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CONVERSION OF HYDROCARBONS OF HIGH BOILING POINT INTO THOSE OF LOWER BOILING POINT

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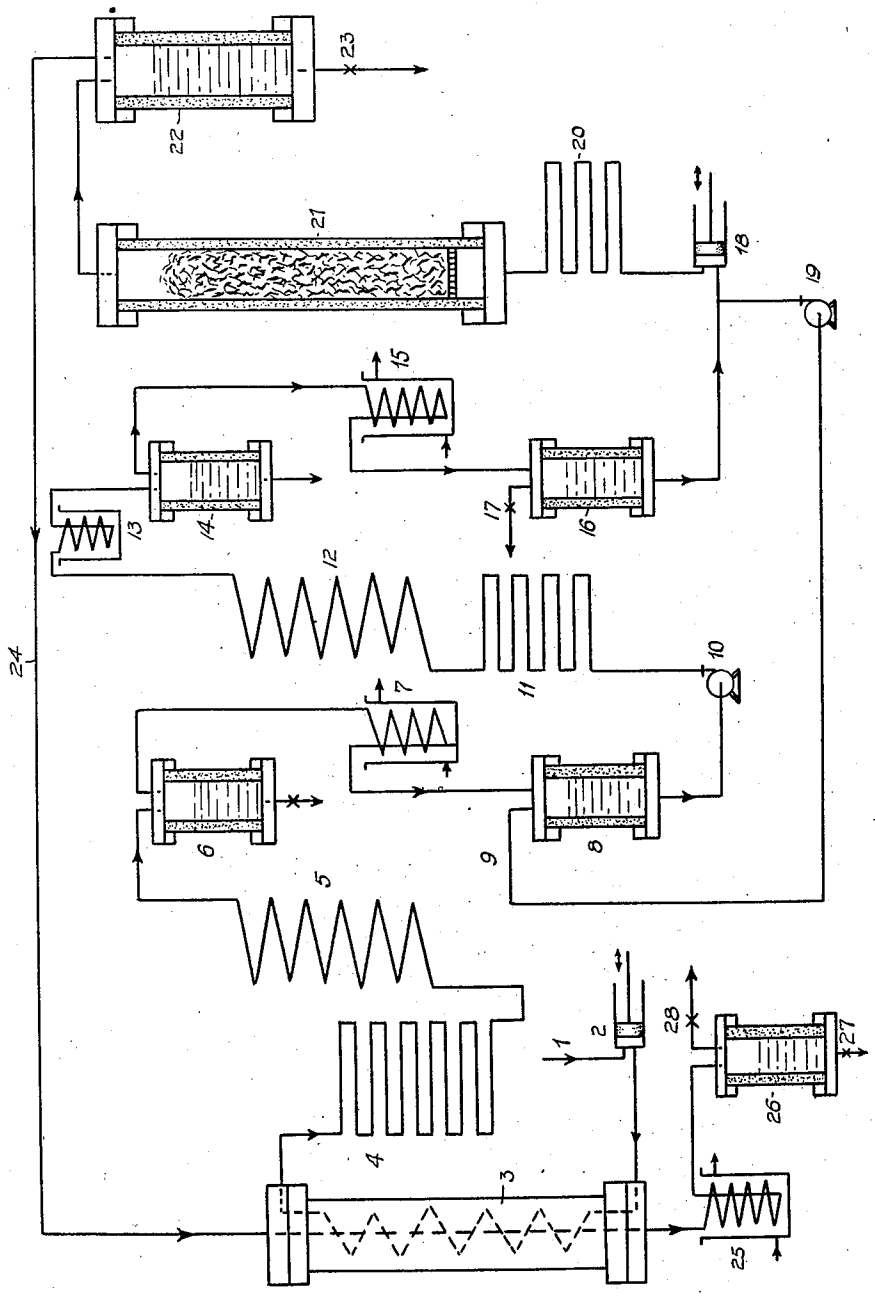


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## CONVERSION OF HYDROCARBONS OF HIGH BOILING POINT INTO THOSE OF LOWER BOILING POINT

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7 Claims. (Cl. 196—52)

This invention relates to improvements in the conversion of hydrocarbons of high boiling point into those of lower boiling point.

