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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Synthesis of Hydrocarbons under Ultra-pressure

We, EDVARD FISCHER, of Stupartska 4, Prague, 1, Czechoslovakia and BRUNO DONATH, Parizska, 10, Prague, Czechoslovakia, both Czechoslovakian citizens, 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:—

This invention relates to the synthetic production of hydrocarbons, particularly liquid hydrocarbons, from mixtures of gases containing hydrogen and carbon monoxide.

Hitherto in the synthetic manufacture of hydrocarbons use has been made of the combined effects of heat and pressure acting in the presence of various suitable catalysts, especially precious metals. The catalytic material, in addition to being expensive, rapidly becomes poisoned if the starting material is not properly freed from sulphurous constituents. A further inconvenience is the periodicity of the process due to the fact that the catalyst has to be rested, cleaned from impurities and regenerated.

These disadvantages naturally cause an increase in the price of the synthetic product, especially in the case of liquid hydrocarbons.

It has already been proposed in the manufacture of hydrocarbons from carbon monoxide and hydrogen, to subject these gases to pressures of a high order at a more or less elevated temperature and in this connection pressures up to 3000 atmospheres (see specification of Letters Patent No. 328,586) and temperatures up to 700° Centigrade have been specifically mentioned although the temperature usually preferred was between 300 and 500° Centigrade. In prior proposals of this character, however, a catalyst has invariably been employed.

The present invention, on the other hand, provides a method for the synthetic production of hydrocarbons from mixtures of gases containing hydrogen and carbon monoxide by the use of high pressures, characterised by the fact that no catalysts are employed and that to effect the reaction the gases are subjected to a pressure exceeding 1500 atmospheres at an elevated temperature, said pressure being developed by compression of the gases in successive stages.

The principle of synthesis by high pressures is based on the physical feature that the volume of a given quantity of gas under pressure is reduced; e.g. at 5000 atmospheres it is approximately 0.001 of the volume at atmospheric pressure. Air at high pressure may thus have a higher density than water but still remains gaseous as its temperature is considerably higher than the critical temperature. The mixture of gases under these conditions is chemically extraordinarily active and they react mutually very intensively at an appropriate temperature.

The proper reaction is dependent upon three main factors, namely, the pressure and temperature of the gases and the time for which they remain at a given pressure and temperature. The optimum temperatures for the reaction have been found to lie between 800 and 1000° C. at which temperatures, with a pressure of 4500—5000 atmospheres the reaction takes place without catalysts. The invention is not, however, limited to the use of these particular temperatures and pressures.

In carrying the invention into effect the reaction is not allowed to take place in the preliminary compression stages but takes place in a reaction chamber connected to said pressure stages. Such reaction chamber may be formed by the compressor of the last stage, and the reaction prevented from taking place prior to reaching the reaction chamber by keeping the temperature of the compressed gases below that necessary for the reaction until the reaction chamber has been reached.

Apparatus for the synthetic production of hydrocarbons in accordance with the invention is represented schematically and by way of example in the accompanying drawing.

Referring to the drawing, *a* designates a generator for water-gas of normal construction having a grate *x* on which burns a layer of combustibles supplied by the charging holes *k*. To the lower part of the generator *a* a tubing *pp* for steam is connected by which steam is led under pressure into the generator.

By the incomplete burning of the combustibles, e.g. coal, cóke, coal waste, wood, straw, peat, oils, tars, charcoal, leaves etc. gases are produced in which carbon monoxide (CO), predominates and other gases as nitrogen methane, quantities of carbonic dioxide, etc. are present. If steam is led to this mixture through the red-hot combustible the water is decomposed by the action of the glowing coal into hydrogen and oxygen so that some heat is taken from the combustible. The water-gas has the following average composition: 40% CO, 45% H_2, 0.5% CH_4, 5% CO_2, 9.5% N_2 as to the volume, in cases where the combustible consists of coke, anthracite or charcoal. If pit coal or brown coal is used, the gas usually contains traces up to 0.2% of hydrocarbons of the olefine group of the general formula C_nH_{2n}, e.g. ethylene.

