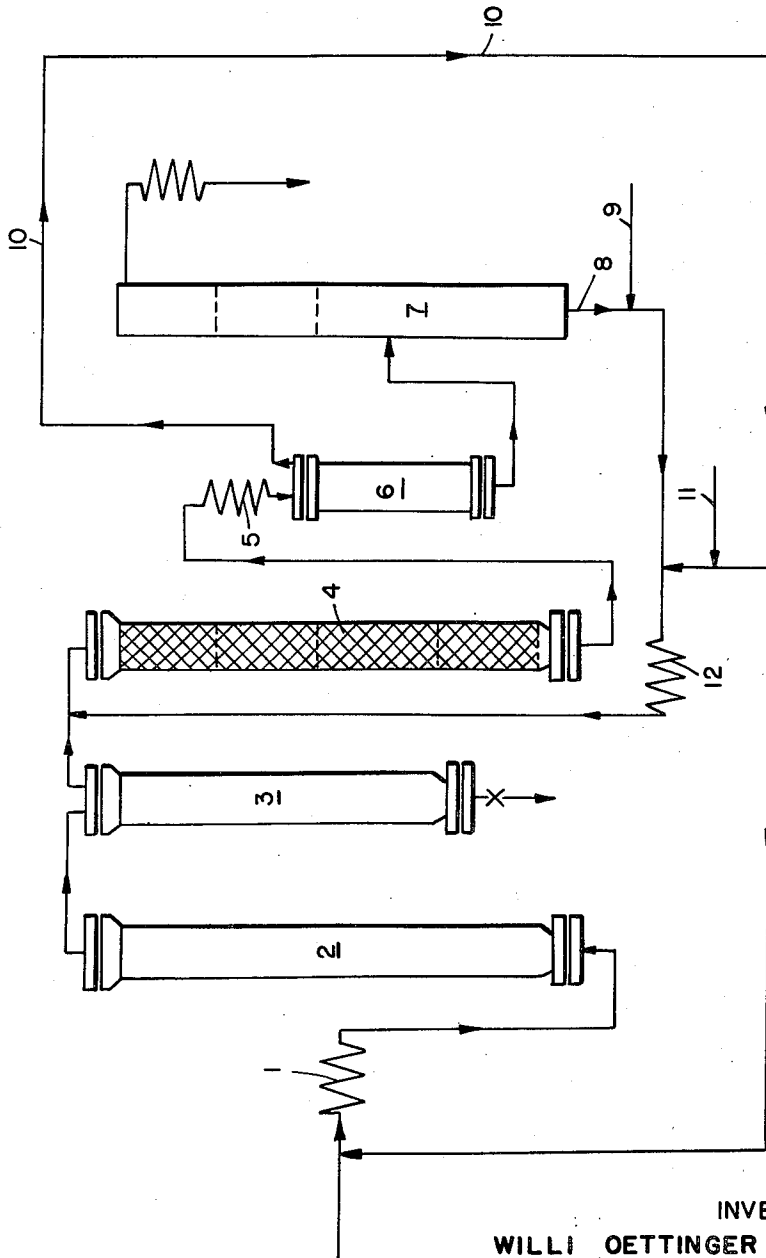


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TWO STAGE DESTRUCTIVE HYDROGENATION PROCESS FOR THE
PRODUCTION OF GASOLINE FROM HYDROCARBON OILS
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TWO STAGE DESTRUCTIVE HYDROGENATION PROCESS FOR THE PRODUCTION OF GASOLINE FROM HYDROCARBON OILS

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16 Claims. (Cl. 196—53)

This invention relates to a new and improved method for the catalytic production of gasoline.

The prior art practice of processing crude oils, in particular their high-boiling components, by the catalytic destructive hydrogenation method consists in first treating the oils in the sump-phase, then distilling the reaction product and recycling the heavy oil components to the sump-phase until the high-boiling oil fraction is substantially converted into middle oil. Among the low-boiling products distilled off, the middle oil is pre-hydrogenated for the removal of the substances which would have a detrimental effect upon the catalyst used in the subsequent hydrogenation stage and then subjected to destructive hydrogenation in the gas phase.

