

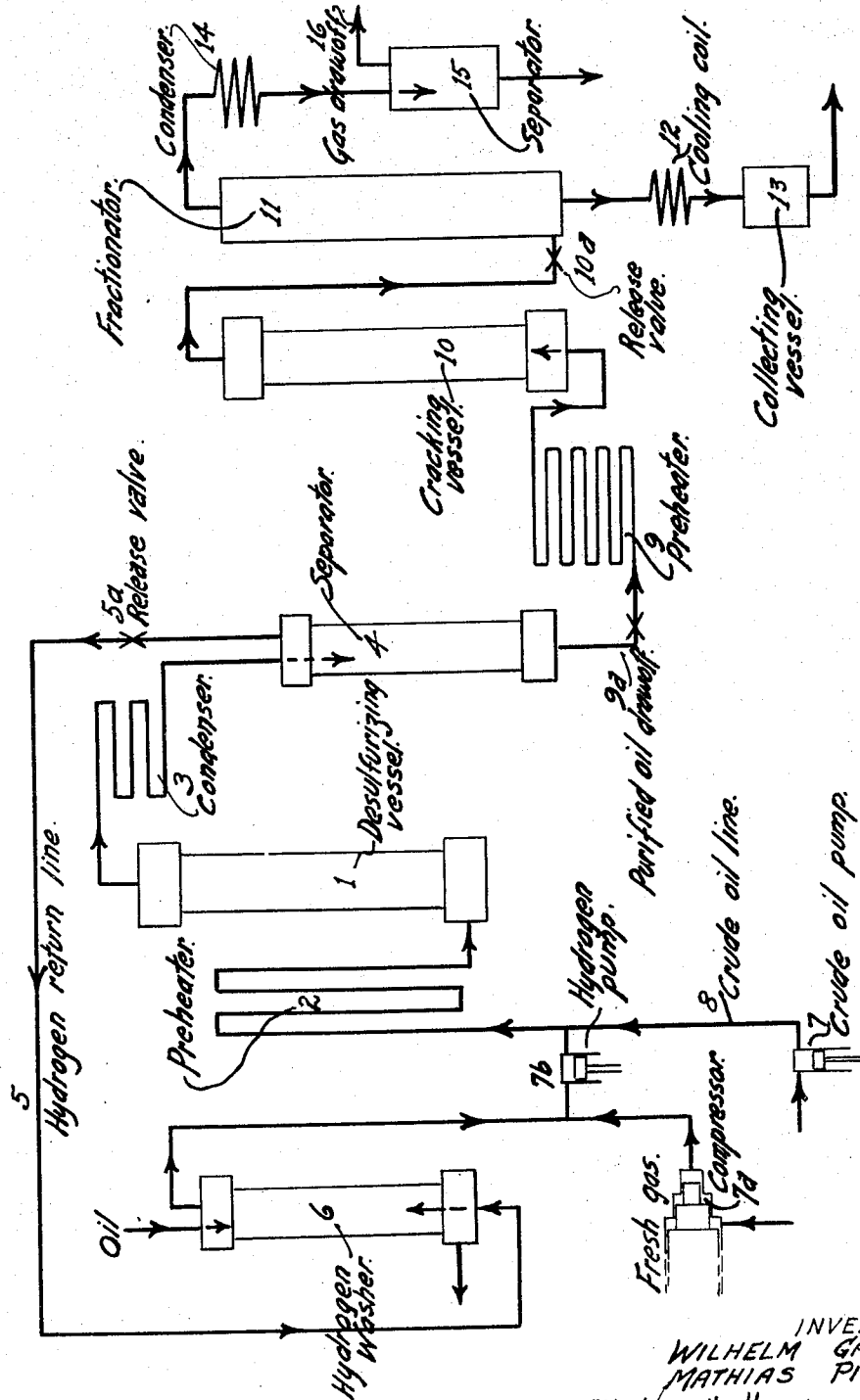
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PRODUCTION OF VALUABLE HYDROCARBONS

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PRODUCTION OF VALUABLE
HYDROCARBONS

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This invention relates to the production of valuable hydrocarbons from liquid carbonaceous materials such as coal pastes, mineral oils, tars and the like and the distillation, conversion products and residues thereof which initial materials contain sulfur compounds or oxygenated products which may be of an asphaltic nature or both.

