

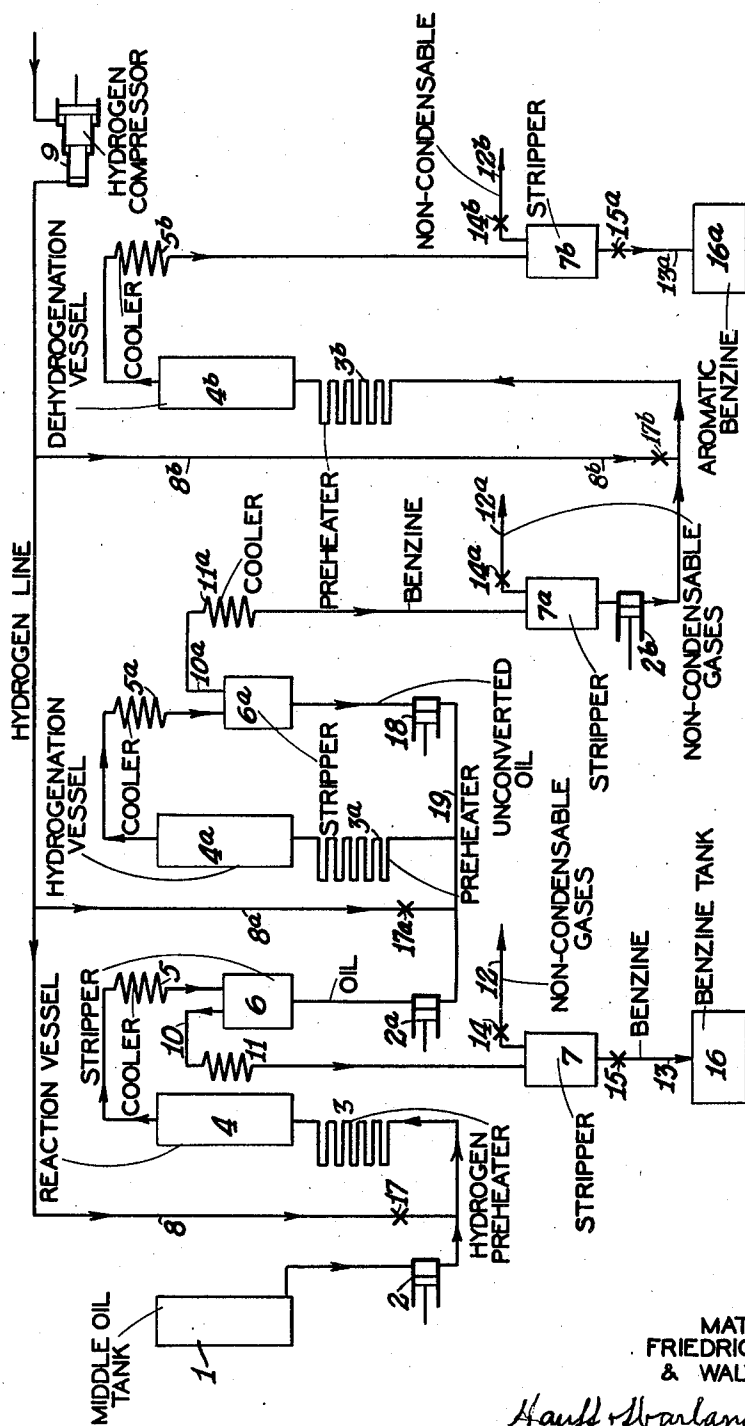
June 30, 1936.

M. PIER ET AL

2,045,795

PRODUCTION OF HYDROCARBONS OF LOW BOILING POINT

Filed July 13, 1932



INVENTORS:
MATHIAS PIER.
FRIEDRICH RINGER.
& WALTER SIMON.

Hauff & Harland

ATTORNEYS.

UNITED STATES PATENT OFFICE

2,045,795

PRODUCTION OF HYDROCARBONS OF
LOW BOILING POINT

Mathias Pier, Heidelberg, and Friedrich Ringer
and Walter Simon, Ludwigshafen-on-the-
Rhine, Germany, assignors to Standard-I. G.
Company, Linden, N. J., a corporation of Dela-
ware

Application July 13, 1932, Serial No. 622,314
In Germany July 16, 1931

2 Claims. (Cl. 196—53)

The present invention relates to improvements in the production of hydrocarbons of low boiling point which are not saturated with hydrogen by destructive hydrogenation and cracking.

