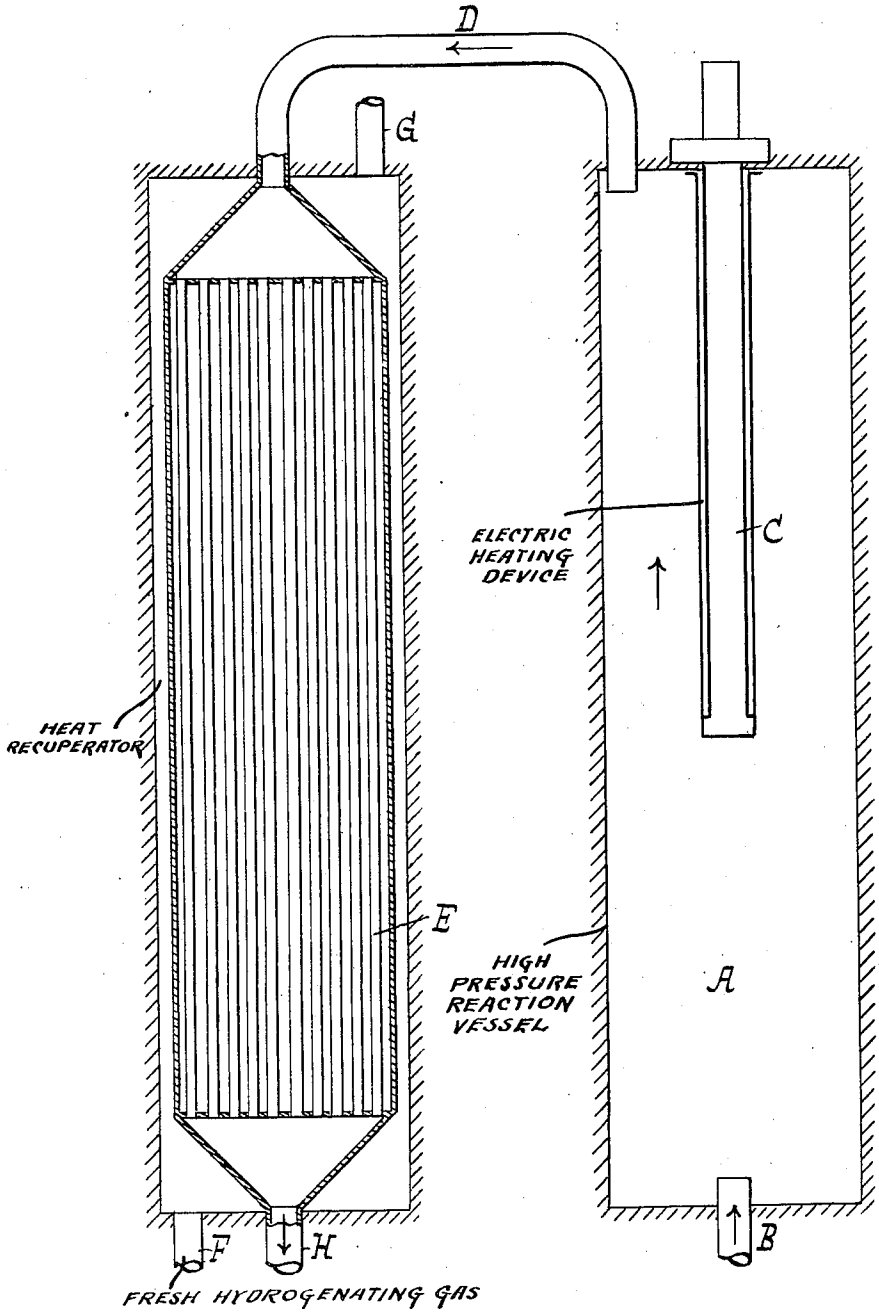
Dec. 8, 1931. M. PIER 1,835,425

DESTRUCTIVE HYDROGENATION OF CARBONACEOUS MATERIALS

Filed Oct. 27, 1927



INVENTOR
Mathias Pier
BY
Haußfeld Warland
ATTORNEYS

Patented Dec. 8, 1931 1,835,425

UNITED STATES PATENT OFFICE

MATHIAS PIER, OF HEIDELBERG, GERMANY, ASSIGNOR, BY MESNE ASSIGNMENTS, TO STANDARD-I. G. COMPANY, OF LINDEN, NEW JERSEY, A CORPORATION OF DELAWARE

DESTRUCTIVE HYDROGENATION OF CARBONACEOUS MATERIALS

Application filed October 27, 1927, Serial No. 229,084, and in Germany August 7, 1926.