Alternatively retorts, either of horizontal or vertical disposition may be used for the manufacture of the initial gases. The retorts, may be arranged for the continual movement of the combustibles so that the process is then uninterrupted, which makes possible on the one hand the reduction of the heat losses to a minimum and on the other hand a far more constant composition of the raw gases. The gas-genous retort has furthermore the advantage that it is possible to supply approximately 40% of the heat energy necessary for the decomposition of water-vapour and compensation for losses to the retort from outside so that the process remains continuous, without the composition being changed periodically as is usually the case in an ordinary generator during the period of aeration.

The raw gas is exhausted by the exhauster *i* and forced into the gas cleaner *b*. The cleaner consists substantially of a vertical container of sheet iron provided at a distance above its base with a grate *j* on which rest pieces of material presenting a large surface area e.g., coke, Raschig-rings or the like so that the gas passing through may not be subjected to a high resistance. The gas enters the container at the base beneath the grate *j* by the tube *p* leading directly from the generator and passes the layer of the charge. Against the gas stream flows water on the surface of the charge, entering the cleaner by a spray situated on the upper lid of the cleaner *b*. In the cleaner *b* the gas is on the one hand cooled and on the other hand freed from gross impurities taken along from the generator or the retort by the stream of gas, such for example as particles of unburned fuel, ashes, mineral dust or the like. Beyond the cleaner *b* is inserted also a fine spraying cleaner *d*, for certainty, by which sharp particles taken along with the stream of gas are prevented from entering the compressing device, the interior contacting and friction surfaces of which would easily be damaged. The interior of the compressors must have very close contact with the contacting surfaces having regard to the extreme pressures.

The cleaned gas is supplied to the mixer *l* with other suitable gases, the composition of the mixture being such as to correspond as nearly as possible with that of the desired final product (the liquid hydrocarbon), and the mixture is sucked-on by the compressing device.

Should the resistance of the whole cleaning section be very considerable an added suction pump, or if necessary two, is inserted between the cleaners *b* and *d*, or behind the cleaner *d* or behind the mixer *l*, so that the first stage of the compressing device sucks at least under atmospheric pressure or under a slight additional pressure.

The compressing device compresses the cleaned gas of suitable mixed composition, from atmospheric pressure. the pressure being regulated by the suction compressors to a final extreme pressure of, for example, 5000 atmospheres. The attainment of this degree of compression is divided into several compressing stages, e.g. five stages with compressing ratios of 1:8, 1:5, 1:5, 1:5, 1:5 and final pressures of 8 atmospheres, 40 atmospheres, 200 atmospheres, 1000 atmospheres and 5000 atmospheres, assuming that the suction of the first stage takes place at atmospheric pressure. The temperature of the gases is kept below that necessary for the reaction by cooling until the final pressure has been reached, whereupon the temperature is allowed to rise to permit the reaction to take place.

The division of the total pressure increase into several parts has the chief advantage of saving energy and also enables a maximum increase in pressure to be obtained with the minimum possible diameter of the cylinders of the last stage for extreme pressures. According to the increasing pressures of the respective degrees the contents of the cylinders diminish. Also the selection of the constructing material depends on the respective zone of pressure so that it is possible to save expensive constructing material for the last compressing degrees.

The function of the compressing device will be evident from the schematic drawing hereunto annexed.

The first degree I sucking the gases from the cleaners *a* and *b* as well as from the mixing device 1, compresses the gases to 8 atmospheres and leads them to a pressure pipe. The compressor is provided with as efficient a water jacket as possible so that the compressing operation approaches as nearly as possible to isothermic compression. The gases compressed in the first stage may be further cooled by making the pressure pipe as a system of ribbed tubes of the required capacity which form at the same time the gas receiver for the second compression stage. The compressor II of the second stage is arranged similarly to compressor I and compresses to 40 atmospheres. From this compressor the gas is led through a steel pipe, arranged in an economiser *e* in which water is warmed and the compressed gas cooled.

