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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Production of Liquid Hydrocarbons and other Organic Bodies from Heavy Organic Materials.

I, GEORGES PATART, 50, rue Spontini, Paris, France, a citizen of the French Republic, 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:—

It has been observed that liquid products of great value may be extracted from the solid fuels such as coal, lignite, peat, wood and the like, and more generally from the organic compounds derived from the carbohydrates if the simple pyrogenic decomposition is replaced by a treatment with liquid solvents, preferably under pressure and at high temperatures, or with hot gases, for instance hydrogen, passing through the material in a continuous and rapid current; it has been further observed that such methods afford a more rapid operation, and the separation of a greater amount of liquid by-products, whilst the amount of methane and hydrogen in the gas products, due to a decomposition of these organic compounds, is much smaller.

The same method applies to the extraction of the by-products of the greatest value from the liquid fuels such as mineral oils or petroleum, shale oil, vegetable or animal oils, or from the residues from manufacturing operations upon fuels of other classes such as tars, mazout, cracking residues, naphthalenes, pitches, rosins and the like; the separation of their different components can also be advantageously effected by dissolving them in more volatile liquid solvents, preferably under pressure and at a high temperature, or by distilling them under pressure in a current of hot gas, for instance in the presence of hydrogen, which will have the effect of counteracting the dehydrogenising of certain compounds.

But it has been hitherto a difficult matter to generalise these improved methods, due to the great cost resulting from the compression of the auxiliary liquids or gases in use, or the recovery of the waste heat.

I have found, however, that in the exothermic synthesizing operations effected under high temperature and pressure, large quantities of hot gases and solvent liquids, brought to a high degree of compression, are available, the composition of the said gases and liquids being quite suitable for the extraction of the valuable by-products contained in the solid or liquid fuels, and in general in the organic compounds derived from the carbohydrates. The invention accordingly consists in treating the raw material (carbonaceous or organic substances in the solid or liquid state) with liquid solvents and/or hot gases in order to extract the by-products contained in said substances, said liquid solvents and/or hot gases proceeding, while compressed and at a high temperature, from the catalytic treatment of an initial gas mixture containing oxides of carbon, hydrogen and, if desired, hydrocarbons rich in hydrogen, for the production of liquid hydrocarbons and hydroxygenated compounds of carbon, or from any other exothermic synthesizing operation effected under pressure and at a high temperature of the class of operations hereinafter referred to.

The exothermic synthesizing operations thus referred to are chiefly those by which hydrocarbons, alcohols, aldehydes, ketones and the like are obtained by the combined action of heat, pressure and catalyzers upon a gas mixture consisting of oxides of carbon, hydrogen, or hydrocarbons rich in hydrogen. The reaction products are discharged from the reaction chamber where the exothermic synthesizing operation is performed, at temperatures varying from about 200 to 600 degrees C., and at very high pressure; upon cooling, various liquids consisting of hydrocarbons, alcohols, ketones and the like are condensed under high pressure and they may be reheated preferably by an exchange of heat with the vapours entering the condenser. The class of exothermic synthesizing operations effected under high temperature and pressure to which the invention relates also comprises the following operations:

Synthetic manufacture of ammonia by means of hydrogen and nitrogen, at high temperature and pressure.

Synthetic manufacture of cyanhydric acid starting from a mixture of carbon monoxide with ammonia.

Synthetic manufacture of urea starting from carbon dioxide and ammonia.

It is obviously impossible to enumerate all the industrial exothermic synthesis effected under high temperature and pressure which are suitable for the treatment referred to. Those skilled in the art will be able to appreciate whether an industrial exothermic synthesizing operation is or not suitable for the process according to the invention, provided it has been ascertained:—

1°) that hot gases under high pressure or vapours of liquid solvents under high pressure and temperature are available at the outlet of the reaction chamber, where the operation is performed.

2°) that such gases or liquids have no destructive action at high temperature and pressure upon the products which are to be extracted from the raw material, and which essentially comprise liquid hydrocarbons.

All the exothermic synthesizing operations for which the two conditions above indicated are fulfilled pertain to the class of operations suitable for the process according to the invention.

