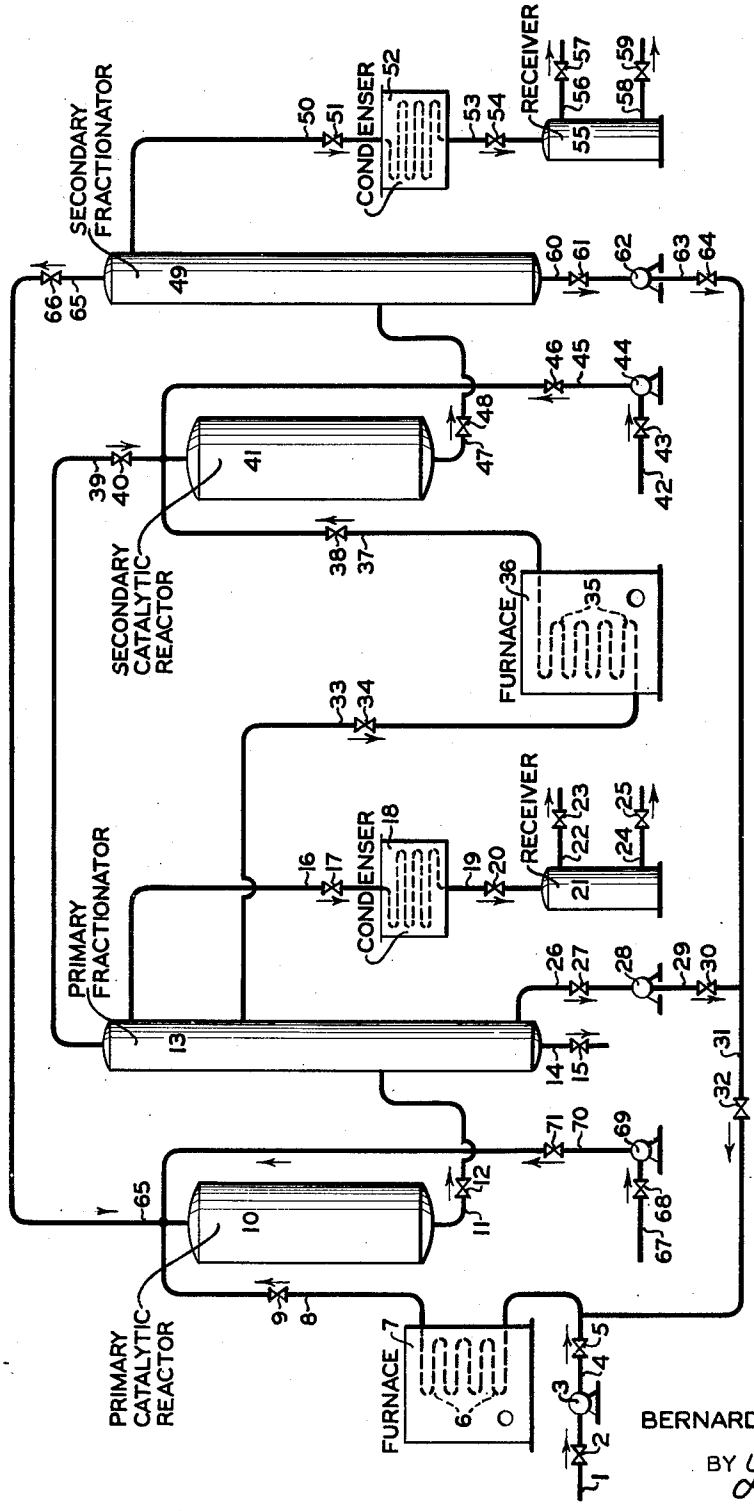
Nov. 9, 1943. B. S. FRIEDMAN 2,334,159

TREATMENT OF HYDROCARBON OILS

Filed Jan. 31, 1941



INVENTOR

BERNARD S. FRIEDMAN

BY Lee J. Barry

ATTORNEY

Patented Nov. 9, 1943

2,334,159

UNITED STATES PATENT OFFICE

2,334,159

TREATMENT OF HYDROCARBON OILS

Bernard S. Friedman, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application January 31, 1941, Serial No. 376,723