The gas passes into the compressor III of the third compression stage which is arranged, for example in the manner of a compressor for the liquefaction of gases, so that a compression to 200 atmospheres takes place. The cooling of the cylinders must be as efficient as possible to prevent the lubrication of cylinders and pistons being spoiled and also to prevent the reaction taking place. The gas subsequently passes into the tubes of an economiser *f* arranged as counter-flow cooler to make use of the warmth of the gases.

The gas compressed to 200 atmospheres and properly cooled in the economiser *f* is extracted by the compressor IV of the fourth stage, in which the final pressure is 1000 atmospheres. The cooling of the cylinders takes place by means of oil under a pressure of 50 to 100 atmospheres to secure the most intensive contact of the oil with the surface of the cylinders and by this means the perfect transmission of the heat. The oil itself is then cooled in counter-flow coolers by water or by any suitable cooling medium, the heat taken from the oil being used for boiling water and for the supply of steam necessary for the generators or retorts.

Finally the gas is extracted from the economiser *g* by the compressor V of the fifth and last degree where an extreme pressure of 5000 atmospheres is attained. The oil-cooling of the compressor V is under a minimum pressure of 100 atmospheres and is cooled down similarly as in the fourth degree just described.

The cooling by oil or glycerine has been chosen in view of possible corrosion, which would render water unsuitable at the high temperatures and pressures employed, although, as oil transmits only approximately 40% of the heat carried away by the same weight of water, it is necessary to consider this circumstance in calculating the flow speed and the flow quantities in a unit of time.

The compressor V also constitutes the reaction chamber and in it the temperature is permitted to rise to the degree requisite for the reaction.

From the last stage the synthetic product passes into an apparatus *h* of known form for fractional condensation where it is divided into its respective fractions according to their boiling-point, which are drawn off at points 1, 2, 3, 4.

It will be evident that the products of the synthesis especially those with a high boiling point or in gaseous form, may be worked up to a gasoline, paraffin, vaseline oil and the like by known processes e.g. by cracking, polymerisation or the like, either with or without catalysts.

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. Method for the synthetic production of hydrocarbons from mixtures of gases containing hydrogen and carbon monoxide by the use of high pressures, characterised by the fact that no catalysts are employed and that to effect the reaction the gases are subjected to a pressure exceeding 1500 atmospheres at an elevated temperature said pressure being developed by compression of the gases in successive stages.

2. Method as claimed in claim 1, wherein the reaction pressure is of the order of 4500 to 5000 atmospheres.

3. Method as claimed in claim 1 or claim 2, wherein the temperature of the compressed gases is kept below that necessary for the reaction to take place until the final pressure stage has been reached, whereupon it is allowed to rise to enable the reaction to take place.

4. Method as claimed in claim 2, or claim 2 and claim 3 wherein the temperature at the reaction pressure stage is of the order of 800—1000° centrigrade.

5. Method as claimed in any preceding claim, wherein the initial mixture of gases is water gas, producer gas or the like, with or without the addition of other gases.

6. Method of synthesis of hydrocarbons according to any of claims 1 to 4, wherein the initial gases are made by incomplete combustion of solid or liquid combustibles, such as coal, wood, peat, oils, tars, charcoal and the like in continuously operating generators or retorts.

7. The method of synthesis of hydrocarbons, substantially as hereinbefore described.

8. Hydrocarbons, when produced by

the process claimed in any of the preceding claims.

9. Method as claimed in any preceding claim, in which the manufacture takes place in an apparatus comprising a generator of water gas, producer gas, or the like supplying a multi-stage compressing plant adapted to raise the pressure of the gases to the requisite degree, and cooling means associated with said plant for cooling the compressed gases at different pressure stages, said cooling means being used for the production of steam for the generator.

10. Method as claimed in any preceding claim, in which the manufacture takes place in an apparatus constructed, arranged and adapted to operate substantially as herein described with reference to the accompanying drawings.

