

UNITED STATES PATENT OFFICE

2,326,799

CONVERSION OF COMBUSTIBLE CARBONACEOUS MATERIALS

Mathias Pier, Heidelberg, and Gerhard Fricé,
Ludwigshafen-on-the-Rhine, Germany; vested
in the Alien Property Custodian

No Drawing. Original application August 12,
1938, Serial No. 224,488. Divided and this ap-
plication July 19, 1939, Serial No. 285,348. In
Germany August 24, 1937

3 Claims. (Cl. 196—52)

The present application is a division of our copending application Ser. No. 224,488, filed August 12, 1938, now Patent No. 2,245,157, dated June 10, 1941, which relates to the conversion of combustible carbonaceous materials and is particularly concerned with the production of liquid and/or solid hydrocarbons by the conversion of liquid and/or solid carbonaceous materials comprising aliphatic compounds at elevated temperatures and with the conversion of carbon monoxide with hydrogen into hydrocarbons containing more than one carbon atom in the molecule and/or solid or liquid oxygen-containing derivatives of hydrocarbons, such as methanol or higher alcohols, as for example propanol or isobutylalcohol, or aldehydes, ketones, acids and the like. The said application generally covers the conversion of combustible carbonaceous materials comprising essentially aliphatic compounds at elevated temperatures by heating such materials in the presence of substantial amounts of added cyclic hydrocarbons and specifically claims the production of heavy fuels stable to knocking by cracking in the vapor phase at a temperature between 400° and 700° C. hydrocarbon oils comprising essentially unsaturated aliphatic hydrocarbon oils boiling at least for their greater part, above the boiling point range of benzene while adding a substantial amount of cyclic hydrocarbons which under the reaction conditions are vaporous, but in the absence of substantial amounts of added hydrogen or of gases supplying hydrogen.

The present application is more particularly concerned with the production of valuable non-knocking motor fuels by subjecting paraffinic hydrocarbons together with low boiling cyclic hydrocarbons to a thermal treatment.

In the said conversions, such as cracking, dehydrogenation or destructive hydrogenation of the said carbonaceous materials or in the hydrogenation of these materials without pressure or in the interaction of carbon monoxide with hydrogen there is often the inconvenience that a considerable amount of undesirable low molecular, in particular gaseous hydrocarbons are formed especially when working in the gas or vapor phase and when using very active catalysts and thereby the yield of the desired products is reduced.

We have now found that this inconvenience may be overcome by carrying out the said conversions of carbonaceous materials essentially comprising aliphatic compounds in the presence of a substantial amount of added cyclic hydro-

carbons. These cyclic hydrocarbons have proved to substantially suppress or diminish the said tendency of gas formation.

Thus the said operation in the presence of added cyclic hydrocarbons is very useful in the production of non-knocking motor fuels, in particular safety fuel, by heating hydrocarbon oils to cracking temperatures, especially when starting from hydrocarbon oils which consist wholly or substantially of unsaturated aliphatic hydrocarbons and boil, at least for their greater part, above the boiling point range of benzene. As additional cyclic hydrocarbons come into consideration in particular mono-nuclear, aromatic hydrocarbons, such as benzene, toluene and xylene.

Oil fractions rich in unsaturated hydrocarbons and boiling mainly above 200° C. may be obtained, for example, by cracking mineral oils, tars or fractions thereof, for example mineral oil or brown coal tar fractions containing paraffin wax, or destructive hydrogenation products of coals, tars, mineral oils and the like. Cracking products of hydrocarbon oils which result from the reduction of carbon monoxide, are also suitable. The said initial materials are mixed, before or during the heating to cracking temperatures, with cyclic, particularly mono-nuclear, aromatic hydrocarbons, such as benzene, toluene, xylene and the like, or also with the hydrogenation products thereof or with hydrogenated naphthalenes. The mixture is passed in gaseous form through a chamber heated to from 400° to 700°, preferably to from 450 to 600° C.