It is already known that hydrocarbons of low boiling point, in particular motor fuels, can be prepared by the cracking of hydrocarbons of high boiling point, such as tars, mineral oils and the like. By the employment of sufficiently high temperatures in the cracking it is possible to obtain products having a considerable content of constituents having an "anti-knocking" action. As a rule, however, when working in this manner, quite a considerable fraction of the initial materials is lost as far as the formation of valuable liquid products is concerned, by gasification and coking.

I have now found that considerable advantages both as regards the yields and the utility of the products as motor fuels are obtained when hydrocarbons of high boiling point, which expression also comprises mixtures containing the same, such as tars, mineral oils and the like, are subjected to consecutive restricted crackings at a pressure of at least 50 atmospheres, that is to say crackings in which only relatively small proportions of the initial materials are cracked, or in which the molecules thereof are split into relatively large parts, if desired in the presence of catalysts, in such a manner that each time fractions having a comparatively narrow boiling point range are subjected to the said treatment, the said range not exceeding 200° C. Such a process may be defined as one involving successive partial crackings, and this latter expression is employed in the claims to cover cracking procedures in which in any single cracking operation only a relatively small portion of the initial material is cracked. It is easy to produce only a comparatively slight conversion in the subsequent cracking stages, by subjecting a fraction having a boiling point range of not more than 200° C., obtained in a previous cracking, to a subsequent cracking if desired under different conditions as regards temperature, pressure and the like. For example lower temperatures may be employed or the duration of the treatment may be reduced, or less active catalysts or any of these factors combined may be employed. Thus, if desired, products having similar boiling points which arise from different initial materials or from various previous crackings can be combined, in order to influence the composition of the final product, in particular as regards its content of aromatic and unsaturated products. For example three crackings, or even more if desired, may be carried out. By the cracking process in accordance with the present invention it is possible to convert products of high boiling point range to a great extent into products of low boiling point range without the occurrence of any appreciable formation of coke or of gas.

The catalysts immune from poisoning by sulphur, namely those which are suitable for the destructive hydrogenation of the initial materials already described may be advantageously employed as catalysts for cracking in accordance with the present invention at least in one stage of the process, especially when employing pressures of at least 50 atmospheres. Particularly suitable for application in the process according to the present invention are catalysts comprising compounds containing sulphur in combination, for example metallic sulphides, in particular the heavy metal sulphides and more especially those of the iron group, either alone or as mixtures with one another or with metals, metalloids, active charcoal, coke or the like or with oxides, hydroxides, or carbonates, or with other materials of a catalytic or of inert nature. The sulphur may also be combined with the catalyst by adding sulphites or sulphates thereto or by the addition of sulphur to metals or oxides. A very suitable catalyst may be obtained by treating iron with hydrogen sulphide at an elevated temperature. Particularly suitable catalysts of this class are for example cobalt sulphide, iron sulphide, zinc sulphide, nickel sulphide, manganese sulphide and the like or mixtures thereof, for example, mixtures of cobalt sulphide with nickel sulphide or of cobalt sulphide with manganese sulphide, or of cobalt sulphide mixed with iron sulphide, or with zinc sulphide or with aluminium sulphide, with or without an addition of inert substances. Catalysts consisting of or containing molybdenum, chromium, tungsten or uranium or the compounds thereof or mixtures of those substances are also particularly suitable. As examples of this type of catalyst may be mentioned molybdic acid or ammonium molybdate, tungsten sulphide, tungstic acid, chromium hydroxide and chromic acid. Mixtures of chromium or tungsten with other catalysts, such as with cobalt, nickel or iron may also be employed. Activation of the catalysts or the addition of substances increasing their mechanical strength may also be of advantage, this being effected for example with substances having a basic action, such as potassium carbonate, aluminium hydroxide or calcium carbonate. Carriers such as lumps of aluminium

