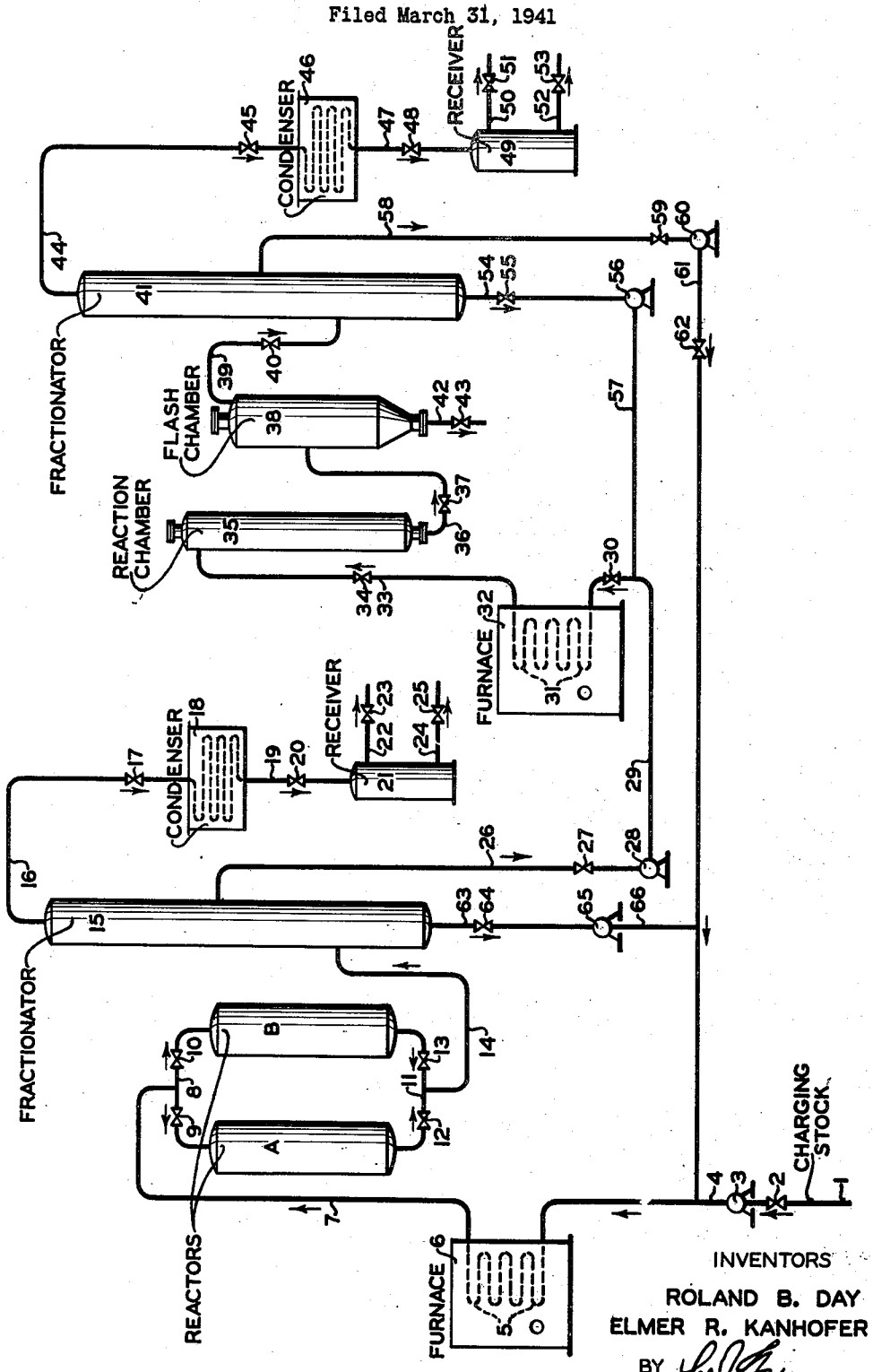
Jan. 25, 1944. R. B. DAY ET AL 2,339,917