The said cracking reaction is preferably carried out in the presence of catalysts, more specifically the metals of the 2nd to the 8th groups of the periodic system or their compounds. As examples of the latter may be mentioned the sulphides, oxides, phosphates, halides or sulphates of iron, cobalt or nickel, and also of chromium, vanadium, aluminum, zinc, tin, manganese, titanium, magnesium, tungsten, molybdenum and the like.

It is of special advantage to apply the metal compounds to carriers, for example substances having large surface areas, such as bleaching earths, active charcoal, brown coal, small coke and the like, which may, if desired, be subjected to a pretreatment with acid substances, as for example hydrogen fluoride. In some cases it is of advantage to carry out the reaction in the presence of halogen or of gaseous or vaporous halogen or sulphur compounds.

The said reaction may also be carried out un-

der increased pressure as for example at 20 to 200 atmospheres or more.

In order to ensure a far-reaching polymerization or condensation of any low boiling unsaturated compounds formed, it may in some cases be of advantage to provide for another zone behind the cracking zone, in which the products are kept for some time at elevated temperature. The products may also, following the cracking zone, be passed over a catalyst which promotes the polymerization or the condensation. With a view to accelerating the polymerization, the splitting catalyst may also be mixed, preferably in the last part of the splitting chamber, with catalysts having a polymerizing action. Catalysts suitable for this purpose are for example certain metal halides, such as aluminium chloride, iron chloride and the like, or phosphoric acid, boric acid, if desired together with oxalic acid and the like.

Another example of conversions which may be carried out with advantage in the above described manner is the conversion of low molecular weight paraffin hydrocarbons, such as ethane, propane, butane or low-boiling liquid paraffin hydrocarbons, into non-knocking motor fuels; also in this conversion the difficulty arises that considerable amounts of low molecular weight hydrocarbons, in particular the lowest member of the series, methane are formed. On the other hand, when using methane itself very high temperatures are necessary. In every case there also takes place considerable deposition of carbon.

We have found that paraffin hydrocarbons can be employed in a very advantageous manner for the preparation of valuable non-knocking fuels by subjecting them together with cyclic hydrocarbons to a thermal treatment at temperatures above 300° C., preferably in the presence of rigidly arranged catalysts. Cyclic hydrocarbons suitable for this purpose are especially low boiling aromatic and hydroaromatic hydrocarbons which may also be employed in admixture with each other. The treatment is preferably carried out in the vapor phase.

As paraffin hydrocarbons there may be mentioned for example benzines or middle oils from paraffin-basic petroleums or from destructive hydrogenation products of coals, such as brown coals, or of tars, in particular brown coal tars, or of mineral oils, or liquid fractions of the products obtained by the reduction of carbon monoxide, and also corresponding fractions of hydrocarbons rich in hydrogen which have been obtained by the treatment of oils with selective solvents. Of the gaseous paraffinic hydrocarbons, pentane, butane and propane are especially suitable for the treatment. They may be taken from any source, as for example from cracking gases or from the gaseous portions of the products obtained by the reduction of carbon monoxide with hydrogen and the like. As low boiling aromatic hydrocarbons there may be employed preferably benzene or its homologues; hydrogenation products of these substances or naphthalene or its hydrogenation products are also suitable. In the mixtures to be treated, the proportion of the aromatic and/or hydroaromatic hydrocarbons advantageously amounts to between about 10 and 50 per cent; in many cases it may be even greater. The aromatic and/or hydroaromatic hydrocarbons should boil substantially in the boiling range of the benzines, i. e. below about 220° C.

The paraffinic hydrocarbons may be mixed with the aromatic and/or hydroaromatic hydro-

carbons in the liquid or vapor phase. The mixture is then subjected to the vapor phase to the thermal treatment at temperatures of between 300° and 700°, advantageously between 450° and 650° C. and preferably in the presence of catalysts.

The liquid mixture or the two boiling paraffinic hydrocarbons, liquid and gaseous hydrocarbons may be present at the same time. In this case it is advantageous to heat the mixture of the liquid paraffins with the aromatics for example to about 480° C. and to heat the gaseous hydrocarbons separately therefrom, for example to from 500° to 700° C., the hot vapors then being united with the heated gases and the whole treated at from 450° to 700° C., preferably in the presence of catalysts.

