to the said troubles and that it is therefore the chief problem to remove more or less completely these constituents from the gases.

When the said gases are heated at atmospheric pressure, the formation of deposits is far less than when they are heated under increased pressure, so that when employing the gases at atmospheric pressure it is hardly necessary to remove the said substances.

The removal of the constituents which lead to the injurious deposits from the gases may be effected in different ways, as for example by employing agents, adsorbing the said constituents, chemical agents and/or catalysts at atmospheric or increased pressure.

For example solid adsorption agents, such as bleaching earth, active carbon, silica gel, and the like may be employed, if desired at moderately elevated temperature, for example between 150° and 300° C.

The said adsorption agents remove part of the organically combined sulphur, have a condensing action on diolefines and promote the reaction between the oxides of nitrogen and diolefines to form high boiling products.

Chemical agents may be employed instead of adsorption agents. For example the unsaturated hydrocarbons may be removed by washing with sulphuric acid, whereby in order to economize with acid, the concentration is preferably regulated so that the unsaturated hydrocarbons which react especially readily, namely the diolefines and acetylenes, are mainly removed while the more difficultly decomposable, simple unsaturated hydrocarbons are left in the gases. In this manner a part of the sulphur compounds are removed at the same time. Instead of sulphuric acid,

other reagents which react with unsaturated hydrocarbons and if desired also with sulphur compounds may be employed, as for example dilute nitric acid, alkaline hypochlorite solution and anhydrous aluminium chloride.

It has further been found that by leading the said gases over hydrogenating catalysts, such as those comprising difficultly reducible metal oxides of the 6th group of the periodic system, as for example oxides of molybdenum, tungsten, uranium or chromium, at atmospheric pressure and/or increased temperature (for example from about 350° to 400° C.) the said injurious constituents of the gases, chiefly the unsaturated hydrocarbons and the oxygen as well as any oxides of nitrogen present, are so far removed that the gases may then be directly employed in continuous operation at elevated temperatures even under increased pressure. The gases may also be treated at temperatures of, for example, from 200° to 300° C. with catalysts containing silver, for example those obtained by precipitating salts of silver on carriers or those composed of salts of silver, such as silver chromate; in this manner the oxygen is removed almost entirely and the unsaturated hydrocarbons to such an extent that the gases may then be heated to high temperatures without trouble. The removal of the oxygen and/or the unsaturated hydrocarbons may also be carried out with different catalysts. Instead of treating the gases at high temperatures, for example between 350° and 700° C., under atmospheric pressure, the purification may be carried out at moderately elevated temperatures, for example between 180° and 300° C., under increased pressures above 10 atmospheres, for example 25, 50, 100, 200, 500 or more atmospheres.

Furthermore, the gases may be freed from injurious constituents by treatment in a liquid carbonaceous medium of high boiling point at temperatures of about 200° C. or more under pressure, as for example from 100 to 200 atmospheres, in the presence of catalysts, such as chromium, uranium or vanadium or compounds thereof, alone or in conjunction with each other or with other elements or compounds, as for example silver, zinc or compounds thereof and the like, or in the presence of catalysts forming methanol, such as vanadic acid, manganese oxide, uranium oxide, titanitic acid, chromic acid, zinc oxide, or mixtures of zinc oxide with uranium oxide, lead oxide, titanitic acid, chromium oxide, or with chromium oxide and manganese oxide, and the like.

It has been found that gases purified in the said manner may be heated to reaction temperatures of for example from 300° to 500° C., even under a pressure of for example 200 atmospheres or more, for example 300, 500, 800 or 1000 atmospheres, without the occurrence of deposits.

Several of the said methods of purification may also be employed. Depending on the extent of the purification effected by the treatment with chemical or adsorption agents, it is in some cases necessary, for example if substances, such as diolefines, are present which give rise to the formation of resins in the presence of oxygen to remove the oxygen before the heating under increased pressure, and this may be carried out for example by the said catalytic methods of purification.

In addition to the said injurious impurities, the said gases usually contain small amounts of iron carbonyl by reason of their content of carbon monoxide. This iron carbonyl is liable to be decomposed in the presence of the catalysts

with the formation of iron depositing on and thereby reducing the activity of the said catalysts. When these impurities are not removed by the pretreatment it is preferable to remove them before heating the gases, especially when catalysts are to be employed in the destructive hydrogenation processes and this may be effected in the usual manner, as for example by means of active carbon.