It has already been proposed to convert coals, tars, mineral oils, their distillation or conversion products, in particular middle oils, into benzines of cyclic, and in particular of aromatic nature by treatment with hydrogen under pressure at temperatures above 500° C. It has also been proposed to convert middle oils by treatment with hydrogen under pressure at elevated temperatures into benzines of aliphatic nature which are saturated with hydrogen, the latter being converted in a second stage at temperatures above 500° C. into benzines which are not saturated with hydrogen.

We have now found that it is advantageous first to convert hydrocarbon oils boiling at least as high as middle oils and which mainly consist of hydrocarbons practically saturated with hydrogen, i. e. those which either have mainly an aliphatic nature or which mainly consist of saturated cyclic hydrocarbons or such cyclic hydrocarbons with side chains in which the aliphatic nature predominates on account of the side chains (especially if the number of carbon atoms in the side chains is substantially greater than of those present in the aromatic nuclei), into hydrocarbons of the nature of middle oil boiling between 200° and 325° C. which are not saturated with hydrogen and which contain considerable amounts for example from 60 to 80 per cent of cyclic hydrocarbons not saturated with hydrogen and in which the cyclic character predominates by heating to temperatures between 500° and 800° C. under pressures above 50 atmospheres, such as 100 or 200 atmospheres or more with or without the addition of hydrogen, and then to convert the latter into benzine-like hydrocarbons of low boiling point, boiling substantially below 250° C., which are practically saturated with hydrogen by treatment under strong hydrogenating conditions at temperatures between 300° C and 500° C., preferably while returning those constituents of the resulting products which boil above 200° C. By hydrocarbon oils mainly consisting of hydrocarbons practically saturated with hydrogen we mean those which contain at least 60 and preferably more than 80 per cent of these hydrocarbons. The benzines thus obtained contain the rings formed in the first stage, as for example as methylated hexahydro aromatics, and in a third stage are dehydrogenated, which operation is

readily carried out without appreciable loss, to form non-knocking motor fuels. It is especially advantageous to employ middle oils the upper boiling limit of which lies at 275° C. The dehydrogenating operation is preferably carried out at a temperature above 500° C., under elevated pressures, as for example from 20 to 200 atmospheres in the presence of hydrogen and in the presence of catalysts, such as compounds, as for example the oxides or sulphides, of metals from groups 4 to 8 of the periodic system.

As initial materials may be mentioned for example fractions of mineral oils, tars obtained by distillation, or extraction products of coals, oil shales or destructive hydrogenation products of any carbonaceous materials which have middle oil or lubricating oil character. It is especially advantageous to employ middle oils rich in hydrogen having an upper boiling limit at about from 270° to 280° C.

These initial materials are converted into middle oils which are not saturated with hydrogen and which contain cyclic hydrocarbons for example by cracking at high temperatures for example between 470° and 500° C. and under a pressure of for example 20 to 50 atmospheres preferably set up by means of an inert gas or hydrogen, or by treatment with hydrogen under pressure at temperatures above 500° C. and with a comparatively high partial pressure of the initial materials (more than 10 per cent). Suitable catalysts for this reaction stage are compounds especially oxides, of the metals of the 3rd, 5th and 6th groups of the periodic system.

The further treatment of the said middle oils which preferably contain no substantial amount of constituents boiling above 275° C. is then carried out by treating them under strong hydrogenating conditions with hydrogen. The said treatment under strong hydrogenating conditions is carried out at temperatures of from 400 to 500° C., preferably from 400° to 450° C., and with the lowest possible partial pressure of the introduced hydrocarbon products, especially one of less than 10 per cent. The particular amount of hydrogen to be employed in each case depends upon the product to be treated and the particular conditions of temperature and pressure employed. It is selected so great that, as aforesaid, the partial pressure of the introduced hydrocarbon products is as a rule less than 10 per cent which may for example be attained by employing from 1.5 to 2 cubic metres of hydrogen per each kilogram of the introduced hydrocarbon products. If catalysts having a strong hydrogenating action are em-

