[Second Edition.]

PATENT SPECIFICATION

Convention Date (France): Dec. 20, 1927.

302,683

Application Date (in United Kingdom): Dec. 5, 1928. No. 35,831/28.

Complete Accepted: Jan. 30, 1930.

425

COMPLETE SPECIFICATION.

Process and Apparatus for the Manufacture of Liquid Fuels by Hydrogenation of Vaporous Substances in the Presence of Catalysts.

We, COMPAGNIE INTERNATIONALE POUR LA FABRICATION DES ESSENCES ET PETROLES, of No. 1, Avenue de Villars, Paris, France, a Body corporate organised under the Laws of France, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to a process and apparatus for the manufacture of liquid fuels by hydrogenation of vaporous substances in the presence of catalysts.

The treatment of vaporous substances derived more particularly from the distillation or the gasification of combustibles of low value (lignites, shales, peats, etc.) or from tars, comprises in principle, on issue from the gas generating apparatus, a catalytic purification designed to eliminate, as fully as possible, the mineral sulphur and the organic sulphur. The vapours thus purified are led into apparatuses wherein, in the presence of active catalytic agents such as metals, mixtures of metals or alloys or oxides thereof, they are reduced in density and in most cases enriched with hydrogen by the addition, in such apparatuses of pure hydrogen or of hydrogenating gases separately manufactured for that purpose, or most generally of water gas and residual gases furnished by the final materials themselves.

The Compagnie Internationale pour la Fabrication des Essences et Petroles have previously indicated how, whilst operating at normal pressure, they have succeeded in carrying out in a continuous manner, a very nearly complete purification, by removing to the greatest extent possible the organic sulphur as well as the mineral sulphur.

In the specification of Patent No. 295,272, it has in particular been indicated how, by harnessing to the end of a plurality of batteries of purifiers alternately in period of activity and in period of regeneration, a protective purifier of far less capacity and of a much longer period of activity, it is able still further to extend the possible limits of purification.

Work recently carried out by Eugene Houdry and the applicants, has demonstrated that, in operating at suitable temperature, gaseous substances not having been subjected to an ideally perfect desulphurisation, can be admitted to a certain extent with impunity, into the hydrogenation apparatuses in the presence of catalytic agents, if care is taken to proceed in a continuous manner, with a regeneration of such catalytic agents.

If, for example, pure nickel is employed as the catalytic agent, such metal will give rise to the formation of a sulphide with all the sulphur not retained by the purification. It is apparent that in principle it would suffice constantly to reduce this sulphide to the extent and measure of its formation, in order to ensure, at every instant, in a continuous manner, a regeneration of pure metal.

This result has been partially obtained by introducing constantly reducing gases, in the form of hydrogen, water gas or residual gas from a preceding operation, into the various elements of the apparatus wherein is effected the catalysis in stages of gases and vapours previously purified.

The applicants and Mr. Houdry have precisely established that the additional gases play the double role of enriching gases and of gases serving to maintain permanent the catalytic agent in the active state. There is produced, in effect, constantly, for example with a catalyst of nickel a reversible reaction.

$$NiS + H_2 \Longleftrightarrow Ni + H_2S$$

Consequently the vapours reduced in density by being saturated with hydrogen, will necessarily carry over a little sulphuretted hydrogen at the outlet from the catalytic apparatus.

The present invention provides a practical utilisation of the scientific observation made by Mr. Houdry and ourselves.

The present invention therefore consists in a process for the hydrogenation, at normal pressure and in the presence of catalysts, of vaporous substances derived from the distillation or gasification of carbonaceous substances, in which the operation of reduction in density and hydrogenation in the presence of catalysts,

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which comprises a constant addition of fresh hydrogenating gas, is interposed between two purifications, a preliminary purification before entry into the catalytic apparatuses and which retains as far as possible all the mineral sulphur and the major portion of the organic sulphur, and a second purification after leaving the catalytic apparatuses whereby the enriched gases are freed from sulphur contained in the sulphuretted hydrogen which through the constant regeneration of the catalyst is constantly formed in the said catalytic apparatuses.

In the second purifier, containing for example copper, the H_2S decomposes and the hydrogen set at liberty will be able to be taken back in part to the catalytic apparatus.

To sum up, the new process comprises a hydrogenation in the presence of catalyst, interposed between two purifications. The preliminary purification is charged with retaining the mineral sulphur, and, to all the extent possible, the organic sulphur. In the course of the hydrogenation in the presence of catalysts the remaining sulphur derived principally from the very stable thiophenes, forms with the fresh enrichment gases, H_2S which, in the presence of the metal catalyst, decomposes, produces a sulphide, which is in turn immediately decomposed by the newly supplied fresh reducing gases. The remaining H_2S escapes with the synthetic hydrocarbons, and the sulphur which it contains finds itself retained in the outlet purifier, the hydrogen set at liberty being able to be taken back in part to the catalytic apparatuses.

Diagrams showing two examples of plants for carrying out the above described process are shown by the figures of the accompanying drawing.