In some cases it may be advantageous to reduce the content of carbon dioxide and carbon monoxide in the gases, especially when catalysts, such as those containing molybdenum or iron, are to be employed in the destructive hydrogenation which decompose carbon monoxide with the formation of carbon black or which promote strongly the reduction of carbon oxides to methane, so that the heat evolved during the reduction is greater than is permissible for maintaining the desired reaction temperature during the destructive hydrogenation and, moreover, the concentration of methane in the gases becomes too high. Since, on the other hand, it may be advantageous in order to maintain the necessary reaction temperature, or in reactions which proceed with but a slight evolution of heat, that certain amounts of carbon monoxide or carbon dioxide should be present in the hydrogenating gas, the oxides of carbon are preferably only so far removed from the said gases that the residue remaining is sufficient to give the desired evolution of heat during its conversion with hydrogen to form methane. As a rule the content of carbon monoxide and carbon dioxide should not be greater than 2 per cent.

The removal of the carbon dioxide may be effected by the usual methods, as for example by washing with water under pressure and the removal of the carbon monoxide by the usual methods of washing with solutions of cuprous salts. Furthermore, the amounts of carbon monoxide and carbon dioxide may be so far reduced by reduction to methane and water by the said purification of the gases by means of catalysts at atmospheric pressure that they are present in the desired amount.

The gases freed from impurities which give rise to the formation of deposits may be employed for different processes for the destructive hydrogenation of carbonaceous substances, especially in the presence of catalysts. For example, the benzene obtained by the low temperature carbonization of brown coal may be freed from the constituents which injuriously affect its employment in motors by catalytic destructive hydrogenation with the purified low temperature carbonization waste gases. The same result is obtained with the crude benzene obtained by the degasification of mineral coals at high temperatures, for example between 900° and 1300° C., when it is treated with the coke oven or illuminating gas formed at the same time, after it has been purified in the said manner. The process according to the present invention may also advantageously be employed, however, for other processes of destructive hydrogenation, such as the conversion of hydrocarbons of high boiling point into those of lower boiling point.

The hydrogenating gases, after their employment for the destructive hydrogenation, have an increased heating value by reason of their content of methane, which has been enriched during the reaction, and of gaseous hydrocarbons of high molecular weight, and, moreover, are practically free from carbon monoxide so that

they may be advantageously employed as heating or illuminating gases. If the gases obtained from the destructive hydrogenation are to be rendered useful for the further treatment of carbonaceous materials, care should be taken by the removal of a part of the gaseous hydrocarbons that the partial pressure of hydrogen is sufficiently high.

An apparatus suitable for carrying out our process is illustrated in diagrammatic form in the accompanying drawing, to which suitable descriptive legends have been applied. The apparatus shown is only one of various types in which our process could be carried out. The manner in which our process is carried out in the apparatus shown in the drawing, is apparent from the following description. The illuminating gas entering pipe 1 is compressed to, for instance, 200 atmospheres, in compressor 2 and is led through active charcoal containing vessel 3. The gas is then conveyed through iron-free pipe 3a, into heating coil 4 and there preheated at a temperature of 250° C. At this temperature it enters the silver chromate containing vessel 5 and may be united in the T-piece 6 with any recycled hydrogenating gas. In the T-piece 7 the product which arrives by way of tank 9 and is compressed in pump 8 to, for example, 200 atmospheres, is mixed with the washed gas issuing from chamber 5a is preheated in coil 10 and then subjected to pressure hydrogenation or pressure refining in high-pressure hydrogenator 11. The reaction products which depart from the hydrogenator are cooled in cooling coil 12 and separated into liquid and gaseous products in separator 13. The liquid portions are released by way of valve 14 and removed from the system through pipe 15, whereas the gaseous portions leave through pipe 16 and are either released in the pressure release valve 17 and removed by way of pipe 18, or else, as stated, are employed for the further treatment of carbonaceous materials by following a circular course, in that they are conducted through pipe 16a into washing vessel 20 and there liberated from a part of the gaseous hydrocarbons by means of the oil pressed into the washer through pipe 21, which oil flows off again through pipe 19, and are re-conveyed into the reaction system by means of pump 22 to the T-piece 6.

The following example will further illustrate the nature of this invention but the invention is not restricted to this example.

