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HYDROCARBON CONVERSION

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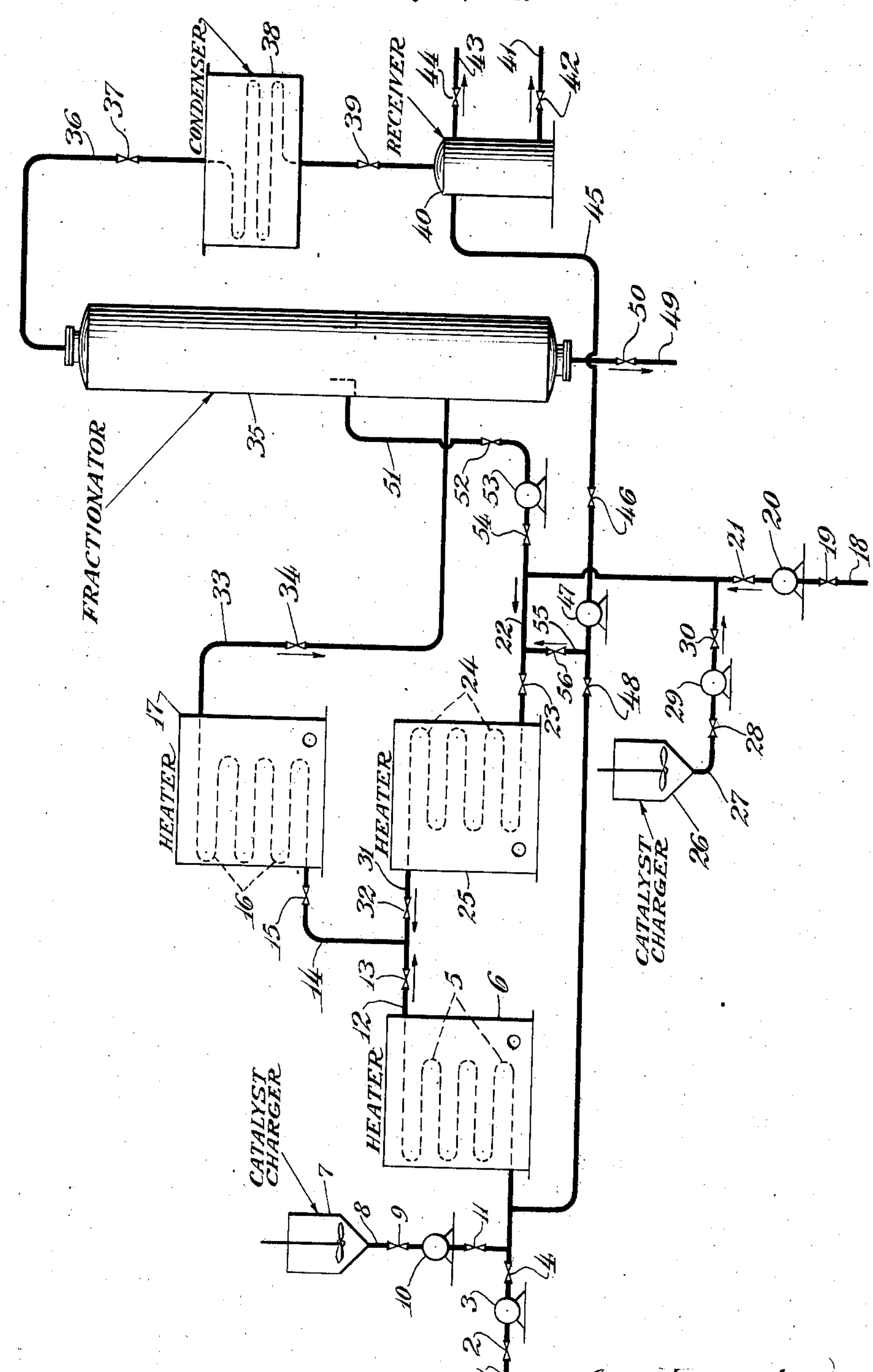

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HYDROCARBON CONVERSION

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4 Claims. (Cl. 196—52)

This invention relates to a process for converting hydrocarbon oil into substantial yields of high antiknock gasoline and further improving the antiknock value of hydrocarbon fractions boiling substantially within the gasoline range.