We have now found that the prior art method of processing crude oils aforesaid can be appreciably simplified and the apparatus needed for the sump-phase hydrogenation be markedly reduced in size as part thereof may now be dispensed with, if the initial material be passed through the reaction zone in the conventional manner together with hydrogen under a pressure of at least 200 atmospheres and at a temperature above 450° C. and the resulting products which substantially consist of heavy oil and middle oil be directly converted, without being returned to the sump-phase, into gasoline by destructive hydrogenation under special conditions after previously stripping it of gasoline, if any. Our invention affords the special advantage that the reaction products, arriving from the sump-phase need not be pre-hydrogenated nor be freed from high-boiling components before their conversion into gasoline. The special conditions within the purport of our invention are meant to include: a pressure between 200, preferably 500, and 800 atmospheres, a quantity of hydrogen of from 1 to 5 cubic metres per kilogram of oil per hour and a throughput of oil of 0.3 to 1.5 kilograms per litre of catalyst space an hour, the catalyst used consisting of an acid carrier substance having incorporated therein a small amount of a molybdenum or tungsten compound and, if desired, a chromium, zinc, iron, nickel or cobalt compound.

Attempts that have already been made in an effort to obtain low-boiling products by a one-stage process from high-boiling oils by passing these over the conventional hydrogenation catalysts, have revealed the fact that the activity of the catalyst always drops off relatively rapidly. Longer periods of activity of the catalyst could only be secured at very low oil partial pressures of for example 0.8 to 1.5 atmospheres and very large amounts of hydrogen of about 10 cubic metres or more per kilogram of oil per hour, but this makes the process uneconomical in full scale operation. It is only by maintaining the above-mentioned limits of pressure and throughout, the use of a relatively small amount of hydrogen and the use of quite a definite catalyst that it is possible to process oils containing heavy oils directly into gasoline in continuous operation. Moreover, the yield and quality of the resulting product are better than in the known processes.

The process allows of reducing the size of the high pressure chamber for the sump-phase hydrogenation considerably, for example by half, because no return of the reaction product to the sump-phase takes place, and of dispensing with the distillation between the hydrogenation stages and with the reaction chamber for a preliminary hydrogenation. Moreover, the process may be operated with only one hydrogen cycle.

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As initial materials for the process there may be used crude oils of any origin or shale oils and also the residues of the same which have been freed from gasoline and middle oil, if any.

The initial materials are led through a reaction chamber at temperatures of 450° to 550° C. together with about 1 to 10 cubic metres of hydrogen under a pressure of more than 200 atmospheres, as for example 200 to 800 atmospheres, at a rate of 0.5 to 2.5 kilograms, more particularly 0.6 to 1.2 kilograms, per litre of reaction space per hour. The operation can be carried out in the absence of catalysts or in the presence of small amounts of catalytically active or inert substances, as for example compounds of the metals of the 6th or 8th groups of the periodic system, which may be applied to carriers, such as lignite coke, or large-surfaced inert substances, as for example silica gel, bleaching earth, kieselguhr or coke. The throughput and temperature are adjusted to each other so that more than 30%, and preferably more than 40%, of middle oil is newly formed.

The product obtained by this method of working, if desired after separation of gasoline, is supplied to the second stage. The process may be simplified by adopting the same pressure for the two stages and allowing the product to flow from the first reaction chamber directly into the second reaction chamber, whereby the cost of compression energy is reduced. In the processing of the crude product in the sump-phase with finely divided catalyst and/or when using crude oils containing relatively high percentages of asphalt, containing for example more than 2% of asphalt (measured by the Holde method), the product of the sump-phase hydrogenation is led through a catch pot into the second stage. In the lower part of the catch pot, the solids, such as catalyst, inert material and ash components and/or unconverted high-boiling asphalts, settle and may be withdrawn continuously or in batches. Only negligible amounts, for example 1 to 2% calculated on the initial material, of carbonaceous substances are thereby removed.

The second stage is carried out by leading the whole of the product from the sump-phase hydrogenation together with 1, in particular 2, to 5 cubic metres of hydrogen per kilogram of oil per hour under a pressure of 400 to 800 atmospheres, in particular 500 to 750 atmospheres, at a temperature of 400° to 550° C., in particular 440° to 520° C., and at a rate of 0.5 to 1.5 kilograms per litre of reaction space per hour over a catalyst. The latter consists of an acid substance, in particular a substance containing silicic acid, such as bleaching earth, which has been pretreated with acids, as for example hydrochloric acid, hydrofluoric acid or other mineral or organic acids or contains synthetic silicates preferably those prepared at a pH below 7, as for example aluminum and/or magnesium silicate, and also aluminas which have been pretreated with acids. When employing activated alumina or synthetic silicates as a carrier, pressures lower than 400 atmospheres may be used, as for example those of 200 to 400 atmospheres.

