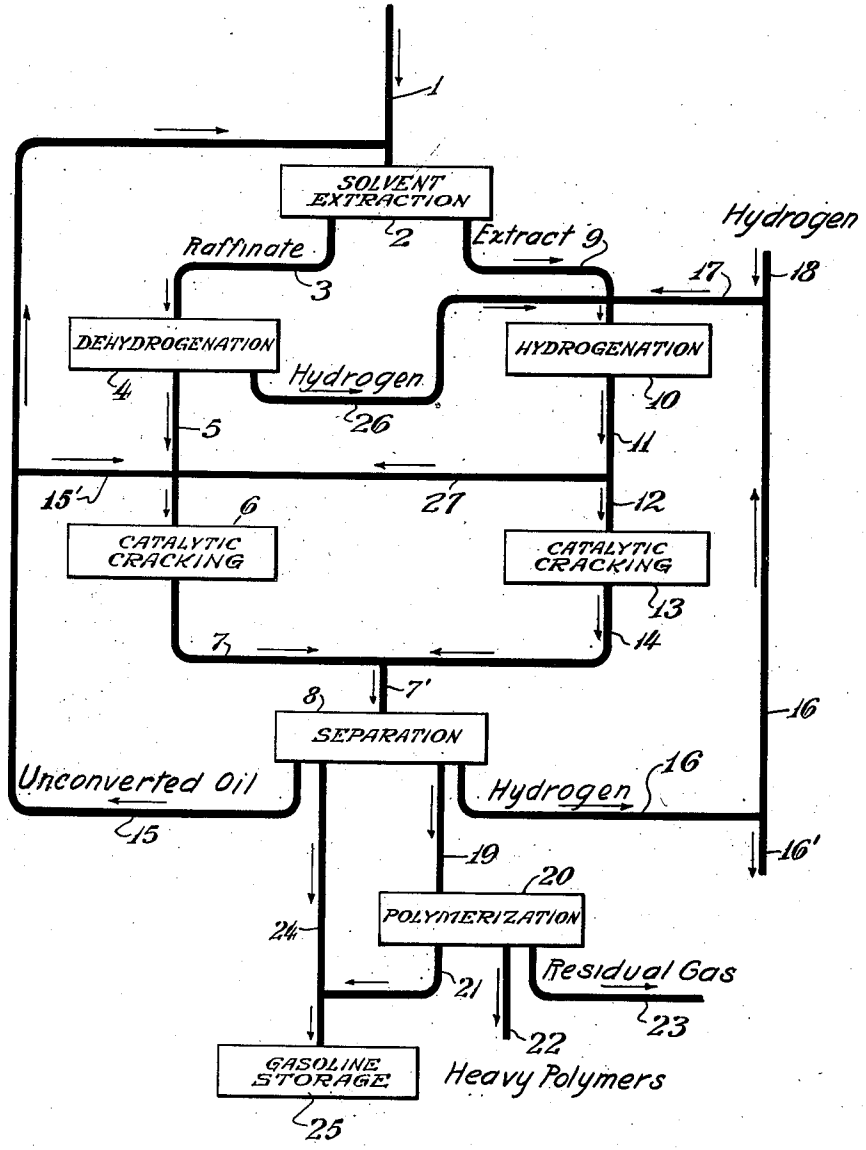
May 20, 1941. W. L. BENEDICT ET AL 2,242,504

CATALYTIC CONVERSION OF HYDROCARBONS

Filed April 29, 1939



Inventors:
Wayne L. Benedict
Jacob Elston Ahlberg
By Lee J. Gary
Attorney

Patented May 20, 1941

2,242,504

UNITED STATES PATENT OFFICE

2,242,504

CATALYTIC CONVERSION OF HYDROCARBONS

Wayne L. Benedict and Jacob Elston Ahlberg, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application April 29, 1939, Serial No. 270,850

11 Claims. (Cl. 196—13)

This invention relates to the catalytic conversion of heavy hydrocarbonaceous materials and more particularly, distillates which are vaporizable without substantial decomposition. More specifically, the invention concerns the conversion of hydrocarbons by means of cracking catalysts which are specific in their action of producing desirable gasoline and gaseous products from heavy hydrocarbon distillates. In general, charging stocks from petroleum sources are converted, although the conversion of similar hydrocarbon fractions produced by the distillation of coal tar, shale oils and the like, may be included within the intended scope of the present invention.