More specifically it relates to a process for producing high antiknock gasoline by contacting hydrocarbon distillates with powdered cracking catalysts under conditions adequate to produce high yields of desirable motor fuel. The fractions contemplated for conversion include naphtha, kerosene, gas oil, wax distillate and the like, preferably of petroleum origin, although similar suitable stocks from other hydrocarbon sources may likewise be employed.

In one specific embodiment the present invention comprises contacting naphtha with a powdered catalytic agent under cracking conditions of temperature and pressure, separately contacting a higher boiling hydrocarbon fraction containing substantially no gasoline with a powdered catalytic agent in a second step, combining the reaction products under conversion conditions of temperature and pressure, fractionating the reaction products, recovering gas and gasoline and recycling a portion of the insufficiently converted oil boiling above the gasoline range. A part of the process gases may also be recycled.

The invention is further understood by reference to the accompanying drawing which is diagrammatic and should not be construed as limiting it to the exact conditions of apparatus shown therein.

Naphtha charging stock which may be cracked or straight run is introduced through line 1, valve 2, pump 3 and valve 4 to coil 5 which is disposed in heater 6. A reforming catalyst is introduced from catalyst charger 7 through line 8, valve 9, pump 10 and valve 11, joining with the naphtha in line 1 and thus being passed to the reforming zone. The mixture is heated to a temperature within the range of approximately 800–1200° F. and a pressure of approximately atmospheric to 300 pounds per square inch or higher. The heated products pass through line 12 and valve 13 to line 14 and valve 15 and thence to coil 16 which is disposed in heater 17. In place of coil 16, a heated or unheated reaction chamber may be used. Although shown as a coil, this may comprise any type of reaction zone, such as a reaction chamber. A gas oil charging stock is introduced through line 18, valve 19, pump 20, valve 21, line 22 and valve 23 to coil 24 which is disposed in heater 25. A powdered cracking catalyst is introduced from catalyst charger 26 through line 27 containing valve 28, pump 29 and valve 30. The mixture is heated to a temperature of approximately 500–1200° F. and usually within the range of approximately 850–1050° F. and then passes through line 31 and valve 32 to line 14 wherein it combines with the mixture from coil 5. Such additional heat as may be required to carry out further conversion may be supplied in heater 17. The temperature maintained in this region is normally within the range of approximately 600–1200° F. The reaction products pass through line 33 containing valve 34 to fractionator 35. Gasoline and gas are recovered through line 36 containing valve 37, condenser 38 and valve 39 entering receiver 40. The gasoline is removed through suitable stabilizers, not shown, through line 41 and valve 42. A portion of the process gases may be removed through line 43 and valve 44. Another portion of the process gases may be recycled through line 45 containing valve 46, pump 47 and valve 48, joining with line 1 and thus being passed through coil 5 for further conversion. Alternatively the recycled process gases may bypass heaters 5 and 24 and pass directly to heater 16. Higher boiling fractionator bottoms may be removed from fractionator 35 through line 49 and valve 50. A part of the insufficiently converted oil boiling above the gasoline range may be passed through line 51, valve 52, pump 53 and valve 54 to line 22 and thence to coil 24. A portion of the receiver gases may be supplied to coil 24. A portion of the receiver gases may be supplied to coil 24 through line 55 containing valve 56 and joining with line 22. The spent catalyst is removed from the process with the fractionator bottoms through line 49 and may be recovered therefrom by suitable means and may be regenerated for further use, or in certain instances may be discarded.

The catalytic agents employed in the present process may vary considerably and it is not essential that the same catalyst be used in the various steps. The amount of catalyst used is approximately 0.1–10% and preferably 0.5–5% by weight of oil. The catalytic agent used in the first step for reforming the naphtha may comprise alumina, bauxite, magnesite, etc., or may comprise one or more of these materials, having deposited thereon promoting oxides of chromium, molybdenum, tungsten, vanadium, titanium, zinc oxide and the like. These agents are used as a fine powder, preferably of particle size approaching colloidal dimensions.

The catalytic agent employed in the second step for cracking the higher boiling oil may comprise the so-called silica-alumina, silica-zirconia and silica-alumina-zirconia catalysts which may have added thereto minor portions of promoting compounds and particularly the oxides of elements such as chromium, molybdenum, vanadium, thorium, titanium and the like, and which are preferably prepared by the separate or simultaneous precipitation of the components under conditions such that finely divided powder results. This may then be followed by suitable washing and drying steps so that alkali metal ions are substantially eliminated. It is within the scope of the invention to use naturally-occurring earths or clays which may or may not have been further activated by chemical treatment, for example, with strong mineral acids.