9 Claims. (Cl. 196—52)

This invention relates broadly to the treatment of relatively heavy petroleum fractions containing substantially no gasoline to convert them into substantial yields of gasoline of relatively high anti-knock value. In a more specific sense, the invention is concerned with a combination of inter-related steps involving a preliminary cracking of a hydrocarbon fraction followed by the selective treatment of a fraction from the first step under conditions designed to increase its anti-knock value to an unusual degree. Other specific features emphasizing the value of the combination will be developed in the following specification.

The art of converting the heavier fractions of petroleum into gasoline by the use of heat, pressure and catalyst is extensive and many combinations of processes and apparatus have been developed which are applicable to different types of charging stocks. The higher anti-knock value of cracked gasolines compared with straight-run gasolines is due to their high content of olefins, cyclic compounds both naphthenic and aromatic, and to some extent the presence of iso-paraffins which are known to have higher anti-knock characteristics than their normal counterparts. Of the groups of hydrocarbons having high anti-knock value the most desirable group comprises obviously the iso-paraffins since these are entirely saturated and exhibit no tendencies toward deterioration by polymerization or other condensation reaction. However, monoolefins of branched chain structure and aromatic hydrocarbons have good anti-knock characteristics and satisfactory motor fuels are in use which contain relatively high percentages of them. The present process is an improvement in the field of catalytic conversion of heavy hydrocarbon fractions to produce gasoline boiling range distillates of high anti-knock value therefrom.

In one specific embodiment, the present invention comprises catalytically cracking intermediate boiling range petroleum fractions in the presence of hydrogen to produce substantial yields of gasoline therefrom, fractionating the products to produce gases, gasoline fractions boiling up to about 300° F., a naphtha fraction boiling from about 300 to about 400° F., intermediate insufficiently converted fractions and residuum, cooling, condensing and collecting said gasoline fraction boiling up to 300° F., returning said intermediate fractions to further catalytic cracking, recovering said residuum, subjecting said fraction boiling from 300 to 400° F. to catalytic aromatization treatment in the presence of a corresponding straight-run fraction in the presence of said gases, fractionating the products from the aromatization treatment to produce gases, gasoline and intermediate refluxes, cooling and condensing said gasoline, and returning said gases and intermediate refluxes to further catalytic cracking.

Features of the invention will be developed more in detail by describing a characteristic operation in connection with the attached diagrammatic drawing which shows in general side elevation, without regard to exact proportion, a system of interconnected units in which the process may be conducted.

Referring to the drawing, a stock for treatment such as a gas oil is introduced to the plant through line 1 containing valve 2 to a charging pump 3 which discharges through a line 4 containing valve 5 into a heating element 6 disposed to receive heat from furnace 7. Intermediate refluxes originating in the succeeding fractionating steps are admitted to line 4 from line 31 as will be later more specifically described. During passage through the primary heating element 6 the temperature of the entering charge plus intermediates is raised to some point from about 700 to about 930° F. and the pressure is maintained by manipulation of valves along the line of flow at a point preferably from about 300 to about 3000 pounds per square inch.

The heated products from coil 6 pass through line 8 containing valve 9 to a primary catalytic reactor 10 which preferably contains a filler of catalyst composed of materials fostering both cracking and hydrogenating reactions. For example, the cracking component may comprise such materials as alumina, zirconia, titania, thoria, silica-alumina, or silica-alumina-zirconia composites, clays, either raw or acid treated, kieselguhr, calcined magnesite, etc., while the hydrogenating component may comprise one or more of the oxides or sulfides of such metals as chromium, molybdenum, zinc, tungsten, manganese, cobalt or copper. The only essential of the material employed as a primary catalytic reactor is that it be able to exert both a cracking and hydrogenating action. The extent of the two types of reaction may be varied by varying the proportions of the ingredients of the catalyst composites employed. A convenient composite includes a prepared alumina-silica composite mixed with an alumina-molybdena composite.