HYDROCARBON CONVERSION PROCESS

Filed March 31, 1941




INVENTORS

ROLAND B. DAY

ELMER R. KANHOFER

BY Lee Gary

ATTORNEY

Patented Jan. 25, 1944 2,339,917

# UNITED STATES PATENT OFFICE

2,339,917

## HYDROCARBON CONVERSION PROCESS

Roland B. Day and Elmer R. Kanhofer, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application March 31, 1941, Serial No. 386,114

5 Claims. (Cl. 196—52)

This invention relates to a process for the conversion of relatively high boiling hydrocarbon oil into lighter and more valuable hydrocarbons and more particularly, it is concerned with a process wherein said relatively high boiling hydrocarbon oil is cracked by a combination of thermal and catalytic steps to produce a high antiknock gasoline.

It has been shown that catalytic cracking by means of siliceous catalysts produces a relatively low boiling fraction which in the case of some charging stocks is highly refractory to further catalytic cracking. In the process of my invention this fraction which comprises the hydrocarbons boiling immediately above the gasoline range is subjected to a thermal cracking step wherein the problem of regeneration of catalyst does not arise. This fraction may be cracked thermally to produce a relatively high octane gasoline and residual material formed in this step is removed as a liquid from the flash chamber instead of forming a carbonaceous deposit on a catalyst from which it would have to be removed by oxidation. The heavy intermediate conversion products obtained by fractionating the mixture from a catalytic cracking step are somewhat less refractory than the light intermediate conversion products and in the process of our invention are returned to the catalytic cracking step for further reacting. The light intermediate conversion products separated from the reaction products of the thermal cracking step are supplied to the catalytic cracking step while the heavy intermediate conversion products separated from the reaction products from the thermal cracking step are returned to the thermal cracking step for further conversion.

In one specific embodiment our invention comprises a process for the production of gasoline by a combination of thermal and catalytic cracking steps wherein a relatively high boiling hydrocarbon oil and recycle streams formed as hereinafter set forth are cracked in the presence of a siliceous cracking catalyst with the formation of substantial quantities of gasoline, the products from said catalytic cracking step fractionated to separate said gasoline, light intermediate conversion products and heavy intermediate conversion products, said heavy intermediate conversion products commingled with the light intermediate conversion products separated from the products of the thermal cracking step and the raw oil charge to form the aforesaid combined feed for the catalytic cracking step and the light intermediate conversion products from the catalytic cracking step and the heavy intermediate conversion products from the thermal cracking step commingled to form the combined feed for the thermal cracking step.

The accompanying diagrammatic drawing illustrates in conventional side elevation one specific form of apparatus which may be used to accomplish the objects of the invention.

Referring to the drawing, a relatively high boiling hydrocarbon oil such as a gas oil, is supplied through line 1, valve 2 to pump 3 which discharges into line 4 wherein said charging stock is commingled with a recycle stream formed by commingling the heavy intermediate conversion products formed in the catalytic cracking step of the system and the light intermediate conversion products formed in the thermal cracking step of the system. This combined feed is directed from line 4 to heating coil 5 so disposed as to receive heat from furnace 6. The oil in passing through heating coil 5 is heated to a temperature within the approximate limits of 900–1100° F. and at a pressure of the order of 50–500 pounds per square inch. This heated oil is directed from coil 5 to line 7 from which it is supplied to one of a plurality of reaction chambers having disposed therein a cracking catalyst of the type of silica-alumina, composites of silica and alumina with other components such as hydrated zirconia or hydrated thoria or blends of hydrated silica with hydrated zirconia or hydrated thoria. Although the process is not limited to any number of reactors, for the sake of simplicity, two are shown in the drawing, one of which in the process being described is used for the conversion of hydrocarbons while the catalyst in the other is being subjected to a regeneration process. This regeneration may be accomplished by oxidizing the carbonaceous deposits by an oxygen-containing gas such as a mixture of air and combustoin gases at temperatures of the order of 850–1200° F. The heated oil in line 7 is then directed to line 8 from which it passes through either valve 9 or valve 10, being supplied to reactor A or B as the case may be. Reactors A and B may be of the adiabatic type, that is the heat adsorbed in the conversion process being obtained from the reactants themselves, or if desired, heat exchange types of reactors may be used. Adiabatic reactors have the advantage of simplicity of construction, although in some cases where it is desired to maintain isothermal conditions throughout the cracking zone, heat may be supplied by means of combustion