As an alternative, a suitable catalyst for the primary reforming step comprises a mixture of the catalysts just mentioned with those described above in connection with the primary reforming step. Thus, for example, when bauxite or alumina is used in the primary step and silica-alumina is used in the secondary step, the two catalysts are mixed and recovered as a mixture. This mixed catalyst may be reactivated by treatment with an oxygen-containing gas whereby the carbonaceous and hydrocarbonaceous deposits are removed, and a portion of the regenerated material may be returned to the primary reforming step, being mixed with the fresh reforming catalyst.

Since comparatively small quantities of catalytic agents are employed and since these catalysts may be relatively inexpensive, it is not necessary to completely recover them and in some instances they may be discarded without further use.

It should be borne in mind that the various catalytic materials described are not necessarily exactly equivalent in their action.

The following example is given to illustrate the practicability and utility of the process, but should not be construed as limiting it to the exact conditions or catalytic materials used therein.

A Pennsylvania naphtha having an octane number of approximately 30 may be mixed with a powdered catalyst consisting essentially of a major portion of alumina having deposited thereon a relatively minor portion of chromia and reformed at a temperature of approximately 1075° F. A gas oil charging stock may be mixed with a silica-alumina composite and converted at a temperature of approximately 1000° F. The reaction products are mixed and may be treated at a temperature of approximately 1050° F. and finally fractionated to recover gasoline and gas. A portion of the insufficiently converted oil boiling above the gasoline range may be returned to the gas oil cracking step. A portion of the process gases may be returned to the naphtha reforming step. A yield of approximately 80% of 79 octane number gasoline, together with small quantities of gas and higher boiling oil suitable for use as a fuel oil, may be recovered in this manner.

I claim as my invention:

1. A process for the production of high antiknock gasoline, which comprises catalytically reforming a relatively light oil in the presence of a powdered dehydrogenating catalyst, simultaneously therewith catalytically cracking a heavier hydrocarbon oil in the presence of a powdered cracking catalyst which is different from the dehydrogenating catalyst, combining products of reaction from both conversion steps, subjecting the mixture to continued conversion in the presence of the mixed dehydrogenating and cracking catalysts, and thereafter separating gasoline from lower and higher boiling conversion products.

2. A process for the production of high antiknock gasoline, which comprises catalytically reforming a relatively light oil in the presence of a powdered dehydrogenating catalyst, simultaneously therewith catalytically cracking a heavier hydrocarbon oil in the presence of a powdered cracking catalyst comprising a siliceous material which is different from the dehydrogenating catalyst, combining products of reaction from both conversion steps, subjecting the mixture to continued conversion in the presence of the mixed dehydrogenating and cracking catalysts, fractionating resultant conversion products to separate fractionated vapors in the gasoline boiling range from higher boiling conversion products and returning at least a portion of said higher boiling conversion products to the second mentioned conversion step.

3. A process for the production of high antiknock gasoline, which comprises catalytically reforming a relatively light oil in the presence of a powdered dehydrogenating catalyst, simultaneously therewith catalytically cracking a heavier hydrocarbon oil in the presence of a powdered cracking catalyst comprising a siliceous material which is different from the dehydrogenating catalyst, combining products of reaction from both conversion steps, subjecting the mixture to continued conversion in the presence of the mixed dehydrogenating and cracking catalysts, separating vaporous conversion products from nonvaporous liquid residue containing the mixed catalysts, fractionating said vaporous conversion products to separate fractionated vapors in the gasoline boiling range from higher boiling conversion products and returning said higher boiling conversion products to the second mentioned conversion step.

4. A process for the production of high antiknock gasoline, which comprises catalytically reforming a relatively light oil in the presence of a powdered dehydrogenating catalyst, simultaneously therewith catalytically cracking a heavier hydrocarbon oil in the presence of a powdered cracking catalyst comprising a siliceous material which is different from the dehydrogenating catalyst, combining products of reaction from both conversion steps, subjecting the mixture to continued conversion in the presence of the mixed dehydrogenating and cracking catalysts, separating vaporous conversion products from nonvaporous liquid residue containing the mixed catalysts, fractionating said vaporous conversion products to separate fractionated vapors in the gasoline boiling range from higher boiling conversion products, returning said higher boiling conversion products to the second mentioned conversion step, cooling and condensing said fractionated vapors, collecting resultant distillate and gas and returning at least a portion of said gas to the first and second mentioned conversion steps.

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