silicate may also be employed with advantage. As further catalysts may be mentioned oxidic catalysts comprising zinc oxide, chromium oxide or manganese oxide or mixtures of these, if desired with an addition of a compound containing fixed nitrogen, such as ammonium sulphide or such nitrides as are comparatively stable against the action of water, for example silicon nitride or titanium nitride. These said oxidic catalysts may be employed in conjunction with other substances, such as lumps of fire-clay, quartz, asbestos, pumice, coke, active charcoal, metals, in particular heavy metals, metalloids, oxides, sulphides, carbides, and the like and mixtures thereof with the said substances. As still further examples of suitable catalysts may be mentioned such containing at least one of the elements silver, copper, cadmium, lead, bismuth, tin in the form of its compounds, further the difficultly reducible metal oxides or carbonates, such as magnesia, lithium carbonate, boric acid, alumina, the rare earths, including the difficultly reducible oxides of metals from the 4th group of the periodic system, or the oxides of zinc, manganese or vanadium. The catalysts may contain several of these substances or also other substances, for example metals from the 8th group of the periodic system, such as iron. As specific examples of these catalysts may be mentioned such obtained by impregnating porous refractory materials with a solution of lead nitrate, of or stannous chloride, silver nitrate or of copper hydroxide, either alone or in admixture with compounds of iron, cobalt and the like. Further may be mentioned catalysts containing the oxides of silver or of titanium, or lithium carbonate, magnesite, manganous oxide, silver borate or mixtures of copper oxide with cerous oxide or of silver with cobalt oxide and the like, and also porous refractory masses coated with vanadium oxide or thorium oxide or with a mixture of compounds of uranium and zinc or of silver and tungsten. These latter compounds may also be employed as such without application to the said porous materials. As further suitable catalysts may be mentioned catalysts containing active charcoal or the metalloids boron, silicon, phosphorus, arsenic, selenium, tellurium or the compounds thereof or halogens. These metalloids may advantageously be employed together with elements from the 2nd to the 8th group of the periodic system, in particular such selected from the 6th group of the periodic system. The catalysts may for example contain the following acids or their salts, namely phosphoric acid, arsenious acid, silicic acid, boric acid, hydrofluoric acid, hydrochloric acid, selenious acid and the like. As specific examples may be mentioned silicon carbide, alder-wood charcoal which has been glowed at 800° C. and impregnated with phosphoric acid, calcium phosphate, molybdenum phosphate, tungsten phosphate, iron phosphate, aluminium phosphate, arsenious acid together with molybdenum or tungsten, silicides, for example iron silicide containing 15 per cent of silicon, active silica, hydrosilicates, borides such as titanium boride or iron boride, calcium fluoride, molybdenum with 10 per cent of aluminium chloride, molybdenum with 10 per cent of cadmium chloride, molybdic acid with sodium selenite. Compounds containing fixed nitrogen may also be employed with advantage in the reaction. Thus ammonia or its salts, for example, ammonium sulphide and in some cases organic compounds of nitrogen may also be advantageous. Such nitrides as are fairly stable against the action of water have been found to give particularly good results. As further examples of suitable catalysts may be mentioned, such containing one or more elements from the *a*) 4th to the 8th group of the periodic system, in particular such from the 6th group of the periodic system and more particularly molybdenum together with *b*) small amounts of other elements from the 2nd to the 7th group of the periodic system or copper or gold or the compounds thereof. The elements from the 2nd and 3rd group may however also be employed in large amounts. Thus mixtures containing molecular proportions of molybdic acid with magnesia or with copper or with aluminium hydroxide, or mixtures of tungstic acid with zinc oxide or of vanadium oxide with magnesia furnish good results. Excellent catalysts are further molybdic acid with about 10 per cent of chromium oxide or of vanadium oxide, molybdic acid with about 10 per cent of uranium oxide or of thorium oxide or of manganous oxide, further tungstic acid containing about 10 per cent of chromium oxide or of a mixture of uranium oxide, cobalt and a small amount of chromium oxide. Again another very suitable class of catalysts is formed by the noble metals or lead or tin or compounds thereof on carriers, in particular on magnesia or magnesite or chromium oxide. As examples of this class of catalyst may be mentioned ruthenium, palladium, platinum, gold, lead or tin on magnesia or magnesite or platinum or gold on chromium oxide. Catalysts containing small amounts of silver or of mixtures of copper with zinc or with cadmium in a free state or in chemical combination and preferably also boron or aluminium or silicon or titanium, or vanadium, or tantalum or chromium or molybdenum or tungsten or cobalt in a free or combined state or mixtures of these are also very suitable. Examples of such catalysts are tantallic acid containing 10 per cent of silver, molybdic acid containing 10 per cent of silver or silica containing 10 per cent of a mixture of copper and zinc. Again another class of catalysts consists of refractory metals or alloys on which small amounts of solid oxides of elements having a catalytic action from the 3rd to the 7th group of the periodic system have been deposited. The said metals or their alloys are preferably employed in an etched condition and preferably acidified solutions of salts of the said oxides are employed as the etching agent.