By the use of the aforesaid gases which proceed, strongly compressed and at a high temperature from the reaction chamber where the synthesizing operation is performed, or by the use of the aforesaid liquids proceeding under high pressure from the condenser of the synthesizing installation and suitably heated, or by the combined use of said gases and liquids, I am enabled to effect the extraction operations above set forth, without the great expense required before, for compressing the said gases and liquids. Moreover, in most cases the heat of said gases is directly recovered, and, in the case of liquids, the heat of the vapours is wholly or partially recovered by an exchange of heat, whereby the expense required for heating the gases and liquids is wholly or partially eliminated.

The substances capable of undergoing the treatment herein described are, as above stated, either carbonaceous substances or liquid or solid organic substances, that is substances containing free or combined carbon, which may be normally subjected to ordinary pyrogenic distillation in order to extract valuable organic by-products, chiefly hydrocarbons, alcohols, acids, etc. By way of example, the following substances may be treated by the process herein described: Coal, lignite, wood, peat, and other organic or carbonaceous compounds derived from the carbohydrates; liquid fuels such as heavy hydrocarbons, mineral oils, raw petroleum, shale oil, vegetable or mineral oils, cracking residues; heavy or raw products from coal distillation such as tar, pitches, rosins, oils containing naphthalene, etc.

The nature of the gases and liquids used depends upon the nature of the synthesizing operation in which said gases and liquids are produced. As above stated, it is indispensable that the gases should be at high temperature and pressure. The presence of hydrogen or gases hydrocarbons rich in hydrogen or gases of a reducing character is preferable in order to avoid oxidation or pyrogenic dehydrogenation of the by-products to be extracted. Mixtures of carbon oxides and hydrogen or hydrocarbons rich in hydrogen, hydrogen and nitrogen, carbon monoxide and ammonia gas, carbon dioxide and ammonia gas, for example, are quite suitable for this purpose. But it is evident that oxidizing media such as pure air or pure water vapour or mixtures of gases susceptible of a destructive action upon the by-products are to be avoided.

A large range of liquids are available for the purpose of the invention and particularly the liquids which are known as solvents for the heavy hydrocarbons, oils, tar, pitch, rosin, naphthalene, fatty substances and the like; said liquids are chiefly alcohols, ketones, ethers, aldehydes, and light hydrocarbons which are obtained at high temperature and pressure in some of the processes of the class referred to.

In carrying out the process according to the invention, the compressed gases discharged from the reaction chamber where the exothermic synthesis is performed may be circulated in a regular current into one or more digesters, which are specially arranged for the purpose, and which contain the organic material to be decomposed such as coal, lignite or wood. Said digesters are disposed between the synthesizing reaction chamber and the condensers of the synthesizing operation. The volatile by-products thus extracted in the digesters, as well as the vapours which have been formed during the exothermic synthesizing operation and were circulated with the gases through the digesters, are withdrawn from the gases in the condensers of the installation for the synthesizing operation. I then separate by evaporation, fractional distillation or (if necessary) by rectification, the various components of the complex condensate thus obtained.

Alternatively, I may use the solvent liquids only and, for this purpose, I first remove from the condensers of the installation for the main synthesis, a part of the condensate if the latter has the required solvent properties; this liquid, which is still under pressure, is first heated to the proper temperature preferably by an exchange of heat with the vapours entering the condenser, or by separate heating or the two methods either simultaneously or consecutively. I then circulate the said liquid—by means of a circulating pump—into the digester or digesters containing the organic material to be decomposed, from which I thus remove the soluble substances. The liquid discharged from the digester may yield up its heat to the liquid entering the said digester.

Obviously, I may utilise at the same time the hot compressed gases from the synthesizing reaction chamber and the liquids under pressure collected in the said condensers and suitably re-heated, and cause them to act simultaneously or successively upon the organic compound to be decomposed. In this case the liquid may be circulated downwardly in the digester, whilst the hot gases are circulated upwardly; before entering the digester, the liquid is heated by contact with the liquid discharged from the said digester.

The movements of the gases or liquids may be combined in a widely varying manner according to the material to be treated, and the same is true for the arrangement of the material in the digesters, and for the construction of the latter.

In the case of pulverulent solid substances, such as coal, lignite and peat, it is preferable to dispose them, in the digester, upon plates or like supports which are finely perforated and through which the ascending gases and the descending liquids will flow. In the case of liquid or pasty substances, the gases may be caused to bubble or the liquids may be caused to flow through the said material under treatment by means of immerged tubes or of suitable plates.