It is known that the cracking of hydrocarbons can only be carried out with difficulty, and in any event uneconomically, if the said products contain an undue proportion of oxygen or sulfur compounds. These initial materials are, in many instances, also so thick and viscous that they can only be distilled with difficulty, if at all. For the same reason it is difficult, or even impossible, to pass them through pipes. Further an excessive content of sulfur renders cracking practically impossible, owing to the rapid destruction of the apparatus by corrosion.

We have now found that the cracking of sulfur bearing or oxygen containing initial materials can be effected in an excellent and also economical manner, if the initial materials, in liquid form, be first treated with gases supplying hydrogen, this term being hereinafter understood also to include hydrogen and also gaseous hydrocarbons or such of low boiling point which can easily be split with evolution of hydrogen, for example methane, ethane and also benzines, under such conditions of temperature and pressure and for so long a time, preferably in the presence of catalysts, that the sulfur and oxygen contained in the materials as such or in the form of compounds are completely or for the most part eliminated but that the molecule does not suffer any substantial disruption of the carbon skeleton contained therein and that only incipient or no substantial destructive hydrogenation of the oil occurs. As a rule temperatures above 300° C. but generally not exceeding 500° C. will be employed, temperatures of between 380° and 480° centigrade having been found particularly suitable for the treatment for the elimination of sulfur and asphaltic compounds. Very high pressures such as 100, 200, 500, 1000 atmospheres may be employed in the treatment, but even pressures of about 50 atmospheres or less, say 20 atmospheres, may suffice.

The duration of the treatment in which the sulfur and oxygen are eliminated and at which destructive hydrogenation becomes substantial is inversely proportional to the temperature and pressure employed and also depends on the na-

ture of the material to be treated and on the degree to which the elimination of sulfur and oxygen is to be carried out. It will be an easy matter for anyone skilled in the art to determine the conditions under which the first stage of our process may be carried out, as for example by an analysis of the gases issuing from the reaction chamber in order to determine the content of the said gases in water and hydrogen sulphide. In cases where the said first stage of the process is carried out continuously it will be necessary to increase the duration of the treatment, if it is found that the content of hydrogen sulphide and water decreases. The said increase in the duration of the treatment may be effected by passing the carbonaceous materials under treatment more slowly through the reaction vessel so that they remain in contact with the catalyst if such be employed for a longer period of time. The initial material itself is also subjected to analysis as regards its content of sulphur and oxygen and therefore the degree of desulphurization and deoxidation can easily be determined from the said gas analysis. Whether any substantial disruption of the carbon skeleton takes place can be determined for example by an examination of the boiling point curve of the products issuing from the first stage of the process prior to their being subjected to cracking or by the determination of the molecular weight of these products. We do not limit ourselves to the process of determination hereinbefore described and those skilled in the art will be able to devise other suitable methods for controlling the temperatures, pressures, duration of the treatment and other conditions of working necessary for carrying out the process according to the present invention. By suitably choosing the conditions of pressure, temperature and of the catalysts and the duration of treatment or of the amount of the product treated in the unit of time, it may be attained that substantially only desulfurization and deoxidation takes place in the first stage without any substantial formation of substances of low boiling point.

The products resulting from this first treatment are then subjected to a cracking treatment, with or without an addition of hydrogen, and with or without catalysts.

Suitable catalysts in particular for employment in the first stage of the process, if any be used, are the "catalysts immune to sulfur poisoning" recommended for the destructive hydrogenation of carbonaceous materials. As typical examples of catalysts of the said kind we mention com-