In the example shown in Fig. 1, the gaseous substances produced in an apparatus A pass, in a continuous manner, into batteries of purifiers B, capable of being regenerated by a reversed flow of gas. At the outlet from each battery of purifiers, wherein are retained, to the full extent possible, the mineral sulphur and the organic sulphur, the gases and vapours pass through a check purifier C which retains the traces of sulphur not retained in B. The whole B and C have preferably the form described and shown in detail in the specification of the above mentioned previous patent application. On leaving the check purifiers, the gaseous substances pass into catalytic apparatuses, D^1, D^2, D^3 disposed to receive, by pipes d^1, d^2, d^3 an addition of fresh hydrogenating gas, which may be constituted, wholly or in part, by residual gas from a preceding operation.

According to the invention, the sulphuretted hydrogen, reformed in the catalytic apparatuses, passes into an outlet purifier, which, in the first example, is disposed immediately at the end of the catalytic apparatuses. This outlet purifier may comprise batteries of purifiers E followed, like the batteries of purifiers B, by check purifiers F. At the outlet from these check purifiers, the gaseous substances, formed then in the major part of condensible enriched hydrocarbons and of a certain quantity of non-condensible light hydrocarbons, are led, in the known manner, into an apparatus G, from whence the non-condensible vapours pass into a retaining apparatus H, charged with an absorbent such as active charcoal or washing oil. The remaining gases, after passage through an apparatus I wherein they are dispossessed of the carbonic acid with which they are charged, pass into a gasometer J. A part of these gases can be led off by a pipe K and be taken back to the inlet element D^1 of the catalytic apparatus, after passage through a heater L which raises them to the temperature suitable for the reaction in the said element.

In the modification shown in Fig. 2, the outlet purifier apparatus E, instead of being placed immediately to follow the catalytic apparatus D^1—D^2—D^3—D^4, is disposed at the end of the group G—H—I. The sulphuretted hydrogen reformed in the catalytic apparatus is here captured only at the outlet from this group. As in the preceding example, the remaining hydrogen, at the outlet from the purifier E, is led to the major extent into a gasometer J, the remainder being taken back into the circuit after passage through a heater L.

It is obvious that the purifying apparatuses at the inlet B—C like the purifying apparatuses at the outlet E or E—F may be of any known type, that is to say they need not necessarily be in accordance with the particular purifiers forming the subject of the previous patents of the applicants.

The outlet purification E may be eventually effected in the cold, the residual gases being, in this case, necessarily reheated before their admission into the catalytic apparatus, as shown in Figs. 1 and 2.

The following is given as an example:—

Lignite is treated in a retort at a maximum temperature of 500° C and the mixture of gases and vapours leaving the retort are led through an inlet purifier charged with a suitable known purifying mass (a metal or metallic oxide on an inert porous carrier) and maintained at a temperature of about 400° C.

On leaving the inlet purifier, the vaporous mass, to which has been added hydrogen or a gas containing hydrogen (for example water gas or residual gas free from sulphur and derived from previously treated vapour), passes through a reaction apparatus charged with a metallic catalyst, such as nickel for example, capable of forming with the sulphur carried by the vapours, an easily reduced sulphide.

The vapour mixture enters such reaction apparatus, which is maintained at a temperature varying between 300 and 350° C, whilst still containing to a slight degree very stable organic sulphur compounds, such as thiophenes which become decomposed by the metallic catalysing agent. By the union of the latter with the sulphur, a sulphide is formed, nickel sulphide in the case of a nickel catalyst, which decomposes in the presence of hydrogen or of a gas which readily yields hydrogen. H_2S is thereby formed, the metallic agent becomes regenerated as and to the extent that it has just fixed the organic sulphur. This action occurs progressively as the vaporous mixture flows through the apparatus. Finally, gases and vapours which have taken up hydrogen leave the catalytic reaction apparatus. At the same time a small quantity of H_2S derived as above explained also issues therefrom. The whole then traverses an outlet purifier preferably charged with a purifying mass comprising a metallic agent such as copper which forms a relatively stable compound with the sulphur. All the previously remaining sulphur is retained in this outlet purifier which is maintained at a temperature of about 250° C.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the hydrogenation, at normal pressure and in the presence of catalysts, of vaporous substances derived from the distillation or gasification of carbonaceous substances, in which the operation of reduction in density and hydrogenation in the presence of catalysts, which comprises a constant addition of fresh hydrogenating gas, is interposed between two purifications, a preliminary purification before entry into the catalytic apparatuses and which retains as far as possible all the mineral sulphur and the major portion of the organic sulphur, and a second purification after leaving the catalytic apparatuses whereby the enriched gases are freed from sulphur contained in the sulphuretted hydrogen which through the constant regeneration of the catalyst is constantly formed in the said catalytic apparatuses.

2. A mode of carrying out the process as set forth in claim 1, in which a part of the hydrogen set at liberty in the outlet purifier is brought back into the cycle, preferably at the inlet to the catalytic hydrogenation apparatuses.

3. A mode of carrying out the process as set forth in claim 1 or 2, in which the outlet purifier follows immediately the catalytic hydrogenation apparatuses.