The substances to be treated and particularly the solid substances, may be preliminarily disposed in cartridges, baskets or like recipients of a slightly tapered shape, the end parts whereof are perforated or not; said recipients fit closely upon the corresponding tapered internal wall of the digester. This latter apparatus may be closed by a movable cover which can be held in place by hydraulic means, so as to provide for its ready opening and closing, so that the basket or like recipient containing the exhausted product can be readily removed and replaced by a similar recipient containing a fresh charge of material to be treated.

I may dispose a plurality of digesters in series or in parallel on the same gas or liquid circuit, so as to proceed more or less methodically with the exhaustion of the material under treatment, or to continue the action of the gases or liquids, or the cooling of the digester for the necessary time without diminishing the total output.

The gaseous products which are produced by the treatment of the material to be decomposed and which are not condensed in the condenser, may be left in the gas circuit pertaining to the main synthesis reaction or may be eliminated by any known means, such as a partial liquefaction, or an expansion with or without external production of work, or a cooling under pressure by separate cooling means.

The solid or liquid residue in the digester may be employed to advantage for the production—by known means—of the whole or a part of the gaseous mixture based upon carbon monoxide, hydrogen, or hydrocarbons rich in hydrogen, which serves for the main synthetic reaction; or otherwise, according to the special quality of this residue, this latter may be employed in a separate manner for other purposes.

For the better understanding of the characteristic features of my invention, I will now set forth how the method according to the invention may be carried out in three particular cases; these are given solely by way of example and are in no wise to be considered as limiting the scope of the invention.

Example I.

It is assumed that the main synthetic reaction consists in the well known process of manufacture of hydrocarbons and of oxygenated derivatives of hydrocarbons by the catalytic hydrogenation of carbon oxide at high temperature and under high pressure. The gases are circulated in a closed circuit by means of a circulating pump by which the gases which have not reacted, and thus are not condensed, are supplied back to the catalyzing chamber, wherein the normal pressure is 250 atmospheres.

According to my invention, I place between the last catalysis chamber and the condenser, one or more digesters which contain the variety of coal known as coking coal, containing for instance 22 per cent. of volatile substances. The gases leave the catalysis chamber at a temperature of 420—450 degrees C. and at 250 atm. pressure, and pass upwardly through the digester. After a three hours' treatment, the coal is reduced to some 60 per cent. of its initial weight, and becomes porous, with a brilliant black appearance, whilst the condensed liquid contains an increased amount of volatile products having a great calorific power, of ammonia and of clear tars. The gases will contain methane and olefines, as the chief addition thereto.

The amount of volatile substances may be much increased by artificially heating up to 750—800 degrees, and before they enter the digester, the gases issuing from the reaction chamber, and the heat which they still possess when issuing from the digester, is recovered for heating the gases entering the latter.

The coke which is collected as a residue in the digester may serve to produce the initial gas mixture for the reaction.

Example II.

It is assumed that the main synthetic reaction consists in the synthetic manufacture of methanol by the combination in the presence of catalyzers of the elements of a gas mixture consisting approximately of one volume of carbon monoxide, two volumes of hydrogen, and variable amounts of methane and nitrogen, the temperature of the reaction chamber being maintained at 300° C. and the pressure at 300 atm.

In this case, between the condenser of the last catalysis apparatus and the condenser for the final product, is or are interposed, one or more digesters which contain broken fragments of pine wood from the Landes region (waste from sawmills, or the small ends of branches of felled trees), and I circulate therethrough at the same time, (1) in the upward direction the gases from the reaction chamber which are not condensed in the methanol condenser, these gases being suitably reheated, and (2) in the downward direction, by means of a small circulating pump, a greater or less amount of the liquid containing methanol which is collected at the bottom of the methanol condenser, said liquid being heated by contact with the gases as well as with the hot liquid discharged from the digester.