The nature of the catalysts to be used depends on the conditions used, in particular on the temperature, and also on the nature of the paraffinic hydrocarbons. The paraffinic hydrocarbons are advantageously treated in the presence of catalysts having a splitting or dehydrogenating action. Catalysts may also be used, however, which have, in addition to a splitting action, also a polymerizing action, or there may be added to splitting catalysts larger or smaller proportions of catalysts having a polymerizing action. The latter may also be brought into reaction separately from the catalysts having a splitting or dehydrogenating action in a second, closed reaction vessel.

At least one of the said actions is exerted by most metals of the 2nd to the 8th groups of the periodic system or their compounds. For example the sulphides, oxides, phosphates, halides or sulphates of iron, cobalt, nickel, chromium, vanadium, aluminum, zinc, tin, manganese, titanium, magnesium, tungsten and molybdenum are suitable as catalysts for the said treatment.

The said metals or metal compounds are advantageously applied to carriers, as for example to bodies having large surfaces, such as fuller's earth, bleaching earths, silicates and silica gel, or active carbons, lignite small coke which may if desired be pretreated with acid substances, in particular hydrogen fluoride.

In many cases it is preferable to carry out the reaction in the presence of halogens or volatile compounds of halogens or other non-metals, as for example volatile sulphur or phosphorus compounds, or of hydrogen, preferably with a low partial pressure of the hydrogen (up to about 30 per cent of the total pressure).

The reaction may be carried out at atmospheric or increased pressure, as for example at from 20 to 200 atmospheres or more.

The gases formed may be led back again to the reaction. The liquid products obtained may be subjected to a refining, as for example a refining destructive hydrogenation.

Very good results are obtained when carrying out the reactions in consideration, while maintaining the gas or vapor phase, in the presence of added cyclic hydrocarbons which under the reaction conditions are at least partly vaporous. Both aromatic hydrocarbons and naphthenes may be used. The most suitable substances are low boiling cyclic hydrocarbons of the boiling range of benzines (benzene, toluene, xylene and cyclohexane) and middle oils or products containing the same, such as mineral coal tar middle oil or middle oil from the liquefaction of mineral coal; substances of higher boiling point

may also be added when under the reaction conditions they have such a vapor pressure that they are present to a considerable extent in the vapor form; this is the case for example with naphthalene and its homologues and also with lower boiling mineral coal tar fractions.

The said cyclic hydrocarbons are generally speaking added in amounts of between 10 and 60 per cent by weight with reference to the throughput of carbonaceous substances. The amount to be added in individual cases depends in particular on the nature of the reaction, on the activity of the catalyst and on the nature of the additional substance. The amounts added are greater in the case of catalysts which tend strongly to form gas than in the case of catalysts having this tendency to a lesser degree.

The cyclic hydrocarbons may be added continuously or at intervals. In the latter case the addition is preferably made when the formation of undesirable low molecular hydrocarbons begins to exceed the desirable degree, which may become evident by the occurrence of great evolution of heat. The additions may also be made at equal intervals of time. When adding the additional substances continuously, the amount added may be constant or variable. The cyclic hydrocarbons may also be added at several places in the reaction chamber. The catalyst may also be laden with cyclic hydrocarbons before use.

We have also found that in the reactions in consideration carried out in the gas or vapor phase the formation of undesirable hydrocarbons of low molecular weight can likewise be considerably reduced by adding at intervals of time cyclic hydrocarbons which at least in part remain liquid under the reaction conditions. Aromatic hydrocarbons and also naphthenes may be mentioned. Cyclic hydrocarbons which boil above 200° C. are most suitable, such as anthracene oil or other mineral coal tar fractions boiling above 200° C. It is, however, also possible to add cyclic hydrocarbons of lower boiling point, as for example xylene, provided the pressure used during the reaction is so high or the temperature used is so low that the added substance remains liquid at least in part.

The amount to be added depends generally speaking on the length of the intervals of time, and also on the nature of the reaction, on the activity of the catalysts and on the nature of the added substances. The amounts added are larger in the case of catalysts having a strong tendency to form gas than in the case of catalysts with which this tendency is less.