Hydrogen necessary for effecting the desired degree of hydrogenation during the cracking of

the charge is introduced from a source not shown through line 67 containing valve 68 to a compressor 69 which discharges through a line 70 containing a valve 71 into the primary catalytic reactor. A gas mixture containing relatively high percentages of hydrogen which may be fractionated to increase the hydrogen content is returned from fractionator 49 through line 65 containing valve 66. The relative proportions of hydrogen used in the primary reaction zone and the amount of make-up hydrogen introduced from line 67 will be varied to produce the best overall results of the process.

Total conversion products from primary catalytic reactor 10 pass through line 11 containing valve 12 to a fractionating zone 13 which is represented in the drawing as a single column although it may comprise any arrangement of fractionators necessary for effecting the desired separations. From this zone gasoline vapors of relatively low boiling points, for example, approximately 100 to 300° F. are removed through line 16 containing valve 17 and condensed during passage through condenser 18, the cooled products passing through line 19 containing valve 20 to a receiver 21 having a gas release line 22 containing valve 23 and a liquid draw line 24 containing valve 25.

Intermediate reflux condensates amenable to further hydro-cracking treatment are represented as being drawn from a point near the bottom of fractionating zone 13 through line 26 containing valve 27 to a recycling pump 28 which discharges through line 29 containing valve 30 and thence into line 31 containing valve 32 and leading to line 4 as already indicated. Residual material too heavy for further efficient conversion is drawn through line 14 containing valve 15.

The naphtha fraction from the primary catalytic step boiling above the previously mentioned fraction which was removed, and usually within the approximate range of 300 to 400° F. or higher, is withdrawn from fractionating zone 13 as a side-cut through line 33 containing valve 34 and passes through a heating coil 35 disposed to receive heat from the furnace 36. In this heater the temperature of the naphtha side-cut is preferably raised to some point from about 932 to 1112° F. while the pressure is reduced to some point below 300 pounds to bring the material to some optimum pressure and temperature combination for its effective catalytic conversion in the second step of the process. Thus the heated products flow through line 37 containing valve 38 and enter a secondary catalytic reactor 41 which also receives the fixed gases from fractionating zone 13 by way of line 39 containing valve 40 and a regulated proportion of straight-run naphtha analogous to that withdrawn from fractionating zone 13 from line 33. This latter straight-run fraction was introduced through line 42 containing valve 43 to pump 44 which discharges through line 45 containing valve 46. The function of the secondary catalytic reactor is to aromatize the naphtha fractions introduced by contact with catalyst having essentially a dehydrogenating action. Such catalysts may comprise, for example, catalysts similar to the hydrogenating component of the mixtures used in the primary catalytic reactor 10 and preferably such compounds as the oxides of chromium, molybdenum, vanadium, tungsten, etc., representing generally numbers of the left-hand colums of groups IV, V and VI of the periodic table. These oxides are preferably supported on relatively inert materials such as alumina, magnesia, clays, etc. In catalytic reactor 41 the naphthenic constituents of the straight-run naphtha are dehydrogenated to form aromatics along with similar cyclic compounds of a partially or totally saturated character found in the cracked naphtha fraction in the first step. There will also be a controlled amount of cyclization reactions tending to convert the aliphatic constituents of both naphtha cuts to cyclic compounds of relatively high anti-knock characteristics.

The products from catalytic reactor 41 pass through line 47 containing valve 48 to a secondary fractionating zone 49 which is preferably adapted to separate a gaseous fraction high in hydrogen, a gasoline boiling range fraction which may be blended with the 300° F. end-point cut from the primary fractionating zone and refluxes for returning to the primary hydro-cracking step for further treatment. Thus, as shown in the drawing the gaseous fractions from the final or secondary fractionating zone are represented as being withdrawn through line 65 containing valve 66 and returned to the primary reactor 10 while the gasoline boiling range material follows line 50 containing valve 51, passes through condenser 52 and run-down line 53 containing valve 54 to receiver 55 which has the conventional gas release line 56 containing valve 57 and a liquid draw line 58 containing valve 59. Heavier materials suitable for further hydro-cracking treatment pass through line 60 containing valve 61 to recycle pump 62 which discharges through line 63 containing valve 64 back to line 31 and thence to the hydro-cracking zone.