The art of producing gasoline and gas by non-catalytic cracking of hydrocarbon oils is extensive, and because of the large amount of investigation has been developed to a point where the principles involved are fairly well understood. The principles of catalytic conversion of hydrocarbons, and more particularly the use of catalysts which assist the thermal cracking of higher-boiling hydrocarbon fractions to produce gasoline and gas, are not so well understood. Such explanations as have been given are largely empirical, and a discussion of the reactions is therefore best confined to a factual basis.

In one specific embodiment the present invention comprises a method for converting hydrocarbon fractions into high yields of gasoline and desirable gas which consists in extracting said fractions with a selective solvent, contacting the raffinate with a dehydrogenation catalyst under conditions adequate to effect substantial dehydrogenation thereof, mixing the extract with a hydrogen-containing gas, contacting the mixture with a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation thereof, contacting the dehydrogenated reaffinate and the hydrogenated extract in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking, separating the reaction products, returning a portion of the hydrogen-containing gas to the hydrogenation step, contacting a fraction of the normally gaseous hydrocarbons with a polymerization catalyst under conditions adequate to convert the olefins therein substantially to the gasoline boiling range and recovering the polymer, recovering the catalytically cracked gasoline, and returning a portion of the unconverted fraction to the solvent extraction step.

It has been found that certain petroleum distillates are rendered more susceptible to catalytic cracking after relatively minor portions of compounds of an unknown character have been removed therefrom by solvent extraction. It has further been found that the unconverted fraction from the catalytic cracking step is similarly improved as a recycle stock when certain portions of it are removed by selective solvents. Proper solvents should have the property of selectively removing olefinic and aromatic hydrocarbons from mixtures thereof with saturated hydrocarbons. After solvent extraction the raffinate is relatively paraffinic. It has been found that partial dehydrogenation of the raffinate yields a stock which is substantially more amenable to catalytic cracking than the original oil. The extracted material is, per se, a relatively difficult stock to crack catalytically to produce high yields of motor fuel. It is improved, however, if it is subjected to a catalytic hydrogenation step and then cracked either in a separate step or in the same step with the dehydrogenated raffinate. The reaction products from the catalytic cracking step, or steps if the two stocks are cracked separately, are separated into unconverted oil which is returned to the solvent extraction step, a hydrogen-containing gas which is returned entirely or in part to the hydrogenation step, a fraction containing C_3 and C_4 olefins which are polymerized into substantial yields of gasoline boiling range material, and a finished gasoline of high octane number.

The solvents which may be used in the extraction step are not a special feature of the present invention, but may comprise any suitable selective solvent, among which are liquid sulfur dioxide, furfural, $\beta\beta$ dichlorethyl ether, nitrobenzene, glycol ethers, etc.

The catalysts used in the dehydrogenation step may comprise any suitable dehydrogenation catalyst such as, for example, alumina or magnesia to which have been added various other metal oxides to increase their dehydrogenating activity, including those of chromium, vanadium, iron, zinc, zirconium, molybdenum, tungsten, etc. The conditions for the dehydrogenation step are substantially atmospheric pressure and temperatures within the range of 900°–1100° F.

The hydrogenation catalyst may comprise any suitable substance known to promote this reaction such as, for example, molybdenum sulfide, molybdenum oxide, or, providing the sulfur content is sufficiently low, the reduced metal catalysts such as nickel, copper, iron, cobalt, etc.

The conditions of hydrogenation may include temperature ranges of 300°–800° F. and pressures of substantially atmospheric to 2000 pounds per square inch, depending to a certain extent upon the catalyst used.

The present process may have more or less applicability when using cracking catalysts produced by the chemical treatment of naturally-occurring clays, or catalysts consisting of specially prepared silica-alumina, silica-zirconia, silica-alumina-zirconia and silica-alumina-thoria composites which have a high degree of activity. These latter composites are prepared by combining the constituents in various ways such as mixing, coprecipitation and the like, under conditions whereby alkali metal ions are excluded. It appears that no one component can be determined as that for which the remaining components may be considered as the promoter according to conventional terminology.

In the present invention the catalysts of the various steps are used in the form of sized particles or formed shapes such as pellets, produced by compression or extrusion methods.

The catalytic cracking step is carried out at temperatures within the range of approximately 800°–1200° F. and pressures sufficient to insure passage of the vapors through the plant.