gases, molten salts, or the like. In the adiabatic reactors, the catalyst may be disposed in relatively wide beds while in the heat exchange type it is usually disposed in a plurality of tubes, or if desired, in beds with closed heat distributing members for supplying the heat needed for the reactions. The temperature at the outlet of the reaction chamber is within the range of 800–1100° F. with a pressure varying from substantially atmospheric to 100 or more pounds per square inch. It is also within the scope of this invention, if desired, to use certain diluents such as steam in the catalytic cracking zone. The conversion products leaving either reactor A or B as the case may be, are directed into line 11 and after passing through either valve 12 or valve 13 are supplied to line 14 discharging into fractionating column 15. The conversion products are preferably cooled before being supplied to the fractionating column which may be done by quenching them with reflux condensate obtained from the fractionating column. Methods for accomplishing this quenching are well known in the art.

Fractionating column 15 separates as an overhead product gasoline boiling range hydrocarbons and normally gaseous products, this mixture being removed by way of line 16 controlled by valve 17 from which it is supplied to cooler and condenser 18. The mixture of liquid, together with undissolved and uncondensed gases, is removed from condenser 18 by way of line 19 and after passing through valve 20 is directed to receiver and separator 21. The gases collected in receiver 21 are removed by way of line 22 and after passing through valve 23 are removed from the system. The olefinic constituents of said gases may be polymerized, if desired, to form gasoline boiling range hydrocarbons, or if desired, the iso-paraffinic constituents of said gases may be alkylated with the olefins to form a saturated motor fuel. The liquid collected in receiver 21 is removed by way of line 24 and after passing through valve 25 is removed from the system. It may be stabilized by well known methods to form a motor fuel of the desired volatility. A light reflux condensate relatively high in aromatic hydrocarbons and boiling immediately above the range of gasoline is removed from fractionating column 15 as a side cut by way of line 26 and after passing through valve 27 is supplied to pump 28, which discharges into line 29. This light reflux condensate is commingled in line 29 with a heavy reflux condensate obtained from the thermal cracking step of the system and the mixture directed through valve 30 to heating coil 31 which receives heat from furnace 32. The products from heating coil 32 are directed into line 33 at a temperature within the approximate limits of 900–1000° F. and at a pressure which may vary from 50 to about 400 pounds per square inch and after passing through valve 34 are supplied to reaction chamber 35. The function of this insulated reaction chamber is the continuance of the cracking reactions begun in heating coil 31. The reaction products from chamber 35 are supplied to line 36 and after passing through valve 37 are directed to flash chamber 38 which operates at a pressure lower than that of the reaction chamber and which may be of the order of 25–200 pounds per square inch. Owing to the reduction of pressure in flash chamber 38, additional vaporization of the hydrocarbons takes place, the mixture of the vapors formed in the cracking step and those due to the flashing operation being removed from the flash chamber by way of line 39 and directed through valve 40 to fractionating column 41. The non-vaporous liquid residue separated from the vapors in the flash chamber is removed from the system by way of line 42 controlled by valve 43. Before being supplied to fractionating column 41, the vapors from the flash chamber are cooled, which may be accomplished by indirect heat exchange but more usually by quenching with a liquid cooling medium, such as a side cut obtained from the fractionator itself. Gasoline boiling range hydrocarbons and normally gaseous products are separated as an overhead from column 41 by way of line 44 and after passing through valve 45 are supplied to cooler and condenser 46 wherein the normally liquid products are condensed. The mixture of liquid, together with undissolved and uncondensed gases, is directed from condenser 46 through line 47, valve 48 to receiver and separator 49. The gases separated in receiver 49 are removed from the system by way of line 50, valve 51. The olefinic constituents of said gases may be polymerized to form a motor fuel or, if desired, these gases may be scrubbed by hydrocarbon oil to separate any normally liquid hydrocarbons present therein as a vapor. The liquid collected in receiver 49 is removed by way of line 52 controlled by valve 53 and constitutes a product of the process, and may be stabilized to form a motor fuel of the desired volatility.