Dated this 9th day of June, 1936.
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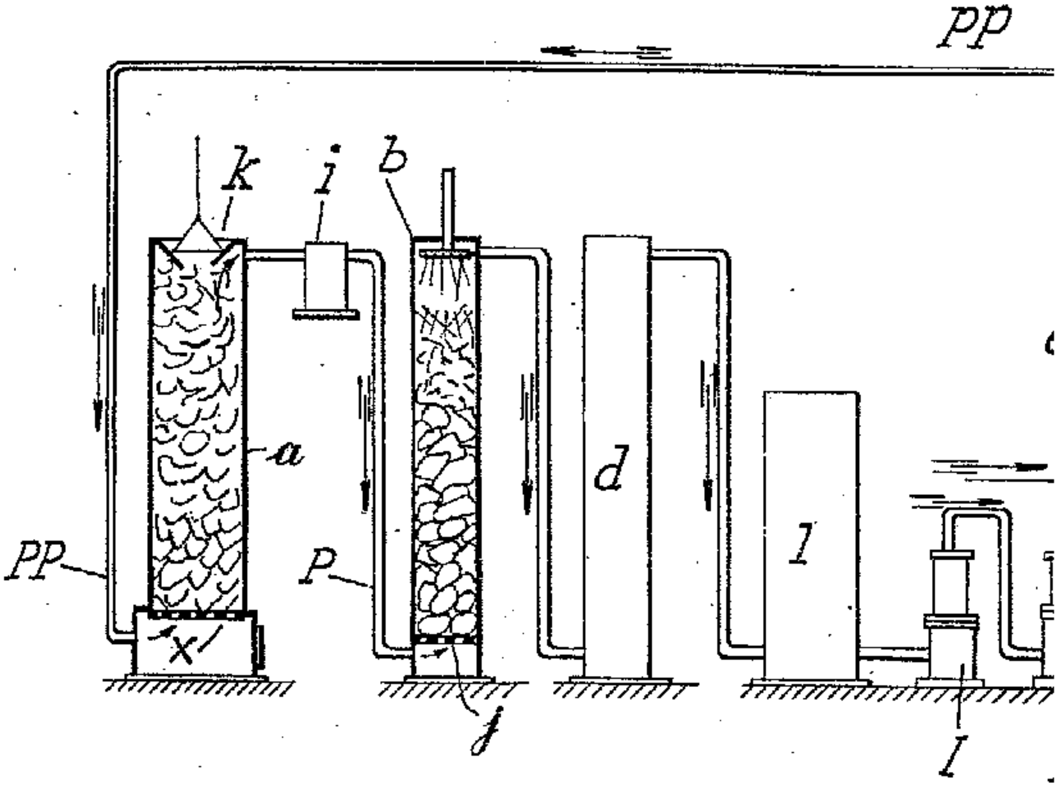
[This Drawing is a full-size reproduction of the Original.]