4. A mode of carrying out the process as set forth in claim 1 or 2, in which the outlet purifier is placed after an apparatus for condensation of the enriched hydrocarbons followed by an apparatus for the retention of non-condensible light hydrocarbon vapours, the fraction of the hydrogenating gases taken away on escape from the outlet purifier being taken back to the catalysers, after passage through a heater which brings them to the temperature of reaction in the said apparatus, whilst the purification is effected in the cold.

Dated this 5th day of December, 1928.
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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 123A.—50/4/1931.]

[This Drawing is a reproduction of the Original on a reduced scale]

Fig. 1

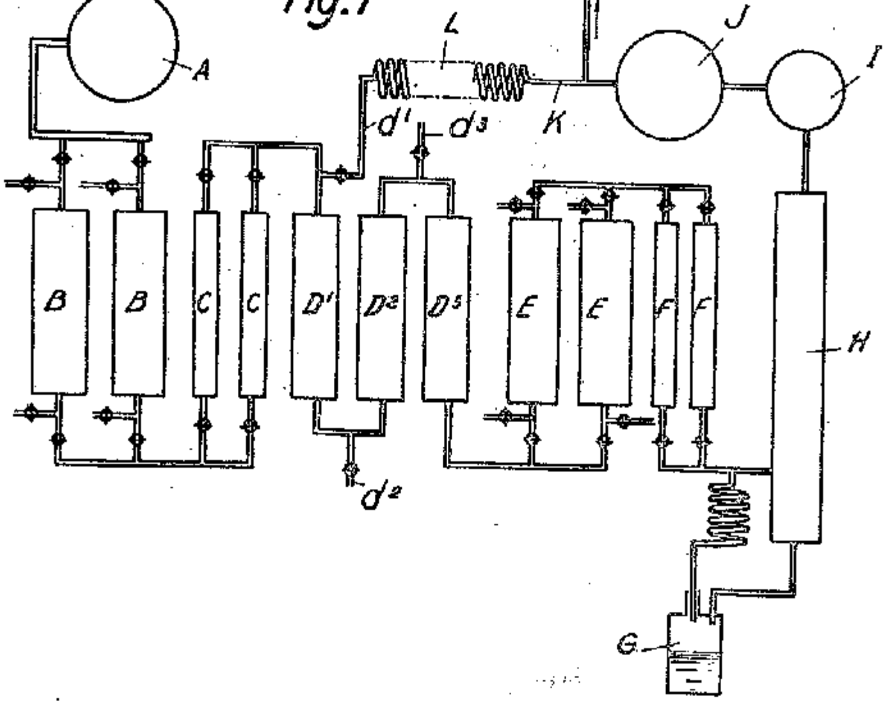
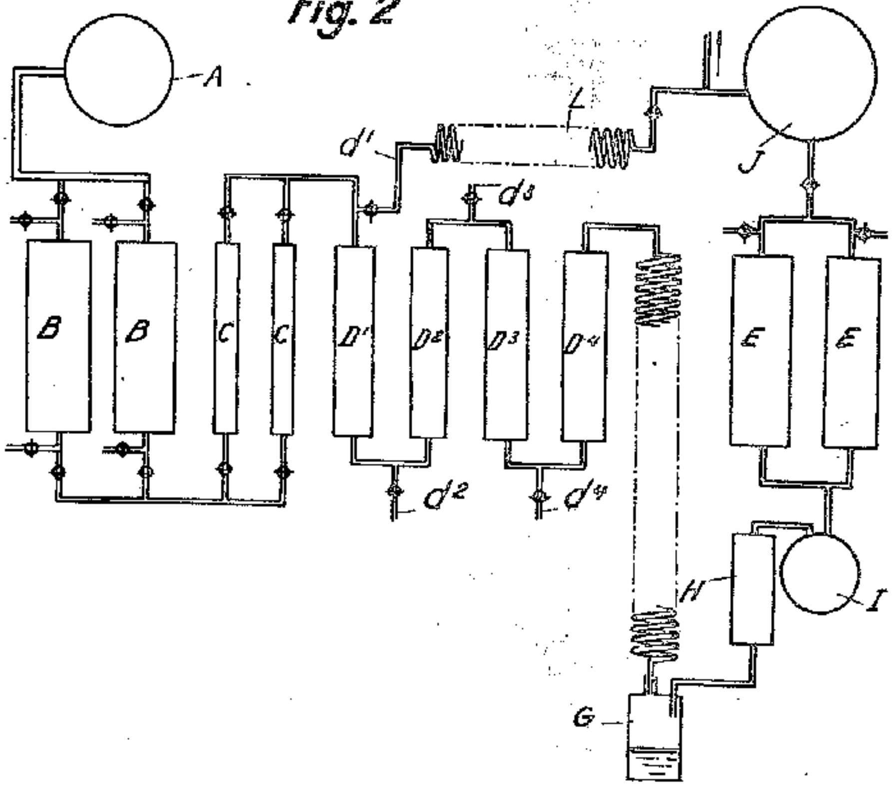


Fig. 2



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