Example

Illuminating gas, compressed to 200 atmospheres, is first led through a high-pressure container filled with active carbon and thus freed from iron carbonyl. The gas is then led through iron-free pipes into a high-pressure chamber which is charged with a catalyst consisting of silver chromate deposited on silica gel. The chamber is kept at a temperature of 250° C. By this treatment the oxygen content of the illuminating gas is reduced from 0.2 per cent to 0.01 per cent or less and the acetylene content is reduced from 0.06 per cent to 0.002 per cent or less. The oxides of nitrogen are converted almost completely into nitrogen or ammonia and water. The content of the other less unsaturated hydrocarbons and of the carbon monoxide is practically unreduced. By this treatment, condensation does not occur either beforehand or on the catalyst. After leaving the chamber the

illuminating gas, thus purified, is led with crude benzene at 390° C. over a catalyst consisting of the oxides of vanadium and zinc. When the gases and vapors leaving the reaction vessel are cooled, a product separates which can be refined to give a pure benzene mixture with only a very small waste, including the crude methanol formed catalytically from the carbon monoxide and hydrogen contained in the illuminating gas. Neither in the preheating chamber nor in the catalyst itself is there any condensation which injures the continuous operation.

Instead of the oxides of vanadium and zinc, the sulphides of these metals prepared by treatment of the metals or the oxides with volatile sulphur compounds in the presence of hydrogen at an elevated temperature and in the absence of hydrocarbons, or catalysts consisting of molybdic acid, zinc oxide and magnesia may also be employed with advantage. In this manner a considerably purer product is obtained which need not be subjected to further purification. The catalyst containing molybdenum has the further advantage that, by virtue of its capacity of promoting the partial conversion of the carbon monoxide contained in the illuminating gas into methane, a considerable amount of heat is evolved, which may be made useful for the maintenance of the reaction temperature.

If, on the contrary, the illuminating gas freed from iron carbonyl, is used directly for carrying out a destructive hydrogenation or pressure refining without passing through the said purifying chamber, the preheating chamber becomes clogged up with deposits of condensation products similar to carbon black even after a few days so that continuous operation is impossible.

What we claim is:—

1. The process for destructively hydrogenating a distillable carbonaceous material with a hydrogenating gas obtained by the degasification of a solid bituminous material, which comprises passing an impure gas from said source which may initially contain iron carbonyl over a catalyst having a hydrogenating action at a pressure ranging upwards from atmospheric pressure and a temperature of from 180 to 700° C., the temperature being within the range of 350 to 700° C. when the pressure is atmospheric and within the range of 180 to 300° C. when the pressure exceeds atmospheric to thereby saturate any highly unsaturated hydrocarbons and convert any sulphur compounds, free oxygen, oxides of nitrogen and undesirable quantities of oxides of carbon into readily removable and non-injurious inorganic substances, removing such of said inorganic substances as may be injurious, any iron carbonyl in said impure gas being removed therefrom at any stage prior to the destructive hydrogenation, and effecting the destructive hydrogenation by contacting the thus purified gas with said carbonaceous material under a temperature and pressure suitable for destructive hydrogenation and in the presence of a destructive hydrogenation catalyst.

2. The process for destructively hydrogenating a distillable carbonaceous material with a hydrogenating gas obtained by the degasification of a solid bituminous material, which comprises passing an impure gas from said source which may initially contain iron carbonyl over a catalyst having a hydrogenating action, at a temperature of about 350 to 700° C. and at atmospheric pressure to thereby saturate any highly unsaturated hydrocarbons and convert any sulphur

compounds, free oxygen, oxides of nitrogen and undesirable quantities of oxides of carbon into readily removable and non-injurious inorganic substances, removing such of said inorganic substances as may be injurious, any iron carbonyl in said impure gas being removed therefrom at any stage prior to the destructive hydrogenation, and effecting the destructive hydrogenation by contacting the thus purified gas with said carbonaceous material under a temperature and pressure suitable for destructive hydrogenation and in the presence of a destructive hydrogenation catalyst.

3. The process for destructively hydrogenating a distillable carbonaceous material with a hydrogenating gas obtained by the degasification of a solid bituminous material which comprises passing an impure gas from said source which may initially contain iron carbonyl over a catalyst having a hydrogenating action, at a temperature of about 180 to 300° C. and a pressure in excess of 10 atmospheres to thereby saturate any highly unsaturated hydrocarbons and convert any sulphur compounds, free oxygen, oxides of nitrogen and undesirable quantities of oxides of carbon into readily removable and non-injurious inorganic substances, removing such of said inorganic substances as may be injurious, any iron carbonyl in said impure gas being removed therefrom at any stage prior to the destructive hydrogenation, and effecting the destructive hydrogenation by contacting the thus purified gas with said carbonaceous material under a temperature and pressure suitable for destructive hydrogenation and in the presence of a destructive hydrogenation catalyst.

4. The process as defined in claim 1 wherein the catalyst having a hydrogenating action is also immune to poisoning by sulphur.