A modification of the process in accordance with the present invention which is suitable in many cases consists in employing catalysts which have chiefly a hydrogenating action for the first cracking or crackings whereby the hydrogen split off in particular from the low molecular constituents causes an enrichment in hydrogen of the higher molecular products which thus can be more easily split. In order to diminish or prevent an undesirable premature splitting it is often advantageous to work in the presence of diluent gases, such as nitrogen or carbonic acid or of water vapor or other substances, which contain or supply oxygen for example carbon dioxide. This manner of working is particularly useful when it is important to have as high a content of aromatic substances in the final product as possible.

The process may be carried out in the liquid or gaseous phase or with the employment of both phases, and different pressures may be employed in the separate crackings, if desired by the use of mechanical compression. When cracking in

the gaseous phase or with the simultaneous employment of both the liquid and gaseous phases, it is preferable to take care that there is a high linear velocity of flow, for example by the addition of gases as already described, in order to prevent local increases in temperature and the condensation of the reaction products on the catalysts.

The process in accordance with the present invention may be carried out in a cycle, if desired in such a manner that no appreciable cooling of the circulating liquid or gaseous or vaporous products occurs. A separation of the final products into their separate constituents may be effected in a simple manner by fractionally releasing the pressure.

The accompanying drawing represents in a diagrammatic manner an elevation of a plant partly in section, which is particularly suitable for carrying out the process according to the present invention.

Referring to the drawing in detail the numeral 1 represents a pipe through which initial oil, for example a mineral oil fraction boiling between 300° and 350° C. is introduced. The oil is then fed by means of a pump, compressing it to a pressure of about 50 atmospheres, into the heat exchanger 3 in which it is preheated by indirect heat exchange with hot vapours issuing from the cracking treatment, and then passed through the preheating coils 4 in which it is brought to a temperature of from 420° to 430° C. The preheated oil is cracked in coils 5. The cracked products are passed into the separator 6 in which the constituents boiling above 325° C. separate, the vaporous products being conveyed to the cooler 7 in which they are cooled to about 225° C., so that the fraction boiling between 225° and 325° C. may be separated in the separating vessel 8 connected with said cooler, while the constituents boiling below 225° C. pass through pipe 9. The fraction boiling between 225° and 325° C. collected in vessel 8 is led by way of pump 10 through coil 11 in which it is preheated to from 420° to 430° C. and then introduced into the second cracking coil 12. The cracked products are conveyed into the cooler 13, maintained at a temperature of 250° C. and then into the separator 14 in which the products condensed in cooler 13 are collected. The uncondensed portion is cooled in cooler 15 to a temperature of 180° C., the fraction boiling between 180° and 250° C., condensed in cooler 15 being collected in separator 16. The vaporous fraction consisting mainly of benzines is removed at 17. The liquid products collected in vessel 16 are compressed, together with the products leaving vessel 8 at 9 and being circulated by circulating pump 19, by means of pump 18 to a pressure of about 80 atmospheres. The compressed mixture is heated to a temperature of 460° C. in the preheating coil 20 and then introduced into a cracking vessel 21, filled with a catalyst consisting of molybdenum and zinc oxide which is rigidly arranged therein. From the products treated in said vessel 21 the higher boiling constituents are collected in separator 22 and may be withdrawn by valve 23. The vapours of the cracked products which are composed of about 60 per cent of benzine are passed through the pipe 24 externally provided with heat insulating material, are then made use of in heat exchanger 3 for preheating the initial materials, and after leaving said heat exchanger are cooled in cooler 25 to ordinary temperature, the condensed products being collected in separator 26 and removed by valve 27. The uncondensed gases are released from pressure by valve 28.