The heavier intermediate conversion products separated from fractionator 41 are removed by way of line 54 and after passing through valve 55 are supplied to pump 56 which discharges through line 57 into line 29 wherein they are commingled with the light intermediate conversion products obtained from the catalytic cracking step, the resulting mixture forming the combined feed for the thermal cracking step. The light intermediate conversion products are separated from fractionating column 41 from which they are removed as a side cut by way of line 58 and are directed through valve 59 into pump 60 which discharges through line 61, valve 62. After passing through valve 62, these light intermediate conversion products from the thermal cracking step are commingled with the heavier intermediate conversion products obtained by fractionating the vapors from the catalytic cracking step. These heavier intermediate conversion products are removed from fractionating column 15 by way of line 63 and after passing through valve 64 are supplied to pump 65 which discharges through line 66 into line 61. This mixture is then directed from line 61 to line 4 wherein it is commingled with the charging stock for the process to form the combined feed for the catalytic cracking step for treatment as hereinbefore set forth.

An example of one specific operation of the process as it may be accomplished in an apparatus such as illustrated and above described is approximately as follows: Charging oil comprising a 35.1 A. P. I. gravity East Texas gas oil is commingled with light intermediate conversion products and heavy intermediate conversion products obtained from thermal cracking and catalytic cracking steps, respectively. This mixture is vaporized and heated to a temperature of about 960° F. and the heated vapors pass in contact with a mass of synthetically prepared silica-alumina catalyst at a pressure of 30 pounds per square inch. The catalytic conversion products

are fractionated to separate vapors of 400° F. end point from the higher boiling and insufficiently converted hydrocarbons. The gasoline is separated from the normally gaseous products and collected as a product of the process.

The insufficiently converted hydrocarbons from this catalytic cracking step are fractionated into light insufficiently converted hydrocarbons and heavy insufficiently converted hydrocarbons. The light insufficiently converted hydrocarbons from the catalytic cracking step are commingled with the heavy insufficiently converted products from the thermal cracking step of the process, the mixture subjected to thermal cracking with a temperature of 920° F. and a pressure of 300 pounds per square inch at the outlet of the heating coil, employing a reaction chamber and utilizing such a time of reaction that approximately 20% of the charge to the thermal cracking step is cracked per pass. The products are then subjected to a flashing operation to separate nonvolatile liquid residue from the vaporous reaction products. The products from the thermal cracking step are then fractionated to separate gasoline, normally gaseous products, light intermediate conversion products and heavy intermediate conversion products. The light intermediate conversion products from the thermal cracking step are then blended with the heavy intermediate conversion products from the catalytic cracking step and with the gas oil charging stock to form the combined feed for the catalytic cracking, while the heavy intermediate conversion products from the thermal cracking step are commingled with the light intermediate conversion products from the catalytic cracking step to form the combined feed for thermal cracking as hereinbefore set forth.

From an operation employing conditions as above mentioned one may obtain approximately 44.1% of 400° end point catalytically cracked gasoline having an octane number of 80, approximately 23.2% of 400° end point thermally cracked gasoline of 70 octane rating and 19.5% of liquid residue of 8.5° A. P. I. gravity, the balance being principally carbon and gaseous products.

We claim as our invention:

1. A process for the production of gasoline which comprises subjecting a combined feed formed as hereinafter set forth to catalytic cracking in the presence of a siliceous cracking catalyst, fractionating from the products of said catalytic cracking step gasoline, light intermediate conversion products and heavy intermediate conversion products, commingling said heavy intermediate conversion products with light intermediate conversion products formed in a thermal cracking step of the process and with a relatively high boiling raw oil charging stock to form the combined feed for the catalytic cracking step, commingling the light intermediate conversion products from the catalytic cracking step with heavy intermediate products from the thermal cracking step, subjecting this mixture to thermal cracking and fractionating from the products of said thermal cracking step gasoline, light intermediate conversion products and heavy intermediate conversion products and commingling said fractions of intermediate conversion products for further treatment as hereinbefore set forth.