The intervals of time between the single additions may be equal. The procedure may, however, also be that cyclic hydrocarbons are added only when the formation of undesirable hydrocarbons of low molecular weight commences to rise beyond the permissible degree, which may become evident by a rise in temperature. The cyclic hydrocarbons may also be added at several points in the reaction chamber. The catalyst may also be laden with cyclic hydrocarbons before use.

The said process is of great advantage in destructive hydrogenations in the presence of catalysts having a strong splitting action. Among such catalysts there may be mentioned for example oxides and sulphides of the metals of the 5th to the 7th groups of the periodic system and the iron group, as well as mixtures containing the same, and, for cracking, activated hydrosilicates, such as bleaching earths, or also

alumina, magnesia, active carbon, lignite small coke or oxides of chromium, molybdenum, tungsten, manganese, iron, nickel, cobalt or titanium or mixtures of these substances.

In dehydrogenations, the process has the advantage that the partial splitting into low molecular hydrocarbons which is unavoidable in most cases is considerably reduced.

In the reaction of carbon monoxide with hydrogen to form liquid or solid hydrocarbons or liquid or solid oxygen-containing derivatives of hydrocarbons, the addition of cyclic hydrocarbons hinders to a considerable extent the formation of gaseous hydrocarbons, in particular methane. When working in this reaction for the formation of high boiling hydrocarbons mixtures and/or paraffin wax, the proportion of high molecular products formed may be considerably increased at the expense of the low molecular hydrocarbons, such as benzine, by the addition of cyclic hydrocarbons.

The said process is of special advantage in the reaction of carbon monoxide with hydrogen when using highly active catalysts having a strong tendency to form gaseous hydrocarbons, in particular methane. Such catalysts are in particular substances containing nickel, as for example those in which the nickel is present in admixture with other catalytically active substances, such as iron, cobalt or the compounds of rare earths, thorium, titanium, copper, zirconium, molybdenum, chromium, tungsten, germanium, manganese or of the alkali or alkaline earth metals, or also with the said metals themselves, and which may also be applied to carriers, such as active silicic acid, alumina, magnesia or zinc oxide. These catalysts containing nickel are prepared in known manner, as for example by reduction from the oxides, the oxalate or carbonate in the presence of reducing gases, such as hydrogen and/or carbon monoxide and at temperatures between 200° and 500° C., or even at higher temperatures, as for example 700°, 800° or 1000° C., whereby the substances may be heated until a partial sintering takes place (for example from about 2 to 4 hours at 850° C.).

Even in the case of catalysts containing no nickel, however, the addition of the said cyclic compounds is of advantage. Among such there may be mentioned in particular substances containing iron, as for example iron obtained by the reduction of fused ferrosferric oxide, which is advantageously provided with additions of other substances, such as titanium or silicon or their compounds, or iron obtained by reduction of non-fused iron compounds and simultaneous or subsequent sintering, which likewise may contain additions of other substances.

The same is true for catalysts containing cobalt.

In the reaction of carbon monoxide with hydrogen to form liquid or solid oxygen-containing derivatives of hydrocarbons, the catalysts known for this reaction are used, in particular the oxides of the alkali, alkaline earth and earth metals or of zinc, chromium, boron, titanium, vanadium, niobium, tantalum or manganese.

The said reactions are carried out under known conditions, the destructive hydrogenations at temperatures between 250° and 600° C. and under increased pressure, advantageously of more than 20 atmospheres the cracking at temperatures between 300° and 700°, advantageously be-

tween 300° and 550° C. and at atmospheric or preferably at increased pressure (as for example 20 to 200 atmospheres or more), the dehydrogenation at temperatures between 400° and 600° C. and the reaction of carbon monoxide with hydrogen at temperatures between 150° and 450°, preferably between 180° and 300° C., at atmospheric or increased pressure, as for example between 5 and 200 atmospheres.

The other conditions, such as time of treatment, relative proportions of the reactants and the like are also as usual. The cracking may be carried out in the presence of gases, such as hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane or ethylene, propylene or butylene, which have preferably been previously heated to the temperatures used in the splitting or to still higher temperatures. The reaction of carbon monoxide and hydrogen may be carried out in the presence of accompanying gases, such as carbon dioxide or methane. The proportion of the carbon monoxide content to the hydrogen content in the initial gas may be different.