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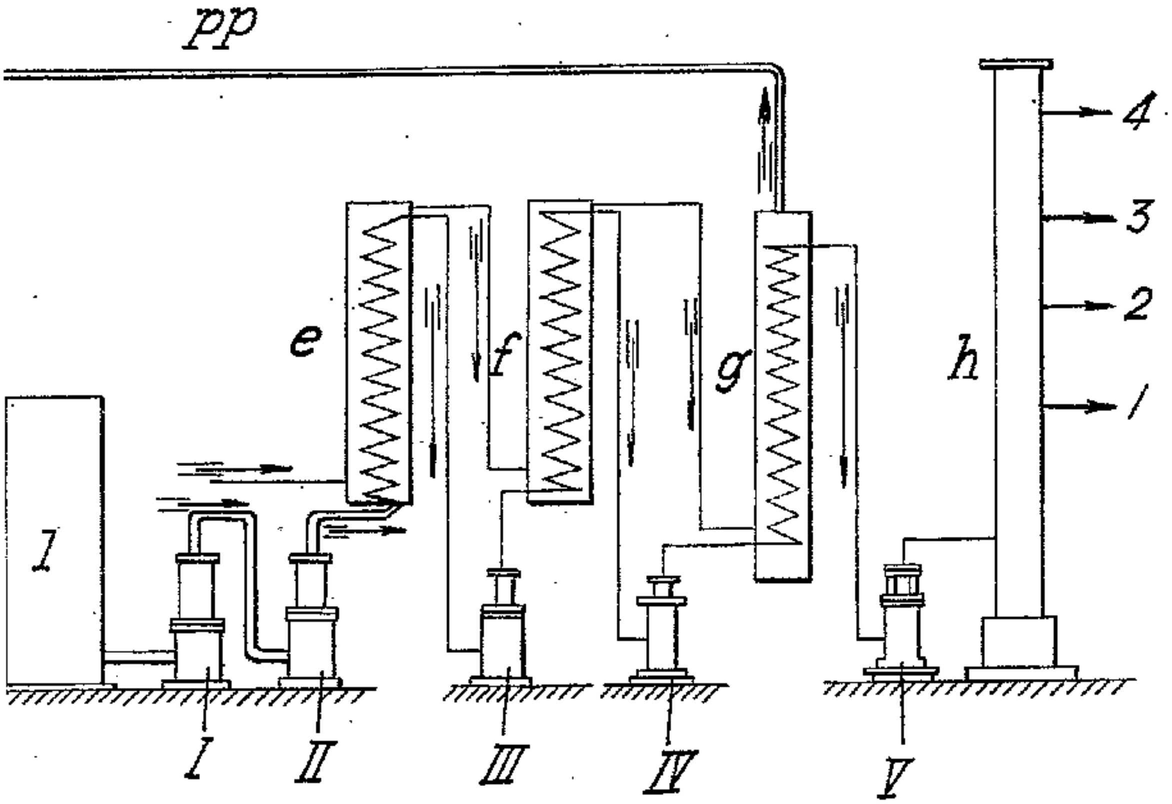

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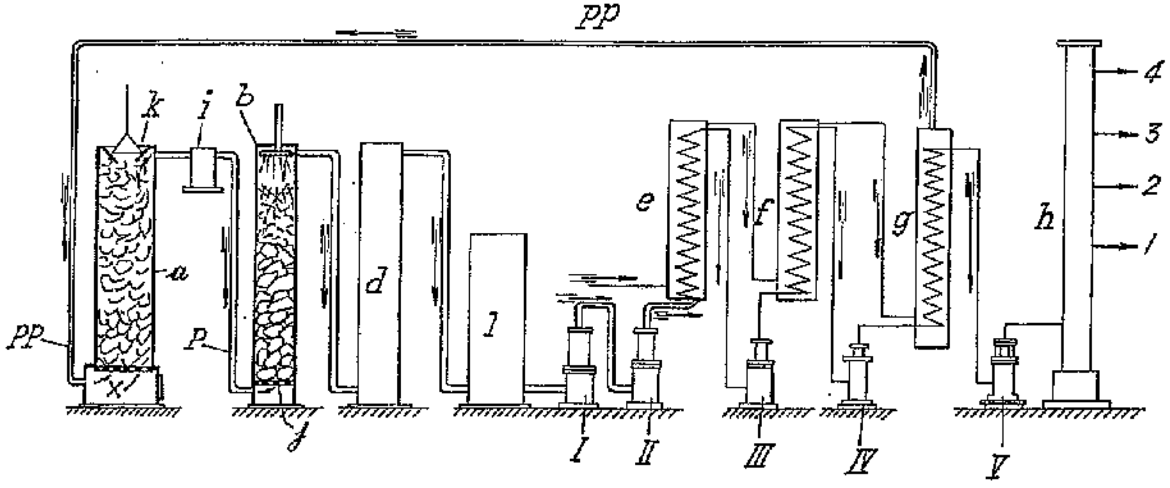

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