pounds containing sulfur in combination, for example metal sulfids, in particular the heavy metal sulfids and more especially those of the iron group, either alone or as mixtures with one
 5 another or with metals, metalloids, active charcoal, coke or the like or with oxids, hydroxids or carbonates or with other materials of a catalytic or of inert nature. The sulfur may also be combined with the catalyst by adding sulfites or sulfates thereto or by the addition of sulfur to metals
 10 or oxids. A very suitable catalyst may be obtained by treating iron with hydrogen sulfid at an elevated temperature. Particularly suitable catalysts of this class are for example cobalt sulfid, iron sulfid, zinc sulfid, nickel sulfid, manganese sulfid and the like or mixtures thereof,
 15 for example, mixtures of cobalt sulfid with nickel sulfid, or of cobalt sulfid with manganese sulfid, or of cobalt sulfid mixed with iron sulfid, or with zinc sulfid or with aluminium sulfid, with or without an addition of inert substances. Catalysts consisting of or containing a metal of the sixth group of the periodic system such as molybdenum, chromium, tungsten or uranium or the
 20 compounds thereof or mixtures of these substances are also particularly suitable. As examples of this type of catalysts may be mentioned molybdic acid or ammonium molybdate, tungsten sulfid, tungstic acid, chromium hydroxid, chromic oxid and chromic acid. Mixtures of molybdenum or chromium or tungsten with other catalysts such as with cobalt, nickel or iron may
 25 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 or calcium carbonate or with aluminium hydroxid. Carriers such as lumps of aluminium silicate may
 30 also be employed with advantage. As further catalysts may be mentioned oxidic catalysts comprising zinc oxid, chromium oxid or manganese oxid or mixtures of these, if desired with an addition of a compound containing fixed nitrogen
 35 such as ammonia or ammonium sulfid, or organic sulfur compounds, or such nitrids as are comparatively stable against the action of water, for example silicon nitrid or titanium nitrid. Compounds containing fixed nitrogen may also be employed as such; for example ammonia or ammonium salts may be added to the materials under
 40 treatment. Further nitrids, in particular such as are stable against the action of water, such as those mentioned by way of example in the foregoing may be employed. Organic compounds of nitrogen or of sulfur may also be employed. The aforesaid oxidic catalysts may be employed in conjunction with other substances
 45 such as lumps of fire-clay, quartz, asbestos, pumice, coke, active charcoal, metals in particular heavy metals, metalloids, oxids, sulfids, carbids, 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,
 50 cadmium, lead, bismuth, tin in the form of its compounds, and further the difficultly reducible metal oxids or carbonates, such as magnesia, lithium carbonate, boric acid, alumina, the rare earths, including the difficultly reducible oxids of metals from the 4th group of the periodic system, or the oxids of zinc, manganese or vanadium. The catalysts may contain several of these substances or also other substances as for example
 55 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 solutions of lead nitrate, or of stannous chlorid, silver nitrate or of copper hydroxid, either alone or
 80 in admixture with compounds of iron, cobalt and the like. Further may be mentioned catalysts containing the oxids of silver or of titanium, or lithium carbonate, magnesite, manganous oxid, silver borate, or mixtures of copper oxid with cerous oxid or of silver with cobalt oxid and the like, and also porous refractory masses coated with vanadium oxid or thorium oxid or with a mixture of compounds of uranium and zinc or of silver and tungsten. These latter compounds
 85 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 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
 90 carbid, 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
 95 with molybdenum or tungsten, silicids, for example iron silicid containing 15 per cent of silicon, active silica, hydrosilicates, borids such as titanium borid or iron borid, calcium fluorid, molybdenum with 10 per cent of aluminium chlorid, molybdenum with 10 per cent of cadmium chlorid, molybdic acid with sodium selenite.

The process according to the present invention is advantageous for the treatment of middle oils containing sulfur or oxygen compounds, and of crude heavy mineral oils, tars and the like.

The said catalysts may be added to the liquid carbonaceous materials to be treated in a fine state of division so that they are more or less uniformly distributed in the said liquid, or they may also be employed fixedly arranged in the reaction space of the reaction vessel deposited for example on grates, wire-gauze, baffles and the like. The reaction vessel employed in the first stage of the process for the desulphurization and disoxidation of the initial materials must have strong pressure bearing walls and will usually consist of an upright vessel for example in the form of a tower.

The products suitable for cracking, obtained in the first stage of the process by desulphurization and disoxidation as herein described may according to the present invention, be cracked, either directly or after removal of the low-boiling products, in the liquid or vapor form, with or without the use of the aforementioned or other catalysts and without damage to the apparatus, benzines, lamp oils and gas oils of good quality being obtained.