ployed, which is the preferred manner of working, the reaction is carried out under a pressure of from 50 to 200 atmospheres; if, however, less strongly hydrogenating catalysts are employed, pressures of more than 250 atmospheres, as for example of 300, 400, 500 or 1000 atmospheres are required. Suitable strongly hydrogenating catalysts are for example the sulphides of heavy metals, such as the sulphides free from oxygen of the metals of the 6th group of the periodic system for example of molybdenum, tungsten, or of nickel, cobalt, rhenium or tungstates such as nickel tungstate with great advantage. Sulphides may be employed which are produced by the decomposition of sulphonic salts, as for example of tungsten, molybdenum and the like according to the application Ser. No. 586,948, filed 15th January 1932, or by treatment of metals, such as chromium, molybdenum, tungsten, rhenium and the like, or metal compounds, with volatile sulphur compounds, as for example hydrogen sulphide, carbon disulphide and the like under pressure, as for example according to the applications Nos. 478,101 and 586,948 filed 27th August 1930 and 15th January 1932 respectively. As catalysts having a less strong hydrogenating action may be mentioned for example the oxides of the metals of groups 5 to 8, in particular group 6 of the periodic system.

The benzines saturated with hydrogen thus obtained contain mainly saturated cyclic hydrocarbons, in particular hydroaromatic hydrocarbons.

In order to obtain a far-reaching conversion into benzines in the second stage it is preferable to return the fractions of the products boiling above 200° C. issuing from this stage to the reaction chamber of the second stage in admixture with fresh middle oil.

In order to improve the properties of the resulting benzines as regards knocking they are dehydrogenated in a third stage, as for example under a pressure of hydrogen. This is preferably effected while employing temperatures of more than 500° C., as for example of from 510° to 560° C. Catalysts, as for example metals or metal compounds, in particular the oxides of the 3rd, 5th and 6th groups of the periodic system may be employed either alone or in admixture with each other or with carrier substances such as active carbon, active silica, bauxite, active alumina, Florida earth, pumice, magnesite, magnesia, chromium oxide and the like. It is preferable to maintain a partial pressure of the products introduced into the reaction chamber of more than 10 per cent, preferably of more than 30 per cent up to 80 per cent. In this manner the benzine is converted into benzine which is not saturated with hydrogen containing cyclic, in particular aromatic hydrocarbons, without any considerable formation of gaseous hydrocarbons.

The present invention has the great advantage of rendering possible the preparation of a non-knocking motor fuel from an aliphatic initial material having a higher boiling point.

Reference is here made to the accompanying drawing, which discloses diagrammatically an apparatus for carrying out our process.

On the drawing:

The middle oil in tank 1 is conducted, with the assistance of pump 2, together with hydrogen, the hydrogen being compressed in compressor 9 to 200 atmospheres and further conducted through conduit 8, over the pre-heater 3, into the reaction furnace 4. The reaction material leaving the oven is cooled in the coil 5 so far that in

the stripper 6 mainly an oil of the boiling point range of middle oil is condensed, whereas any low boiling portions, especially benzine, together with the excess hydrogen, leave the stripper through conduit 10, pass through the cooler 11, into a second stripper 7, in which the benzine is separated. The separated benzine is drawn off by way of the tension release valve 15 through conduit 13 and conducted into the tank 16, whereas the non-condensable parts together with the hydrogen are released through valve 14 and removed by way of conduit 12.

The oil in the stripper 6 is conducted by pump 2a together with fresh hydrogen, which is fed through conduit 8a, through the pre-heater 3a, into a second reaction vessel 4a and there subjected to pressure hydrogenation, according to the conditions set forth in the example. The reaction material leaving the oven is cooled in cooler 5a, the condensed unchanged oil separated in the stripper 6a is returned with the assistance of pump 18 through conduit 19 into the reaction chamber 4a, whereas the benzine condensed in cooler 11a is collected in the stripper 7a. Non-condensable parts and hydrogen undergo a pressure release by way of valve 14a and leave the stripper through conduit 12a.

The benzine is drawn off from the stripper 7a with the assistance of pump 2b and is conducted, together with the hydrogen from conduit 8b through the pre-heater 3b into the reaction vessel 4b. The obtained aromatic benzine is condensed in the cooler 5b and collected in the stripper 7b. The fluid parts are conducted through the pressure release valve 15a through conduit 13a into the tank 16a, whereas the gaseous, non-condensable parts are released by valve 14b and removed through conduit 12b.

The amount of the hydrogen necessary in the various steps is regulated by valves 17, 17a and 17b.

The following example will further illustrate the nature of this invention but the invention is not restricted to this example.