In the copending application of Mittasch, Stern and Galle, Ser. No. 179,391, filed March 29, 1927, it has been shown that in cracking operations, i. e. the conversion of hydrocarbons of high boiling point into others of lower boiling point with or without the aid of hydrogen, the results hitherto obtained have been considerably impaired by the deposition of carbon on the metallic surfaces in the reaction vessel. According to the said application the said drawbacks are overcome by avoiding in the hot parts of the apparatus the presence of materials, in particular metals, which are capable of causing a deposition of carbon when hot.

Now, the present invention relates to the application of a similar principle to the manufacture of valuable hydrocarbons and derivatives by the destructive hydrogenation of carbonaceous materials, such as the various kinds of coal, tars, mineral oils and distillation, extraction and conversion products and residues thereof and the like, that is the treatment of the said materials with hydrogen or gases containing or giving off hydrogen, at elevated temperatures and under high pressure of 50 atmospheres or more, in the absence or presence of catalysts. Also in this reaction the economy of the process is often considerably reduced by undesirable by-reactions such as the formation of methane which is usually accompanied by the separation of carbon and often also by a strong attack of the reacting materials and the apparatus. These undesirable by-reactions which occur chiefly in the reaction vessel itself, but also in the hot parts adjacent thereto such as pipings, heat regenerators and the like, are caused by the action of hydrogen and sulfur on the material of the apparatus which is usually iron (steel) or copper; from these metals spongy sulfurous masses are formed which exert the said obnoxious influence on the course of the process. The formation of methane which can be utilized only after a tedious and expensive process of separation and combustion, by conversion into hydrogen causes in particular a highly uneconomical, useless consumption of hydrogen and a separation of carbon, giving rise to choking of the pipings and the like.

The iron, or steel usually employed for the construction of chemical apparatus has been found to be particularly obnoxious as it is strongly attacked for example by sulfur and by hydrogen and gives rise to the formation of methane, both on the parts which have suffered chemical attack and those parts which were not exposed to such attack. When working with initial materials containing sulfur, similar undesirable by-reactions occur after a short time also when employing copper, as the material of the apparatus.

I have now found that in the said process the formation of methane and also the deposition of carbon can be avoided practically completely when working with streaming gases and with a large excess of hydrogenating gas and excluding such substances as would give rise under the conditions of working to the formation of methane and deposition of carbon. Accordingly care must be taken that the reaction vessel including the catalyst, the walls of the vessel and, if such be arranged therein, the heating devices, and preferably also the other hot parts of the apparatus such as the pipings, heat regenerators and the like which come into contact with the organic reacting materials, are free from such substances as would cause the obnoxious by-reactions. It is also necessary to prevent the initial materials and especially the gases from conveying obnoxious substances into the reaction vessel or the other hot parts of the apparatus.

For the construction of the said parts of the apparatus or for coating these parts, alloys containing cobalt, molybdenum, tungsten, vanadium or manganese, or several of these elements and in addition thereto, if desired, a considerable percentage of nickel, in particular alloyed steels containing the said elements, are very suitable materials. Silver or its alloys are also suitable for the construction of the apparatus.

Those parts of the apparatus which come into contact with hot organic materials may also be provided with a content in certain

metalloids such as boron, arsenic, antimony, silicon, bismuth, phosphorus, selenium and the like. These metalloids may be alloyed with the metals, or they may be incorporated only with the surfaces thereof, for example by the action of compounds of the said metalloids on the surfaces of the apparatus. Also by this means the formation of methane and the separation of carbon are considerably reduced.

When the initial materials contain sulfur, copper is obnoxious as has already been pointed out above. However, when working with initial materials free from sulfur or when removing the sulfur therefrom before subjecting them to the treatment, also this metal may be employed.