The treatment for the removal of the oxygen and sulfur compounds or the cracking treatment or both are preferably carried out in apparatus in which at least the hot parts of the apparatus are not constructed of materials, liable to lead to the formation of methane and deposition of coke

under the conditions employed. Even when cracking, the operation can be carried out without any appreciable formation of coke and gas, this being the more readily possible by reason of the sulfur and oxygen compounds, which are the chief causes of undesirable action, having been removed.

The advantage of the process therefore consists in the fact that products which are unsuitable for cracking, are converted into products which can be further worked up into valuable products in a simple manner by cracking.

Either in the first stage for the elimination of sulphur and oxygen or in the second cracking stage or in both stages the carbonaceous materials may be exposed to the treatment in the form of thin layers. For example the materials under treatment may flow in thin layers over plates. The materials under treatment may also be treated in the form of a spray or of a shower of drops. The cracking treatment in the second stage is usually carried out at temperatures ranging between about 400 and about 800° C. The cracking process may be carried out at ordinary or elevated pressure. Pressures of 10 or 20 atmospheres may be employed but also pressures of 50 atmospheres and even higher. Generally speaking the higher are the pressures the smaller will be the amount of gaseous products formed but working at higher pressures requires a stronger plant, so that it will largely depend on economical circumstances what pressures are employed.

The present invention will be further explained with reference to the accompanying drawing showing in a somewhat diagrammatic manner an elevation, partly in section, of a plant in which the process according to the present invention may be carried out with particular advantage.

Referring to this drawing in detail numeral 7 denotes a pump by which the crude initial oil to be desulphurized and cracked is led through pipe 8 and then through preheater 2 in which it is preheated together with hydrogen supplied by pump 7b. From thence the mixture of oil and hydrogen passes into the vessel 1 filled with a catalyst immune from poisoning in which under the conditions specified desulphurization and de-oxidation takes place. The purified oils are then condensed in condenser 3 and thereupon separated from unused hydrogen in separator 4. This hydrogen is drawn off through pipe 5, pressure release valve 5a, passed through pipe 5 and washed in washer 6 with a middle oil absorbing the hydrogen sulphide formed in vessel 1 and like impurities. The purified hydrogen is then supplied to pump 7b together with fresh hydrogen introduced by compressor 7a. The liquid products collecting in separator 4 are drawn off at the bottom thereof through line 9a and then heated up to cracking temperatures in preheater 9. Cracking is effected in cracking vessel 10. The cracked products are then conveyed by way of pressure release valve 10a into the distillation column 11 in which they are separated into higher boiling and lower boiling fractions. The higher boiling fraction is drawn off at the bottom of column 11, cooled in cooler 12 and collected in vessel 13. The lower boiling fractions are distilled in column 11, pass through condenser 14, in which the normally liquid products are condensed, and are separated from uncondensed constituents in vessel 15. These uncondensed constituents leave vessel 15 at 16, while the liquid portions may be removed from the bottom of this vessel.

The following examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted thereto.

Example 1

A topped Venezuela oil, which contains only about 5 per cent of constituents boiling below 350° centigrade, and as much as 90 per cent of residues rich in sulphur and oxygen compounds, is treated with hydrogen for about one hour at 480° centigrade and under a pressure of 200 atmospheres, in the presence of a catalyst containing molybdenum and chromium. The whole of the residues contained in the initial material are converted into distillable liquid products, the sulfur content of which is over 70 per cent lower than that of the initial materials. The reaction is controlled by gas analysis of the gases issuing from the reaction vessel.

The product thus obtained is cracked at a temperature of about 400°-500° C. A reaction product is obtained containing about 30 per cent of benzene. The constituents which have not been converted into benzene are returned to the cracking plant and are also converted to a considerable extent into benzene.