The 300° F. end-point gasoline from receiver 21 constitutes a good aviation base fuel and may be used as such. The product from receiver 55 from the second step is satisfactory for blending with motor fuels. If desired the two fractions may be combined and the blend used as motor fuel.

The following example is given of the results as obtained in a typical run according to the process of the invention although the invention's scope is not intended to be unduly limited by the data thus presented:

A Mid-Continent gas oil was treated by passing its vapors at a temperature of 752° F. under a pressure of 700 pounds per square inch over a mixed catalyst comprising essentially a silica-alumina-zirconia composite impregnated with 2 percent by weight of molybdenum trioxide. Three mols of hydrogen per mol of gas oil vapors were mixed therewith and the rate of flow over the catalyst was adjusted to correspond to a liquid space velocity of 1 per hour per volume of catalyst space.

In continuous operation the following fractions were obtained in the first steps:

Product:		Once-through yield
Dry gas	weight per cent	1.67
300° F. E. P. gasoline	volume per cent	24.5
300–400° F. naphtha	do	12.7
Recycle stock	do	56.4
Carbon	weight per cent	0.41

The 300° F. end-point gasoline had an octane number of 75.5, a Reid vapor pressure of 7 pounds, a bromine number of 1, and an A. P. I. gravity of 66.7°.

The 300 to 400° F. naphtha cut was processed by passing it over a catalyst consisting of 3.8 per cent of molybdenum tri-oxide deposited upon

alumina using a temperature of 1022° F., a pressure of 50 pounds per square inch, a liquid space velocity of 0.5, and 3 moles of hydrogen per mole of naphtha. The original naphtha cut had an A. P. I. gravity of 44.5° and an octane number of 52.5, and there was obtained a 78.5 volume per cent yield of 84 octane number fraction which had a Reid vapor pressure of 2.6 pounds.

By ultimate recycling of insufficiently converted materials according to the general process shown in the drawing there is produced a total yield of 73% by volume of 80 octane number gasoline having an end boiling point of 400° F.

I claim as my invention:

1. A process for the conversion of hydrocarbon oil which comprises subjecting said oil to conversion in the presence of a catalyst having hydrogenating activity and cracking activity, fractionating the resultant vaporous conversion products to form reflux condensate and to separate a gas fraction comprising normally gaseous products, a gasoline fraction and a naphtha fraction, subjecting said naphtha fraction to aromatization, fractionating the resulting products from the aromatization step to form reflux condensate and to separate a gas rich in free hydrogen and a gasoline fraction, and supplying the last-mentioned reflux condensate to the first-mentioned conversion step.

2. The process of claim 1 further characterized in that at least a portion of the gas rich in free hydrogen is supplied to the first-mentioned conversion step.

3. The process of claim 1 further characterized in that at least a portion of said gas fraction is supplied to the aromatization step.

4. The process of claim 1 further characterized in that a straight-run naphtha is combined with the naphtha formed in the first conversion step and the mixture introduced to the aromatization step.

5. A process for the conversion of hydrocarbon oil which comprises subjecting said oil to conversion in the presence of a catalyst having cracking activity and a catalyst having hydrogenating activity, fractionating the resultant vaporous conversion products to form reflux condensate and to separate a gas fraction comprising normally gaseous products, a gasoline fraction and a naphtha fraction, subjecting said naphtha fraction to aromatization, fractionating the resulting products from the aromatization step to form reflux condensate and to separate a gas rich in free hydrogen and a gasoline fraction, and supplying the last-mentioned reflux condensate to the first-mentioned conversion step.