Activated aluminas which have been prepared in the following manner have proved especially suitable:

The aluminum salt solution and the precipitant are poured without preheating into a heated vessel or a heated liquid. It is necessary to keep the temperature above 40° C., advantageously above 50° C., preferably above 80° C. and the pH value between 7 and 10. The precipitate is separated from the liquid, preferably while the latter is still hot, and then washed out. It may readily be washed free from salts in a relatively short time with hot water. The alumina hydrate thus prepared may, after drying, be made without difficulty in a press into shapes which are remarkable for their great hardness. Rigidly-shaped activated alumina is obtained by heating to 300° to 600° C.

In the preparation of the activated alumina below 80° C., the aqueous solutions of the aluminum salts may be precipitated with ammonia.

When starting from an alkali aluminate solution, the hydroxide is preferably precipitated by adding acid until a pH value below 7 is set up. The separated hydroxide is practically freed from alkali by washing. The resulting precipitate, if desired after a preliminary drying, is

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peptised with acid to form a paste or sludge, shaped, dried and activated by cautiously heating it to 450° to 500° C. The oxide may then be washed with ammonia water and again calcined at about 450° C. In certain cases it may be advantageous then to raise the temperature further to 500° to 700° C. It is especially advantageous to use nitric acid both for the peptization and for the precipitation of the aluminate solution.

To the said carriers there are applied small amounts, as for example 2 to 20, advantageously 3 to 15%, of a molybdenum compound, preferably molybdenum oxide or sulfide, or 1 to 30%, more particularly 1 to 17%, of a tungsten compound, as for example tungsten trioxide or sulfide. Good results are obtained when the catalyst contains, in addition to the molybdenum or tungsten compound, a chromium, zinc, iron, nickel or cobalt compound, as for example the oxides or sulfides of the said metals. These latter compounds, however, are advantageously applied in smaller proportion than the molybdenum or tungsten compounds. In the usual case, 5 to 50%, more particularly 15 to 40%, of the said compounds are used with reference to the molybdenum or tungsten compound.

By working in the said manner, about 35 to 60% of gasoline are formed by a single pass through the reaction chamber. The high-boiling components which substantially consist of middle oil, are recycled to the second stage until the initial material is completely converted into gasoline. If, in addition to gasoline, diesel oil is wanted as an end product, a proper amount of middle oil is not returned.

The single figure shown in the drawing illustrates diagrammatically one of the preferred methods of practicing the invention.

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

Example 1

From a German mixed-base crude oil, 25% of gasoline and middle oil are distilled off.

To the distillation residue there is added 1% of lignite coke which is provided with 10% of iron sulfate and it is then led with 2 cubic metres of hydrogen per kilogram of residue per hour and under a pressure of 700 atmospheres over a preheater 1, illustrated in the drawing, through a high pressure chamber 2 at a rate of 1 kilogram per litre of reaction space at 475° C. without any of the product being returned to the chamber. The liquid product consists of 16% of gasoline boiling up to 180° C., 42% of middle oil boiling up to 350° C. and 42% of heavy oil.

This product is led into a separator 3 placed under the same pressure and in which a temperature of about 460° C. prevails. From the lower part of the separator about 1.5 to 2% (with reference to the product introduced) of a fraction consisting substantially of solid substances is withdrawn. From this vessel the whole product then passes directly into an adjacent reaction vessel 4 charged with shaped catalyst. This consists of a commercial bleaching earth which has been treated for about half an hour at room temperature with 10% hydrofluoric acid while stirring and then dried and shaped. This bleaching earth is impregnated with a solution of ammonium molybdate and chromic acid and heated to 400° to 450° C. The ready-for-use catalyst contains 6% of molybdenum oxide and 2.75% of chromium oxide.

Over this catalyst, the first stage product is passed together with the gasoline and middle oil separated in the distillation of the crude oil, and with 3 cubic metres of hydrogen to each kilogram of oil per hour, under the same pressure as in the first stage, at a rate of 1 kilogram per litre of catalyst space per hour and a temperature of 460° C.