Example 2

A middle oil containing about 2.7 per cent of sulfur which has been obtained by fractionation from a crude Mexican oil rich in sulfur and which on account of its said high content in sulfur is unsuitable for direct cracking since the products thus obtained have a very unpleasant odour and the costs of refinery would be very high and further because the cracking plant would be very much corroded, is passed together with hydrogen at about 430° centigrade and under a pressure of 180 to 200 atmospheres over a catalyst containing molybdenum, zinc and magnesium at such a rate of flow that the oil remains about 40 seconds in contact with the catalyst. The quantity of oil passed through per hour amounts to about 5 to 10 times the volume of the catalyst. In this manner about 75 to 90 per cent of the sulfur contained in the oil is removed. The operation is preferably carried out in such a manner that after the separation of the gaseous from the liquid products the heat of the issuing gases is utilized for preheating fresh oil, whilst the hot oil is directly passed into a cracking plant for further treatment. The products of lower boiling point contained in the gases are condensed therefrom after cooling and are separated in a stripping vessel. The hydrogen sulfide which is carried along with the gases is in part washed out therefrom when the said products are condensed. The remainder must be removed in a separate scrubber with the aid of a scrubbing oil. The gas which has thus been freed from hydrogen sulfide is again returned to the process.

The reaction vessels which are employed according to the process of this case are either composed of or lined with a special steel, such as a chromium steel.

What we claim is:—

1. The process for the production of valuable hydrocarbons from crude heavy petroleum hydrocarbons containing sulphur which comprises subjecting said crude hydrocarbons to the action of a gas containing hydrogen under a temperature of from 300 to 500° C. and a pressure of from 20 to 1000 atmospheres in the presence of a catalyst immune to sulphur poisoning selected

- from the class consisting of metallic sulphides, difficultly reducible metal oxides and metals of the sixth group of the periodic system for only such a period of time that no substantial decomposition of said hydrocarbons into hydrocarbons of lower boiling point ensues to thereby remove the sulphur in the form of hydrogen sulphide and produce hydrocarbon oils of substantially the same boiling point and viscosity range as the crude starting materials and then subjecting said oils to a cracking treatment.
2. The process as defined in claim 1 wherein the first step is effected at a temperature ranging from 380 to 480° C.
3. The process for the production of valuable hydrocarbons from crude heavy petroleum hydrocarbons containing sulphur which comprises subjecting said crude hydrocarbons to the action of a gas containing hydrogen at a temperature of about 430° C. and a pressure of from 180 to 200 atmospheres in the presence of a catalyst containing a metal from the sixth group of the periodic system for only such a period of time that no substantial decomposition of said hydrocarbons into hydrocarbons of lower boiling point ensues to thereby remove the sulphur in the form of hydrogen sulphide and produce hydrocarbon oils of substantially the same boiling point and viscosity range as the starting materials and then subjecting said oils to a cracking treatment.
4. The process of refining crude heavy petroleum hydrocarbons containing sulphur which comprises subjecting said hydrocarbons to the action of a gas containing hydrogen in the presence of a catalyst immune to sulphur poisoning at a temperature lying within the range of temperatures usually employed in liquid phase cracking and at a pressure in excess of 20 atmospheres for only such a period of time that no substantial decomposition of said hydrocarbons into hydrocarbons of lower boiling point ensues to thereby remove the sulphur in the form of hydrogen sulphide and produce hydrocarbon oils of substantially the same boiling point and viscosity range as the crude starting materials.
5. The process as defined in claim 4 wherein a temperature of from 300° to 500° C. is employed.
6. A process as defined in claim 4 wherein the temperature employed ranges from 380° to 480° C.
7. The process as defined in claim 4 wherein the temperature employed ranges from 300° to 500° C. and the catalyst is one selected from the class consisting of metallic sulphides, difficultly reducible metal oxides and metals of the sixth group of the periodic system.
8. A process as defined in claim 4 wherein the temperature employed ranges from 300° to 500° C. and the catalyst comprises a metal from the sixth group of the periodic system.
9. The process for refining crude, heavy, petroleum hydrocarbons containing sulphur which comprises subjecting said hydrocarbons to the action of a gas containing hydrogen at a temperature of about 430° C. and a pressure of from 180 to 200 atmospheres in the presence of a catalyst comprising molybdenum for only such a period of time that no substantial decomposition of said hydrocarbons into hydrocarbons of lower boiling point ensues to thereby remove the sulphur in the form of hydrogen sulphide and produce hydrocarbon oils of substantially the same boiling point and viscosity range as the starting materials.
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