Such metals and alloys are also very suitable in which the boundaries of the crystalline grains are substantially free from impurities as can be determined by microscopic examination. By such absence of impurities a stable crystal structure is obtained, as a consequence of which the material is not attacked even when the apparatus is subjected to a very severe treatment for a very long period. In some cases, for example when the initial materials to be treated contain sulfur, such substantially pure metals or alloys are attacked but such attack takes place only superficially, and accordingly, when the superficial layer which as been exposed to attack, peels off, a smooth surface free from pores is formed again which does not give rise to any obnoxious actions, whereas with the usual metals the entire structure would be loosened and accordingly the material would become porous. In the case of the said superficial attack of the metals or alloys free from impurities, the surfaces thereof may be kept clean and suitable for working in any suitable way for example by scraping. Metals and alloys which have been prepared by fusion in vacuo are particularly suitable as they are particularly free from the said impurities in the boundaries of the crystal grains.

I have further found that the said materials which do not give rise to the formation of methane and separation of carbon, may also be employed as catalysts in the process according to my present invention. It is advantageous to employ catalysts with a large and preferably smooth surface. For this purpose the catalysts may be constructed in any suitable manner for example they may be sheets or wires which may be heated to the temperature of the reaction for example by electric resistance heating. Catalysts of this kind are distinguished by their excellent stability in continued use. In order to keep the catalytically acting surfaces clean and smooth, it is advantageous to maintain a high speed of the reacting materials or gases so that a great relative movement between the catalytic surfaces and the reacting materials is established. This may be furthered by mechanically setting the catalysts into movement.

The initial materials may be employed in solid or liquid and preferably in a finely divided, for example atomized, state, or in the form of vapor. It is advantageous to work with the hydrogenating gas in a circulatory course and to provide an intimate contact of the said hydrogenating gas with the materials to be treated for example by employing the later in the form of thin layers or by stirring, atomizing and the like.

The process according to this invention is especially suitable for the production of valuable liquid fuels such as benzine, heavy oils for Diesel engines and the like, for the production of benzene and its homologues and also in the manufacture of valuable lubricants, solvents and the like.

My invention will be further illustrated with reference to the accompanying drawing which illustrates by way of example one form of apparatus suitable for carrying out my invention.

In the drawing A indicates the reaction vessel into which hot hydrogenating gas is introduced at B. The material to be treated may be introduced in the vapor state together with the hydrogenating gas or it may be fed in any other suitable manner. Heat is supplied to the reacting materials by an electric heating device C. The gases and vapors having undergone the reaction leave the reaction vessel by a pipe D and are passed through the tube system E of a heat regenerator, to which a cooling medium, for example fresh hydrogenating gas is supplied at F, which medium is withdrawn at G. The cooled gases and vapors leave the heat regenerator at H. According to the present invention at least the inner surfaces of the reaction vessel A, the pipe D and the tube system E are made of one of the aforesaid materials which do not lead to the formation of methane and separation of carbon. Also the heating device C is made of such a metal, preferably of a highly alloyed steel.

I claim:

1. In the destructive hydrogenation of bituminous materials at an elevated temperature and a pressure of at least 50 atmospheres, the steps which comprise working with a large excess of a hydrogenating gas in the form of a stream and effecting the hydrogenation in a vessel lined with an alloy resistant to corrosion and containing a considerable percentage of nickel and at least one metal selected from the class consisting of molybdenum, tungsten, vanadium and manganese, said alloy being substantially free from impurities in the boundaries of the crystal grains and said alloy containing, at

least at its surface, at least one metalloid capable of alloying with the constituents of said alloy selected from the class consisting of boron, arsenic, antimony, silicon, bismuth, phosphorus and selenium.

2. In the destructive hydrogenation of bituminous materials at an elevated temperature and a pressure of at least 50 atmospheres, the steps which comprise working with a large excess of a hydrogenating gas in the form of a stream and effecting the hydrogenation in a vessel lined with an alloy resistant to corrosion and containing a considerable percentage of nickel and at least one metal selected from the class consisting of molybdenum, tungsten, vanadium and manganese, said alloy being substantially free from impurities in the boundaries of the crystal grains and said alloy containing, at least at its surface, the metalloid boron.

3. In the destructive hydrogenation of bituminous materials at an elevated temperature and a pressure of at least 50 atmospheres, the steps which comprise working with a large excess of a hydrogenating gas in the form of a stream and effecting the hydrogenation in a vessel lined with an alloy resistant to corrosion and containing a considerable percentage of nickel and at least one metal selected from the class consisting of molybdenum, tungsten, vanadium and manganese, said alloy being substantially free from impurities in the boundaries of the crystal grains and said alloy containing, at least at its surface, the metalloid silicon.

In testimony whereof I have hereunto set my hand.

MATHIAS PIER.