Example

A middle oil rich in hydrogen obtained from German petroleum by distillation, of which 65 per cent consist of hydrocarbons saturated with hydrogen, is led together with hydrogen under a total pressure of 200 atmospheres at 510° C. over a catalyst prepared from molybdic acid, chromium oxide and manganese carbonate at such a velocity of flow that over each liter of catalyst 4 kilograms of middle oil are passed per hour, whereby the partial pressure of the initial material within the reaction vessel amounts to 35 atmospheres. In addition to the formation of small amounts of benzine, a middle oil is obtained of which 85 per cent consists of hydrocarbons not saturated with hydrogen and which contains mainly cyclic compounds. The said middle oil is freed from benzine fractions by fractional condensation and is led from the condensation vessel without releasing the pressure together with an excess of hydrogen under the same pressure as in the first stage and at 425° C. over a catalyst consisting of tungsten sulphide which has been prepared according to the application Ser. No. 586,948, filed 15th January 1932. The partial pressure of the product introduced into the reaction vessel amounts to 8 atmospheres. The effluent fractions boiling above 200° C. are condensed and, after the addition of fresh middle oil, re-introduced into the

reaction chamber in order that the conversion into benzine may be complete. The benzine obtained consists of 90 per cent of hydrocarbons completely saturated with hydrogen of which about one half consists of saturated cyclic, in particular hydroaromatic, hydrocarbons. After condensation this product is led under the same pressure with hydrogen at 530° C. over a catalyst consisting of 80 per cent of tungstic acid and of 20 per cent of magnesium oxide. The partial pressure of the benzine within the reaction chamber is 50 atmospheres. In this manner a benzine is formed which contains about 33 per cent of aromatic hydrocarbons and other hydrocarbons not saturated with hydrogen and which has excellent properties as regards non-knocking in motors.

What we claim is:

1. A process for the production of valuable liquid hydrocarbons of low boiling point from higher boiling hydrocarbons which comprises heating a hydrocarbon oil boiling at least as high as middle oil and which mainly consists of hydrocarbons practically saturated with hydrogen, to a temperature between 500° and 800° C. under a pressure of at least 50 atmospheres while maintaining a partial pressure of said hydrocarbon oil of more than 10 per cent of the total pressure, for a length of time sufficient that said hydrocarbon oil is converted into a hydrocarbon product of which at least the essential part boils within the boiling point range of middle oil and which contains considerable amounts of cyclic hydrocarbons not saturated with hydrogen, then subjecting this hydrocarbon product to strong hydrogenating conditions at a temperature between 300° and 500° C. while maintaining a partial pressure of this hydrocarbon product of less than 10 per cent of the total pressure, said product thus being converted into a benzine-like hydrocarbon oil of low boiling point which is practically saturated with hydrogen, and then dehydrogenating the said benzine-like hydrocarbon oil by treatment at a temperature between 500° and 750° C. in the presence of a dehydrogenating catalyst while maintaining a partial pressure of said benzine-like hydrocarbon oil of at least 10 per cent of the total pressure.

drocarbon oil of low boiling point which is practically saturated with hydrogen, and then dehydrogenating the said benzine-like hydrocarbon oil by treatment at a temperature between 500° and 750° C. in the presence of a dehydrogenating catalyst while maintaining a partial pressure of said benzine-like hydrocarbon oil of at least 10 per cent of the total pressure.

2. A process for the production of valuable liquid hydrocarbons of low boiling point from higher boiling hydrocarbons which comprises heating a middle oil which mainly consists of hydrocarbons practically saturated with hydrogen to a temperature between 500° and 800° C. under a pressure of at least 50 atmospheres while maintaining a partial pressure of said middle oil of more than 10 per cent of the total pressure for a length of time such that said middle oil is converted into a hydrocarbon product of which at least the essential part boils within the boiling point range of middle oil and which contains considerable amounts of cyclic hydrocarbons not saturated with hydrogen, then subjecting this hydrocarbon product to strong hydrogenating conditions at a temperature between 300° and 500° C. while maintaining a partial pressure of this hydrocarbon product of less than 10 per cent of the total pressure, said product thus being converted into a benzine-like hydrocarbon oil of low boiling point which is practically saturated with hydrogen, and then dehydrogenating the said benzine-like hydrocarbon oil by treatment at a temperature between 500° and 750° C. in the presence of a dehydrogenating catalyst while maintaining a partial pressure of said benzine-like hydrocarbon oil of at least 10 per cent of the total pressure.

MATHIAS PIER.
FRIEDRICH RINGER.
WALTER SIMON.