In this manner I obtain, in the liquid discharged from the digesters—in addition to the undecomposed methanol—pine oil, acetone, isopropyl alcohol and acetic acid which are extracted from the wood, while the gases will draw over an additional amount of hydrogen, carbon monoxide and methane together with an appreciable amount of ethylene and its homologues, which latter will be subsequently condensed upon the catalyzer in the form of liquid hydrocarbons, as set forth in my copending Application No. 247,178 for "Method for the simultaneous production of methyl alcohol and liquid hydrocarbons by synthesis". The charcoal collected from the digester may be employed for the production of the initial gas mixture or for other uses.

Example III.

It is assumed that the main synthetic reaction is carried out as set forth in my said copending Application No. 247,178 for "Method for the simultaneous production of methyl alcohol and liquid hydrocarbons by synthesis" employing for the purpose a gas mixture consisting of one volume of ethylene, one volume of carbon monoxide and two volumes of hydrogen, the standard pressure being 850 atm., and the catalysis chamber being maintained at a temperature of 300 degrees C.

Between the last catalysis apparatus and the condenser, I interpose one or more digesters containing heavy petroleum oil, naphthalene, or the residues from the distillation of vegetable or mineral oils, and the gases from the reaction chamber will be caused to bubble through the same before they enter the condenser, after optionally raising their temperature up to 430—450 degrees C. I thus greatly increase the production of light oils in the condensate, due to the fact that a part of the material placed in the digester is drawn off and also that the proportion of olefinic hydrocarbons contained in the gases is increased.

In addition to the preceding indications and those which result from the above-mentioned examples, the method according to the invention can be adapted to all forms of operation which may be required for extracting from the organic substances thus treated, any by-products preferably desired, and this, without departing from the principle of the invention. For instance, the gases or liquids produced by the main synthetic operation may be employed only partially for the treatment of the fuel or other organic substance to be decomposed. The liquid or gaseous products of this latter treatment might be collected apart from the products or gases obtained during the main operation. Furthermore, the gases discharged from the reaction chamber might be preliminarily and wholly freed from the products of condensation which they contain before being circulated into the digester or digesters containing the organic material to be treated, and after they have been heated by their contact with the gases issuing from the reaction chamber and the digesters. The same is true for the liquids. The exchanges of heat between the gases or between the liquids, or between the gases and the liquids, will be much facilitated by reason of the considerable specific gravity given to the gases by the high compression.

Certain special catalyzers may be incorporated into the solid fuels under treatment or may be immersed in the liquids which are treated by the method according to the present invention. According to the nature of the raw material, of the gases or liquids used, of the by-products to be obtained, use may be made of hydrogenating catalysts, condensing agents, etc., the chemist being able to select the suitable known catalysts whose properties have been ascertained.

Obviously, it is not possible to set forth in this Specification all the details applying to each particular case; those skilled in the art will easily carry the present process into practice, along the line above explained by treating the fuel or the organic material with the hot gases or the solvent liquids under high pressure which may be derived from the cycle of the main synthetic reaction preferably recovering the heat of the reagent, either directly in the case of hot gases, or by exchanges of heat in the case of liquid solvents and sometimes also in the case of gases.

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

1. Method for the distillation or hydrogenation of carbonaceous or organic substances in the solid or liquid state, which consists in treating the said substances with liquid solvents and/or hot gases in order to extract the by-products contained in said substances, said liquid solvents and/or hot gases proceeding, while compressed and at a high temperature, from the catalytic treatment of an initial gas mixture containing oxides of carbon, hydrogen and, if desired, hydrocarbons rich in hydrogen, for the production of liquid hydrocarbons and hydroxygenated compounds of carbon, or from any other exothermic synthesizing operation effected under pressure and at a high temperature of the class of operations referred to.

2. Method according to Claim 1, wherein suitable catalyzers are incorporated into the solid substances or immersed within the liquid substances constituting the raw material.

3. Method according to Claim 1, in which the residue of the treatment of the carbonaceous or organic substances is utilised, for instance is burned incompletely, for generating a part of the initial gas mixture used in said exothermic synthesizing operation.

4. Installation for carrying out the method according to the Claims 1 and 2, wherein the carbonaceous or organic substances to be treated are disposed within separate receptacles which are removably disposed within digesters adapted to be passed through by the said liquid solvents or hot gases.

5. Method for the treatment of carbonaceous or organic substances, substantially as described.

Dated this 15th day of March, 1926.

MARKS & CLERK.

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