The catalyst used for the polymerization step may be sulfuric acid, the so-called solid phosphoric acid catalyst, or other suitable polymerization catalysts. When sulfuric acid is used the reaction is carried out with 60% or stronger acid at a temperature within the range of approximately 65°–250° F. The solid phosphoric acid catalyst consists of a mixture of liquid phosphoric acid catalyst with kieselguhr or similar suitable siliceous materials which is extruded and may be precalcined. The polymerization step using this catalyst is carried out at a temperature within the range of approximately 250°–450° F. and pressures of 100–1000 pounds per square inch.

The attached drawing diagrammatically exemplifies one embodiment of the present invention. It should not be interpreted as limiting the invention to the exact conditions given therein.

The raw oil charge enters the system through line 1, passes into the solvent extraction step 2 wherein it is divided into a raffinate and an extract fraction. These fractions are freed of solvent by any convenient method. The raffinate is passed through line 3 to the dehydrogenation step 4 wherein it is contacted in vaporous form with a dehydrogenation catalyst under conditions adequate to effect partial dehydrogenation. The reaction products pass through line 5 to catalytic cracking step 6 wherein the oil is contacted in vaporous form with a cracking catalyst and partially converted to gasoline and gas. The reaction products leave the catalytic cracking step through lines 7 and 7' and pass to separation step 8. The extract from the solvent extraction step 2 passes through line 9 to hydrogenation step 10 wherein it is subjected to the action of hydrogen in the presence of a catalyst under suitable conditions to effect hydrogenation. The hydrogenated oil passes through lines 11 and 12 to catalytic cracking step 13, which is similar in character to catalytic cracking step 6. The reaction products leave the cracking step through line 14 and enter the separation step 8 through line 7'. From the separation step the unconverted fractions from the catalytic cracking steps pass through line 15 to line 1 and thence to primary solvent extraction step 2. A portion of the unconverted fraction may be returned to catalytic cracking step 6 by means of lines 15, 15' and 5. Separated hydrogen-containing gas passes through lines 16 and 17 combining with line 3, and thence to hydrogenation step 10. A portion of the hydrogen-containing gas may be withdrawn through line 16' or, if so desired, the gas may be enriched with hydrogen from an outside source from line 18. The polymerization olefins from separation step 8 which include the C_3 and C_4 hydrocarbons pass through line 19 to polymerization step 20 where they are subjected to catalytic polymerization. The gasoline boiling range polymer is recovered through line 21 and may be blended with the finished gasoline from the cracking step. Polymer of higher than gasoline boiling range may be withdrawn through line 22 and returned by means not shown to the catalytic cracking step or may be used for other purposes if so desired. The residual C_3 and C_4 hydrocarbons are withdrawn through line 23. The finished gasoline from the separation step 8 passes through line 24, combining with polymer from line 21, and passes to gasoline storage 25.

As one alternative of the above-mentioned operation, the hydrogen-containing gas from dehydrogenation step 4 may be passed to hydrogenation step 10 by means of line 26 which joins with line 9.

In another alternative mode of operation, the hydrogenated oil from hydrogenation step 10 may pass through lines 11 and 27 to catalytic cracking step 6 in which case catalytic cracking step 13 is eliminated.

The following example is given to illustrate the usefulness of the invention, but should not be interpreted as limiting it to the exact conditions described therein.

A Mid-Continent gas oil of 35.9° A. P. I. gravity was catalytically converted according to the above-described process after liquid sulfur dioxide was used in a primary selective solvent extraction step. The dehydrogenation catalyst consisted of activated alumina containing 8% of chromia and dehydrogenation was carried out at 932° F. at substantially atmospheric pressure. The cracking catalyst was a sodium-free synthetic silica-alumina composite and the cracking step was carried out at 932° F. and substantially atmospheric pressure. The hydrogenation catalyst was essentially molybdenum oxide, the operation being carried out at 1000 pounds pressure and 730° F. The polymerization step was carried out using a solid phosphoric acid catalyst at a temperature of 375° F. and pressure of 250 pounds per square inch.

The total yield of 400° F. end-point, 81.5 octane number gasoline amounted to 86.5% of the original raw oil fraction charged.

We claim as our invention:

1. A process for the production of high antiknock value gasoline which comprises extracting a hydrocarbon oil with a selective solvent, separating the raffinate and extract, contacting the raffinate with a dehydrogenation catalyst under conditions adequate to effect substantial dehydrogenation thereof, mixing the extract with a hydrogen-containing gas and contacting the mixture with a hydrogenation catalyst under conditions adequate to effect hydrogenation thereof, contacting the dehydrogenated raffinate and the hydrogenated extract in vaporous form with a cracking catalyst under conditions ade-

quate to effect catalytic cracking, recovering the gas and gasoline, and returning the insufficiently converted oil to the solvent extraction step.