6. The process of claim 1 further characterized in that said hydrocarbon oil comprises a straight-run gas oil.

7. A process for the production of substantial yields of gasoline boiling range materials of relatively high antiknock values from a petroleum fraction substantially devoid of gasoline which comprises subjecting an intermediate boiling range petroleum fraction in the presence of hydrogen at a temperature of from about 700° F. to about 930° F. under a pressure of from about 300 to about 3000 pounds per square inch to contact with a catalyst having hydrogenating activity and a catalyst having cracking activity selected from the group consisting of composites of silica-alumina and silica-alumina-zirconia to produce substantial yields of gasoline therefrom, fractionating the products to produce gases, a gasoline fraction boiling up to about 300° F., a naphtha fraction boiling from about 300° F. to about 400° F. intermediate insufficiently converted fractions and residuum, cooling, condensing and collecting said gasoline fraction, returning said intermediate fractions to further catalytic cracking, and recovering said residuum, subjecting said naphtha fraction to catalytic aromatization treatment at a temperature of from about 932 to about 1112° F., under a pressure of less than 300 pounds per square inch in contact with an oxide of chromium in the presence of a corresponding straight-run fraction and in the presence of said gases, fractionating the products from the aromatization treatment to produce gases, gasoline and intermediate refluxes, cooling and condensing said gasoline, and returning said gases and intermediate refluxes to further catalytic cracking.

8. A process for the production of substantial yields of gasoline boiling range materials of relatively high antiknock values from a petroleum fraction substantially devoid of gasoline which comprises subjecting an intermediate boiling range petroleum fraction in the presence of hydrogen at a temperature of from about 700° F. to about 930° F. under a pressure of from about 300 to about 3000 pounds per square inch to contact with a catalyst having hydrogenating activity and a catalyst having cracking activity selected from the group consisting of composites of silica-alumina and silica-alumina-zirconia to produce substantial yields of gasoline therefrom, fractionating the products to produce gases, a gasoline fraction boiling up to about 300° F., a naphtha fraction boiling from about 300° F. to about 400° F. intermediate insufficiently converted fractions and residuum, cooling, condensing and collecting said gasoline fraction, returning said intermediate fractions to further catalytic cracking, and recovering said residuum, subjecting said naphtha fraction to catalytic aromatization treatment at a temperature of from about 932 to about 1112° F., under a pressure of less than 300 pounds per square inch in contact with an oxide of vanadium in the presence of a corresponding straight-run fraction and in the presence of said gases, fractionating the products from the aromatization treatment to produce gases, gasoline and intermediate refluxes, cooling and condensing said gasoline, and returning said gases and intermediate refluxes to further catalytic cracking.

9. A process for the production of substantial yields of gasoline boiling range materials of relatively high antiknock values from a petroleum fraction substantially devoid of gasoline which comprises subjecting an intermediate boiling range petroleum fraction in the presence of hydrogen at a temperature of from about 700° F. to about 930° F. under a pressure of from about 300 to about 3000 pounds per square inch to contact with a catalyst having hydrogenating activity and a catalyst having cracking activity selected from the group consisting of composites of silica-alumina and silica-alumina-zirconia to produce substantial yields of gasoline therefrom, fractionating the products to produce gases, a gasoline fraction boiling up to about 300° F., a naphtha fraction boiling from about 300° F. to about 400° F. intermediate insufficiently converted fractions and residuum, cooling, condensing and collecting said gasoline fraction, returning said intermediate fractions to further cata-

lytic cracking, and recovering said residuum, subjecting said naphtha fraction to catalytic aromatization treatment at a temperature of from about 932 to about 1112° F., under a pressure of less than 300 pounds per square inch in contact with an oxide of molybdenum in the presence of a corresponding straight-run fraction and in the presence of said gases, fractionating the products from the aromatization treatment to produce gases, gasoline and intermediate refluxes, cooling and condensing said gasoline, and returning said gases and intermediate refluxes to further catalytic cracking.

BERNARD S. FRIEDMAN.