In the reactions in which no building up into products of higher molecular weight, as in the reduction of carbon monoxide, takes place, i. e. in destructive hydrogenation, cracking and dehydrogenation, vaporizable substances are used as initial materials, as for example petroleums, tar oils, liquid carbon monoxide reduction products and oils obtained by destructive hydrogenation of coals or by polymerization of olefines.

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

Example 1

A fraction, boiling between 150° and 300° C., of a cracking product of brown coal paraffin wax and an equal proportion of benzene are heated to 510° C. in a tubular reaction chamber, under a pressure of 150 atmospheres. The reaction product obtained is then subjected to a fractional distillation. The fraction boiling between 140° and 200° C. is, after it has been refined with sulphuric acid or bleaching earth, an efficient anti-knock safety fuel having a high flash-point.

Example 2

Butane is heated to 530° C. under a pressure of 250 atmospheres and at a speed of throughput of 2 kilograms per liter of heated spiral volume and per hour in an externally heated tubular spiral. With each kilogram of the butane thus heated there are mixed 0.25 kilogram of benzene and 40 liters of hydrogen. The mixture is then led at 530° C. over a sulphurized mixture of molybdic acid, zinc oxide and magnesia as a catalyst. There is thus formed a product the fraction of which boiling up to 180° may be used very advantageously as an addition for improving the non-knocking properties of motor fuels. By subjecting the product to hydrogenating refining, a valuable motor fuel having very good non-knocking properties is obtained.

Example 3

A hydrocarbon mixture boiling between 200° and 350° C., obtained by reduction of carbon monoxide, is led together with 10 per cent by volume of crude benzene at 460° C. over a catalyst consisting of aluminum hydrosilicate. The addition of crude benzene effects a reduction in the gasification to hydrocarbons having 3 and 4 carbon atoms by 35 per cent.

Example 4

A gas consisting of carbon monoxide and hydrogen in the ratio of 1:2 is led at 330° C. together with 5 kilograms of sulphur-free benzene vapor per 100 cubic meters of gas under a pressure of 5 atmospheres over a multi-substance catalyst containing mainly nickel. 110 grams of liquid hydrocarbons are obtained per cubic meter of gas; without the addition of benzene the greater part of the reaction products consists of gaseous hydrocarbons.

Example 5

A hydrocarbon mixture boiling between 200° and 350° C. obtained by reduction of carbon monoxide is led at 460° C. and under a pressure of 30 atmospheres over a catalyst of aluminium hydrosilicate. There are thus formed from 100 kilograms of initial product, 18 kilograms of benzene and 15 kilograms of gaseous hydrocarbons. If, in addition to the abovementioned hydrocarbon mixture, there be added for 5 minutes at 30 minute intervals a mineral coal tar oil fraction boiling between 225° and 380° C. in an amount of 10 per cent by weight of the hourly throughput of the hydrocarbon mixture to be treated, only 1 kilogram of gaseous hydrocarbons is formed.

Example 6

A gas consisting of carbon monoxide and hydrogen in the ratio of 1:2 is led under a pressure of 50 atmospheres at 230° C. over a multi-substance catalyst containing mainly nickel.

At intervals of from 15 to 30 minutes, from 3 to 10 grams of tetrahydronaphthalene are supplied to the reaction chamber per cubic meter of gas. The waste due to the formation of gaseous hydrocarbons is considerably reduced.

What we claim is:

1. A process for the production of valuable non-knocking motor fuels which comprises subjecting normally gaseous paraffin hydrocarbons together with added cyclic hydrocarbons selected from the group consisting of benzene and its low boiling homologues and low boiling hydroaromatic hydrocarbons in the vapor phase to a thermal treatment, at a temperature between 400° and 700° C. using a silicate having a splitting action as the sole catalyst.

2. In the process as claimed in claim 1 operating in the presence of hydrogen.

3. In the process as claimed in claim 1 operating at a temperature between 450° and 600° C.

MATHIAS PIER.
GERHARD FREE.