Over a cooler 5 the reaction product passes into a cold separator 6. At the top of this the excess circulatory gas is drawn off. From the bottom of the cold separator the product is conducted into a distillation column 7 and is split up into 72% gasoline (boiling point range up to 180° C.) and 28% constituents boiling at from 180° to 320° C. The latter are conducted through the pipe 8 and together with the gasoline and middle oil separated at the distillation of the crude oil and carried by the pipe 9 together with the circulating hydrogen coming from the pipe 10 and fresh hydrogen from the pipe 11 are

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conducted over a preheater 12 back into the reaction tank 4 of the second stage.

By working in this way, 84 parts of gasoline and 10 parts of fuel gas are obtained from the crude oil.

Example 2

From a mixed-base crude oil, 25% of gasoline and middle oil are distilled off. The distillation residue is mixed with 1% of lignite coke which has been provided with 10% of iron sulfate and then led together with 2 cubic metres of hydrogen per kilogram of residue per hour under a pressure of 700 atmospheres at a rate of 1 kilogram per litre of reaction space at 475° C. through a high pressure vessel without returning any of the product to the vessel. After separating the solid substances, a liquid product is obtained consisting of 16% of gasoline (boiling point range up to 180° C.), 42% of middle oil (boiling point range up to 350° C.) and 42% of heavy oil.

From this product the gasoline fraction boiling up to 180° C., is distilled off and the middle oil and heavy oil led over the catalyst defined below together with 3 cubic metres of hydrogen to each kilogram of oil per hour under a pressure of 700 atmospheres at a rate of 1 kilogram per litre of catalyst space and at a temperature of 425° C. By a single pass, a liquid product is obtained which consists of 60% gasoline (boiling point range up to 180° C.) and 40% of components (boiling point range from 180° to 330° C.). The latter are returned to the vessel.

The catalyst consists of a commercial bleaching earth which has been treated at room temperature with 10% hydrofluoric acid for about half an hour while stirring and then dried and shaped. This bleaching earth is impregnated with a solution of ammonium tungstate and cobalt sulfate and treated at 400° C. while passing there-over a mixture of hydrogen sulfide and hydrogen. The ready-for-use catalyst contains 14% of tungsten sulfide and 1.3% of cobalt sulfide.

By working in this way, 63 parts of gasoline and 8 parts of fuel gas are obtained from the crude oil in addition to the 25 parts of gasoline and middle oil separated by distillation.

Example 3

50% of gasoline and middle oil are distilled off from a mixer-base crude oil from Near-Eastern sources. The distillation residue has added to it 1% of lignite coke which has been provided with 10% of iron sulfate and is passed through a high pressure vessel with 1.8 cubic metres of hydrogen per kilogram of residue per hour under a pressure of 700 atmospheres at a rate of a 1 kilogram per litre of reaction space at 475° C., without any of the product being returned to the vessel. The liquid product which leaves at the top of a separator under the same pressure at a temperature of about 460° C. consists of 20% of gasoline (boiling point range up to 180° C.), 40% of middle oil (boiling point range up to 350° C.) and 40% of heavy oil. From the lower part of the separator 1 to 2% (calculated on the initial material) of mainly solid constituents are withdrawn.

The liquid product, together with the gasoline and middle oil separated by distillation of the crude oil, is passed over the catalyst defined below, together with 3 cubic metres of hydrogen to each kilogram of oil per hour under a pressure of 300 atmospheres at a rate of 0.8 kilogram per litre of reaction space per hour and at a temperature of 478° C. By a single pass, a liquid product is obtained which consists of 48% of gasoline (boiling point range up to 180° C.) and 52% of components (boiling point range from 180° to 350° C.). The latter are returned to the vessel.

The catalyst is prepared in the following way:

To a sodium aluminate solution containing 100 grams of Al₂O₃ per litre, dilute nitric acid is added while vigorously stirring, up to a temperature of 50° C. to the extent of imparting the mixture a pH of 5.5. The precipitate is filtered off, made into a suspension with distilled water and washed until free from alkali. The cake is dried at 200° C., ground and peptized with about 2% nitric acid to form a paste. The paste is spread on plates, preliminarily dried, cut into cubes, slowly dried and calcined at 400° to 500° C. The cubes are washed with 5% ammonia and heated at 450° C. for 6 hours. They are then impregnated with

an ammoniacal solution of MoO_3 so that about 16% of MoO_3 are absorbed. After their impregnation they are dried at 140°C . and heated for 6 to 8 hours at 400°C .