2. A process for the production of high anti-knock value gasoline which comprises extracting a hydrocarbon oil with a selective solvent, separating the raffinate and extract, contacting the raffinate with a dehydrogenation catalyst under conditions adequate to effect substantial dehydrogenation thereof, mixing the extract with a hydrogen-containing gas, and contacting the mixture with a hydrogenation catalyst under conditions adequate to effect hydrogenation thereof, separately contacting the dehydrogenated raffinate and the hydrogenated extract in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking of each, recovering the gas and gasoline, and returning the insufficiently converted oil to the solvent extraction step.

3. A process for the production of high anti-knock value gasoline which comprises extracting hydrocarbon oil with a selective solvent, separating the raffinate and extract, contacting the raffinate with a dehydrogenation catalyst under conditions adequate to effect substantial dehydrogenation thereof, contacting the dehydrogenated oil in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking, mixing the extracted oil with a hydrogen-containing gas and contacting the mixture with a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation thereof, contacting the hydrogenated extract in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking, combining the reaction products from the catalytic cracking steps, separating a hydrogen-containing gas therefrom and returning a portion of it to the aforementioned hydrogenation step, recovering the catalytically cracked gasoline, and returning a portion of the insufficiently converted oil to the solvent extraction step.

4. The process of claim 1 wherein the cracking catalyst comprises a composite consisting essentially of a major portion of precipitated silica containing a minor portion of a compound selected from the group consisting of alumina and zirconia, said composite being substantially free of alkali metal compounds.

5. A process for the production of high anti-knock value gasoline which comprises extracting a hydrocarbon fraction with a selective solvent, recovering the raffinate and extracted oil, contacting the raffinate with a dehydrogenation catalyst under conditions adequate to effect substantial dehydrogenation thereof, combining the extract with the hydrogen-containing gas produced in the dehydrogenation step, contacting the mixture with a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation thereof, contacting the dehydrogenated raffinate and the hydrogenated extract in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking, separating the reaction products, and returning the insufficiently converted oil to the solvent extraction step.

6. A process for the production of high anti-knock value gasoline which comprises extracting a hydrocarbon fraction with a selective solvent, recovering the raffinate and extracted oil, contacting the raffinate with a dehydrogenation catalyst under conditions adequate to effect dehydrogenation thereof, mixing the extract with a hydrogen-containing gas, contacting the mixture with a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation thereof, contacting the dehydrogenated raffinate and the hydrogenated extract in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking, separating the reaction products, returning the unconverted oil to the solvent extraction step, supplying hydrogen formed by the cracking to the hydrogenation step, and recovering the gasoline and gas.

7. The process of claim 1 wherein the solvent used in the extraction step is liquid sulfur dioxide.

8. A process for the production of high anti-knock value gasoline which comprises extracting a hydrocarbon oil with a selective solvent, separating the raffinate and extract, contacting the raffinate with a dehydrogenation catalyst under conditions adequate to effect substantial dehydrogenation thereof, mixing the extract with a hydrogen-containing gas and contacting the mixture with a hydrogenation catalyst under conditions adequate to effect substantial hydrogenation thereof, contacting the dehydrogenated raffinate and the hydrogenated extract in vaporous form with a cracking catalyst under conditions adequate to effect catalytic cracking, recovering the gas and gasoline, returning a portion of the insufficiently converted oil to the catalytic cracking step, and returning a further portion of the insufficiently converted oil to the solvent extraction step.

9. A process for producing anti-knock gasoline which comprises extracting hydrocarbon oil with a selective solvent, separating the resultant raffinate and extract, subjecting the raffinate to dehydrogenation, hydrogenating the extract, catalytically cracking the dehydrogenated raffinate and the hydrogenated extract, and recovering the resultant gasoline.

10. A process for producing anti-knock gasoline which comprises extracting hydrocarbon oil with a selective solvent, separating the resultant raffinate and extract, subjecting the raffinate to dehydrogenation, hydrogenating the extract, catalytically cracking the dehydrogenated raffinate and the hydrogenated extract, separating gasoline and a hydrogen-containing gas from the cracked products, recovering the gasoline and supplying at least a portion of said gas to the aforesaid hydrogenating step.

11. The process as defined in claim 9 further characterized in that hydrogen formed in the dehydrogenating step is supplied to the dehydrogenating step.

WAYNE L. BENEDICT.
JACOB ELSTON AHLBERG.