5. The process as defined in claim 1 wherein the catalyst having a hydrogenating action comprises a metal of group 6 of the periodic system.

6. The process for destructively hydrogenating a distillable carbonaceous material with a hydrogenating gas obtained by the degasification of a solid bituminous material which comprises passing an impure gas from said source which may initially contain iron carbonyl over a catalyst comprising an oxide of a metal of group 6 at a temperature of from 350 to 700° C. and at atmospheric pressure to thereby saturate any highly unsaturated hydrocarbons and convert any sulphur compounds, free oxygen, oxides of nitrogen and undesirable quantities of oxides of carbon into readily removable and non-injurious inorganic substances, removing such of said inorganic substances as may be injurious, any iron carbonyl in said impure gas being removed therefrom at any stage prior to the destructive hydrogenation, and effecting the destructive hydrogenation by contacting the thus purified gas with said carbonaceous material under a temperature and pressure suitable for destructive hydrogenation and in the presence of a destructive hydrogenation catalyst.

7. The process as defined in claim 3 wherein the catalyst having a hydrogenating action comprises an oxide of a metal of group 6 of the periodic system.

8. The process as defined in claim 1 wherein the catalyst having a hydrogenating action comprises silver.

9. The process as defined in claim 2 wherein the catalyst having a hydrogenating action comprises silver.

10. The process as defined in claim 3 wherein the catalyst having a hydrogenating action comprises silver.

11. The process as defined in claim 1 wherein the temperature employed is selected from the range of 200 to 270° C., the pressure is at least 10 atmospheres and the catalyst having a hydrogenating action is silver chromate.

12. The process as defined in claim 1 wherein the temperature employed is selected from the range of 200 to 270° C., the pressure is about 200 atmospheres and the catalyst having a hydrogenating action is silver chromate deposited on silica gel.

13. The process as defined in claim 5 wherein the degasification gas is treated with an adsorption agent prior to being passed over the catalyst having a hydrogenating action.

14. The process as defined in claim 6 wherein the degasification gas is treated with sulphuric acid prior to being passed over a catalyst having a hydrogenating action.

15. The process for destructively hydrogenating a distillable carbonaceous material with a hydrogenating gas obtained by the degasification of a solid bituminous material which comprises treating an impure gas from said source containing iron carbonyl with active carbon to remove said iron carbonyl and then passing said gas over a catalyst comprising silver chromate at a temperature of from about 200 to 270° C. and a pressure of at least 10 atmospheres to thereby saturate any highly unsaturated hydrocarbons and convert any sulphur compounds, free oxygen, oxides of nitrogen and undesirable quantities of oxides of carbon into readily removable and non-injurious inorganic substances, removing such of said inorganic substances as may be injurious and contacting the thus purified gas with said carbonaceous material under a temperature and pressure suitable for destructive hydrogenation and in the presence of a destructive hydrogenation catalyst.

16. The process for destructively hydrogenating a distillable carbonaceous material with a hydrogenating gas obtained by the degasification of a solid bituminous material which comprises removing any iron carbonyl from an impure gas from said source and passing said gas over a catalyst comprising an oxide of a metal of group 6 of the periodic system at a pressure ranging upwards from 180 to 700° C., the temperature being within the range of 350 to 700° C. when the pressure is atmospheric and within the range of 180 to 300° C. when the pressure exceeds atmospheric to thereby saturate any highly unsaturated hydrocarbons and convert any sulphur compounds, free oxygen, oxides of nitrogen and undesirable quantities of oxides of carbon into readily removable and non-injurious inorganic substances, removing such of said inorganic substances as may be injurious and contacting the thus purified gas with said carbonaceous material under a temperature and pressure suitable for destructive hydrogenation and in the presence of a destructive hydrogenation catalyst.

17. The process for destructively hydrogenating a distillable carbonaceous material with a hydrogenating gas obtained by the degasification of a solid bituminous material which comprises removing any iron carbonyl from an impure gas from said source and passing said gas over a catalyst comprising silver at a pressure ranging upwards from 180 to 700° C., the temperature being within the range of 350 to 700° C. when

the pressure is atmospheric and within the range of 180 to 300° C. when the pressure exceeds atmospheric to thereby saturate any highly unsaturated hydrocarbons and convert any sulphur compounds, free oxygen, oxides of nitrogen and undesirable quantities of oxides of carbon into readily removable and non-injurious inorganic substances, removing such of said inorganic sub-

stances as may be injurious and contacting the thus purified gas with said carbonaceous material under a temperature and pressure suitable for destructive hydrogenation and in the presence of a destructive hydrogenation catalyst.

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