2. A process for the production of gasoline which comprises subjecting a combined feed formed as hereinafter set forth to catalytic cracking in the presence of a siliceous cracking catalyst, fractionating the products of said catalytic cracking step to separate normally gaseous products, gasoline, light intermediate conversion products and heavy intermediate conversion products, commingling said heavy intermediate conversion products with light intermediate conversion products formed in a thermal cracking step as hereinafter set forth and with raw oil charging stock to form the combined feed for the catalytic cracking step, commingling the aforesaid light intermediate conversion products from the catalytic cracking step with heavy intermediate products formed in the thermal cracking step, subjecting this mixture to thermal cracking to form substantial quantities of gasoline, subjecting the products from the thermal cracking step to a vaporizing and separating step to separate a non-volatile liquid residue from the vapors, fractionating said vapors to separate normally gaseous products, gasoline, light intermediate conversion products, heavy intermediate conversion products and commingling said fractions of intermediate conversion products for further treatment as hereinbefore set forth.

3. A process for the production of gasoline which comprises subjecting a combined feed formed as hereinafter set forth to the action of a catalyst comprising a synthetically prepared composite of silica and alumina under conditions adequate to the formation of substantial quantities of gasoline, fractionating the products to separate normally gaseous products, gasoline, light intermediate conversion products and heavy intermediate conversion products, commingling said heavy intermediate conversion products with light intermediate conversion products formed in a thermal cracking step as hereinafter set forth and with raw oil charging stock to form the combined feed for the catalytic cracking step, commingling the light intermediate conversion products from the catalytic cracking step with heavy intermediate products formed in the thermal cracking step, subjecting this mixture to thermal cracking to form substantial quantities of gasoline, subjecting the products from the thermal cracking step to a vaporizing and separating step to separate a non-volatile liquid residue from the vapors, fractionating said vapors to separate normally gaseous products, gasoline, light intermediate conversion products, and heavy intermediate conversion products and commingling said fractions of intermediate conversion products for further treatment as hereinbefore set forth.

4. A process for the production of gasoline which comprises maintaining a catalytic cracking step and a thermal cracking step, subjecting hydrocarbon oil conversion products from the thermal cracking step to a vaporizing and separating step to separate a non-volatile liquid residue from the vapors, fractionating the vapors to separate gasoline and normally gaseous products, light intermediate conversion products and heavy intermediate conversion products, fractionating the products from the catalytic cracking step to separate gasoline, light intermediate conversion products and heavy intermediate conversion products, commingling the light intermediate conversion products from the catalytic cracking step with the heavy intermediate conversion products from the thermal cracking step to form a combined feed for the thermal cracking step and commingling the light intermediate conversion products from the thermal cracking step with the heavy intermediate conversion products from the catalytic cracking step and with a raw oil

charging stock comprising fractions boiling above the range of gasoline and subjecting this mixture to cracking in the presence of a silicous cracking catalyst in the aforesaid catalytic cracking step.

5. A process for the conversion of hydrocarbon oil which comprises subjecting a charging stock comprising a straight-run distillate fraction to catalytic cracking, fractionating the resulting conversion products to separate fractionated vapors, light reflux condensate and a heavier reflux condensate, removing said fractionated vapors, supplying the heavier reflux condensate to the catalytic cracking step, subjecting said light reflux condensate to thermal cracking, fractionating the resulting vaporous thermal conversion products independently of the first mentioned conversion products to form light reflux condensate and a heavier reflux condensate, returning the last-mentioned heavier reflux condensate to the thermal cracking step and supplying the last-mentioned light reflux condensate to the catalytic cracking step.

ROLAND B. DAY.
ELMER R. KANHOFER.