By working in this way, 85 parts of gasoline and 8 parts of fuel gas are obtained.

What we claim is:

1. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450°C . to 550°C . together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% of middle oil boiling in the range of 180°C . to 350°C . is formed; and leading the resulting product containing gasoline, heavy oil and middle oil, without returning it to the said reaction zone, into a second reaction zone together with hydrogen in an amount of from about 1 to 5 cubic metres per kilogram of oil per hour under a pressure of 200–800 atmospheres, at a temperature of 400°C . to 550°C . and at a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten, the reaction in said second zone being carried out in the gaseous state.

2. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450°C . to 550°C . together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% of the middle oil boiling in the range of 180°C . to 350°C . is formed; then leading the resulting product containing gasoline, heavy oil and middle oil, without returning it to the said reaction zone, into a catch pot and withdrawing the settled materials in the lower part of the catch pot; passing the entire remainder of the product together with the hydrogen and without essential alteration of the amount of hydrogen directly into a second reaction zone under a pressure of 200–800 atmospheres, at a temperature of 400°C . to 550°C . and at a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over a shaped catalyst of an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten, the reaction in said second zone being carried out in the gaseous state; and returning at least the high-boiling fraction of the product thus obtained to the second zone.

3. A process as claimed in claim 1, wherein the carrier substance is an activated alumina which has been prepared by precipitating alumina hydrate from an aluminum salt solution having a pH value of between 7 and 10 at a temperature above 40°C . and heating the precipitate formed.

4. A process as claimed in claim 1, wherein the carrier substance is an activated alumina which has been prepared by precipitating alumina hydrate from an aluminum salt solution having a pH value of between 7 and 10 at a temperature above 80°C . and heating the precipitate formed.

5. A process as claimed in claim 1, wherein the carrier substance is an activated alumina which has been prepared by precipitation from a solution of an aluminum compound subjected to a peptizing treatment and dried.

6. A process as claimed in claim 1, wherein the carrier substance is an activated alumina which has been prepared from an alkali aluminate solution by precipitation with acid to set up a pH inferior to 7, washing

out of the alkali, peptizing the precipitate and heating to about 450° to 500°C .

7. A process as claimed in claim 1, wherein the reaction in the first reaction zone is carried out in the presence of a small amount of a compound of a metal of the 6th and 8th groups of the periodic system.

8. A process as claimed in claim 1, wherein the reaction in the first reaction zone is carried out in the presence of a small amount of a large-surfaced inert substance provided with a compound of a metal of the 6th and 8th groups of the periodic system.

9. A process as claimed in claim 1, wherein gasoline and middle oil are separated from the initial crude oil and supplied directly to the second reaction zone.

10. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450°C . to 550°C . together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% of middle oil boiling in the range of 180°C . to 350°C . is formed; then leading the resulting product containing gasoline, heavy oil and middle oil, without returning it to the said reaction zone, into a catch pot and withdrawing the settled materials in the lower part of the catch pot; passing the entire remainder of the product directly into a second reaction zone together with hydrogen in an amount of from about 1 to 5 cubic metres per kilogram of oil per hour, under nearly the same pressure as that in the first zone, at a temperature of 400°C . to 550°C . and at a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over a shaped catalyst of an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten, the reaction in said second zone being carried out in the gaseous state; and returning at least the high-boiling fraction of the product thus obtained to the second zone.

11. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450°C . to 550°C . together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% of middle oil boiling in the range of 180°C . to 350°C . is formed; leading the resulting product gasoline containing heavy oil and middle oil, without returning it to the said reaction zone, together with the hydrogen and without essential alteration of the amount of hydrogen into a second reaction zone under nearly the same pressure as that in the first zone, at a temperature of 400°C . to 550°C . and a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten, the reaction in said second zone being carried out in the gaseous state; and returning at least the high-boiling fraction of the product thus obtained to the second zone.

12. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450°C . to 550°C . together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% of middle oil boiling in the range of 180°C . to 350°C . is formed; then leading the resulting product containing gasoline, heavy oil and middle oil, without returning it to the said reaction zone,

into a catch pot and withdrawing the settled materials in the lower part of the catch pot; passing the entire remainder of the product directly into a second reaction zone together with hydrogen in an amount of from about 1 to 5 cubic metres per kilogram of oil per hour under a pressure of 200-800 atmospheres, without essential alteration of the temperature and at a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over a shaped catalyst of an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten, the reaction in said second zone being carried out in the gaseous state; and returning at least the high-boiling fraction of the product thus obtained to the second zone.

13. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450° C. to 550° C. together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% of middle oil boiling in the range of 180° C. to 350° C. is formed; and leading the resulting product containing gasoline, heavy oil and middle oil, without returning it to the said reaction zone, into a second reaction zone together with hydrogen in an amount of from about 1 to 5 cubic metres per kilogram of oil per hour under nearly the same pressure as that in the first zone, without essential alteration of the temperature and at a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten, the reaction in said second zone being carried out in the gaseous state.
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14. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450° C. to 550° C. together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% of middle oil boiling in the range of 180° C. to 350° C. is formed; then leading the resulting product containing gasoline, heavy oil and middle oil, without returning it to the said reaction zone, into a catch pot and withdrawing the settled materials in the lower part of the catch pot; passing the entire remainder of the product together with the hydrogen and without essential alteration of the amount of hydrogen directly into a second reaction zone under nearly the same pressure as that in the first zone, without essential alteration of the temperature and at a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over a shaped catalyst of an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten, the reaction in said second zone being car-

ried out in the gaseous state; and returning at least the high-boiling fraction of the product thus obtained to the second zone.

15. A process for the production of gasoline from mineral oils and shale oils by destructive hydrogenation in two stages which comprises leading the initial materials in the liquid phase through a reaction zone at a temperature of 450° C. to 550° C. together with 1 to 10 cubic metres of hydrogen per kilogram of materials per hour, under a pressure of 200 to 800 atmospheres and at a rate of 0.5 to 2.5 kilograms per litre of reaction space per hour, adjusting the throughput and temperature so that more than 30% middle oil boiling in the range of 180° C. to 350° C. is formed; leading the resulting product containing heavy oil, middle oil and gasoline, without returning it to the said reaction zone, into a catch pot and withdrawing the settled materials in the lower part of the catch pot; passing the remainder of the product into a second reaction zone together with hydrogen in an amount of from about 1 to 5 cubic metres per kilogram of oil per hour under a pressure of 200-800 atmospheres, at a temperature of 400° C. to 550° C. and at a rate of 0.3 to 1.5 kilograms per litre of catalyst volume per hour over an activated acid carrier substance from the group consisting of acid-treated natural substances containing silicic acid, acid synthetic silicates, and activated acid aluminas which is provided with a small amount of a compound of a metal of the group consisting of molybdenum and tungsten; and carrying out the reaction in said second zone in the gaseous state.

16. A process for the production of gasoline by destructive hydrogenation of mineral oil in two stages which comprises adding about 1% of lignite coke which is provided with about 10% of an iron compound to a mineral oil from which the gasoline and middle oil have been removed, leading the resulting mixture in the liquid phase through a reaction zone at a temperature of 450° C. to 550° C. together with approximately 2 cubic metres of hydrogen per kilogram of said mineral oil per hour, under a pressure of 200 to 800 atmospheres and at a rate of approximately 1 kilogram per litre of reaction space per hour, adjusting the throughput and temperature so that more than about 40% of middle oil boiling in the range of 180° C. to 350° C. is formed; then leading the resulting product containing heavy oil, middle oil and gasoline, without returning it to the said reaction zone, into a catch pot and withdrawing the settled materials in the lower part of the catch pot; passing the entire remainder of the product directly into a second reaction zone together with hydrogen in an amount of approximately 3 cubic metres per kilogram of oil per hour under approximately the same pressure and at approximately the same temperature as those in the first zone and at a rate of approximately 1 kilogram per litre of catalyst volume per hour over a shaped catalyst of hydrofluoric acid treated bleaching earth provided with a small amount of molybdenum oxide, the reaction in said second zone being carried out in the gaseous state; and returning the components of the product thus obtained boiling above gasoline to the second zone.

References Cited in the file of this patent

UNITED STATES PATENTS

1,984,596	Pier et al. -----	Dec. 18, 1934
2,326,800	Pier et al. -----	Aug. 17, 1943
2,541,317	Wilson -----	Feb. 13, 1951

FOREIGN PATENTS

320,473	Great Britain -----	Oct. 17, 1929
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