The following example will further illustrate the nature of the said invention but the invention is not restricted thereto.

*Example*

A petroleum distillate which boils above 250° C. and the major portion of which boils between 300° and 350° C. is subjected to cracking at a temperature of from about 420° to 430° C. and at a pressure of about 50 atmospheres. The product thus obtained contains from about 70 to 80 per cent of constituents which boil up to 325° C. The fraction which boils between 225° and 325° C. is again subjected to a cracking at a temperature of from 420° to 430° C. and at a pressure of about 50 atmospheres. The product thus obtained contains small quantities of constituents which boil below 180° C. and above 325° C. and from about 65 to 75 per cent of constituents which boil between 180° and 250° C. These latter, together with the fraction from the first cracking which boils below 225° C. and which is also poor in benzines, are subjected to another cracking at 460° C. and at 80 atmospheres pressure, preferably in the presence of a catalyst prepared from a mixture of about 66 per cent of molybdic acid and 33 per cent of zinc oxide, and a product is obtained which contains about 60 per cent of benzines and which constitutes an excellent non-knocking motor fuel. The whole of the cracking stages can be carried out with a high throughput with practically no loss occurring by reason of the separation of coke.

What I claim is:—

1. A process for the conversion of hydrocarbons of high boiling point into those of lower boiling point, which comprises subjecting a petroleum distillate which boils above 250° C. to cracking at a temperature of from about 420° to 430° C. and under a pressure of about 50 atmospheres, subjecting that fraction of the product thus obtained which boils between 225° and 325° C. to cracking at a temperature of from 420° to 430° C. and at a pressure of about 50 atmospheres and subjecting that fraction of the product thus obtained which boils between 180° and 250° C. together with those fractions from the product of the first cracking which boil below 225° C. and which are poor in benzines to another cracking at 460° C. and at 80 atmospheres pressure in the presence of a catalyst prepared from a mixture of molybdic acid and zinc oxide.

2. A process for the conversion of hydrocarbons of high boiling point into those of lower boiling point by subjecting hydrocarbons of high boiling point to separate consecutive restricted crackings under pressures of at least 50 atmospheres and at a temperature above the critical temperature of kerosene which comprises partially cracking a high boiling hydrocarbon fraction having a boiling point range not exceeding 200 centigrade degrees and having an initial boiling point above the end point of gasoline, while avoiding the formation of substantial amounts of permanent gases and coking, separating a fraction having a boiling point range not exceeding 200 centigrade degrees and having an average boiling point below that of the fraction treated in the first stage from the partially cracked products and partially cracking the said fraction at a temperature above the critical temperature of

kerosene to form products of lower average boiling point, no hydrogen being present except that which may be split off in the cracking of the hydrocarbons under treatment.

3. A process for the conversion of hydrocarbons of high boiling point into those of lower boiling point by subjecting hydrocarbons of high boiling point to separate consecutive restricted crackings under pressures of at least 50 atmospheres and at a temperature above the critical temperature of kerosene which comprises partially cracking a high boiling hydrocarbon fraction having a boiling point range not exceeding 200 centigrade degrees and having an initial boiling point above the end point of gasoline, while avoiding the formation of substantial amounts of permanent gases and coking, separating a fraction having a boiling point range not exceeding 200 centigrade degrees and having an average boiling point below that of the fraction treated in the first stage from the partially cracked products and partially cracking the said fraction at a temperature above the critical temperature of kerosene to form products of lower average boiling point, at least one stage of the process being carried out in the presence of a catalyst immune to poisoning by sulphur, no hydrogen being present except that which may be split off in the cracking of the hydrocarbons under treatment.

4. A process for the conversion of hydrocarbons of high boiling point into those of lower boiling point by subjecting hydrocarbons of high boiling point to separate consecutive restricted crackings under pressures of at least 50 atmospheres and at a temperature above the critical temperature of kerosene which comprises partially cracking a high boiling hydrocarbon fraction having a boiling point range not exceeding 200 centigrade degrees and having an initial boiling point above the end point of gasoline, while avoiding the formation of substantial amounts of permanent gases and coking, separating a fraction having a boiling point range not exceeding 200 centigrade degrees and having an average boiling point below that of the fraction treated in the first stage from the partially cracked products and partially cracking the said fraction at a temperature above the critical temperature of kerosene to form products of lower average boiling point, at least one stage of the process being carried out in the presence of a catalyst having chiefly a hydrogenating action and being immune to poisoning by sulphur, no hydrogen being present except that which may be split off in the cracking of the hydrocarbons under treatment.

5. A process for the conversion of hydrocarbons of high boiling point into those of lower boiling point by subjecting hydrocarbons of high boiling point to separate consecutive restricted crackings under pressures of at least 50 atmospheres and at a temperature above about 420° C. which comprises partially cracking a high boiling hydrocarbon fraction having a boiling point range not exceeding 200 centigrade degrees and having an initial boiling point above the end point of gasoline, while avoiding the formation of substantial amounts of permanent gases and coking, separating a fraction having a boiling point range not exceeding 200 centigrade degrees and having an average boiling point below that of the fraction treated in the first stage from the partially cracked products and partially cracking the said fraction at a temperature above about 420° C. to form products of lower average boiling point, no hydrogen being present except that which may be split off in the cracking of the hydrocarbons under treatment.

6. A process for the conversion of hydrocarbons of high boiling point into those of lower boiling point by subjecting hydrocarbons of high boiling point to separate consecutive restricted crackings under pressures of at least 50 atmospheres and at a temperature above about 420° C. which comprises partially cracking a high boiling hydrocarbon fraction having a boiling point range not exceeding 200 centigrade degrees and having an initial boiling point above the end point of gasoline, while avoiding the formation of substantial amounts of permanent gases and coking, separating a fraction having a boiling point range not exceeding 200 centigrade degrees and having an average boiling point below that of the fraction treated in the first stage from the partially cracked products and partially cracking the said fraction at a temperature above about 420° C. to form products of lower average boiling point, at least one stage of the process being carried out in the presence of a catalyst immune to poisoning by sulphur, no hydrogen being present except that which may be split off in the cracking of the hydrocarbons under treatment.

7. A process for the conversion of hydrocarbons of high boiling point into those of lower boiling point by subjecting hydrocarbons of high boiling point to separate consecutive restricted crackings under pressures of at least 50 atmospheres and at a temperature above about 420° C. which comprises partially cracking a high boiling hydrocarbon fraction having a boiling point range not exceeding 200 centigrade degrees and having an initial boiling point above the end point of gasoline, while avoiding the formation of substantial amounts of permanent gases and coking, separating a fraction having a boiling point range not exceeding 200 centigrade degrees and having an average boiling point below that of the fraction treated in the first stage from the partially cracked products and partially cracking the said fraction at a temperature above about 420° C. to form products of lower average boiling point, at least one stage of the process being carried out in the presence of a catalyst having chiefly a hydrogenating action and being immune to poisoning by sulphur, no hydrogen being present except that which may be split off in the cracking of the hydrocarbons under treatment.

MATHIAS PIER.

# CERTIFICATE OF CORRECTION.

Patent No. 1,963,245. June 19, 1934.

MATHIAS PIER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 38, after the period insert the following sentence: The cracking is generally carried out at a temperature above the critical temperature of kerosene.; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of October, A. D. 1934.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.