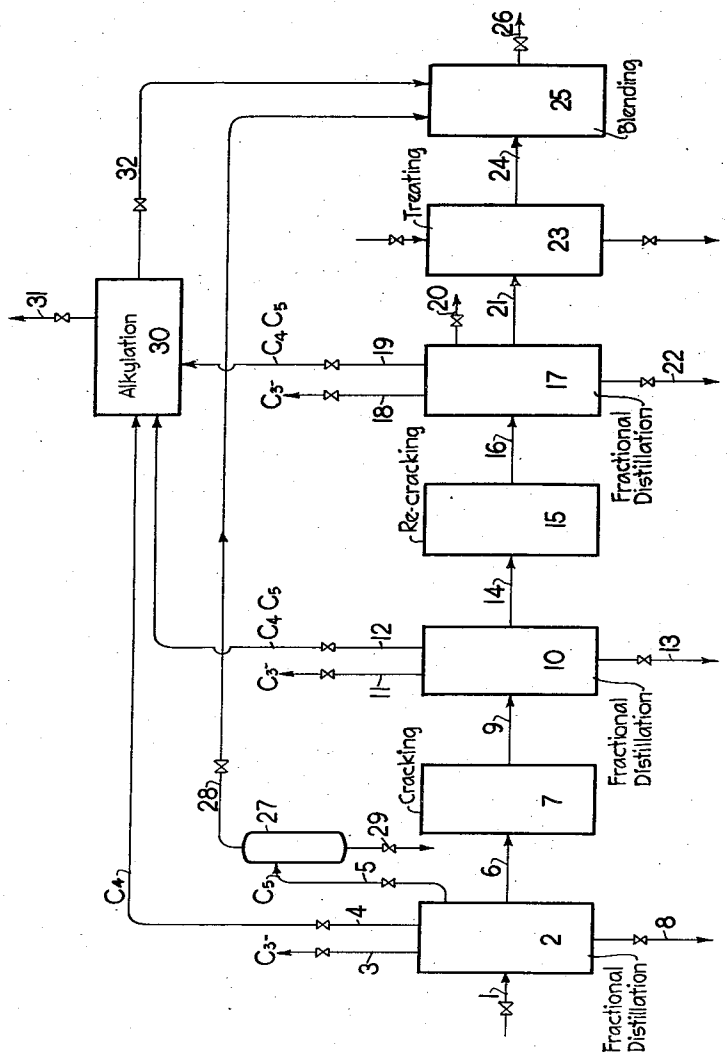
Feb. 27, 1945. H. GERSHINOWITZ 2,370,533

CRACKING AND REFORMING OF HYDROCARBONS

Filed Nov. 23, 1942



Inventor: Harold Gershinowitz

By his Attorney: [signature]

Patented Feb. 27, 1945 2,370,533

UNITED STATES PATENT OFFICE

2,370,533

CRACKING AND REFORMING OF HYDROCARBONS

Harold Gershinowitz, New York, N. Y., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application November 23, 1942, Serial No. 466,681

2 Claims. (Cl. 196—49)

This invention relates to the manufacture of motor fuels by cracking of hydrocarbon distillates and especially to the art of cracking low octane naphtha to produce a motor fuel having improved properties and high anti-knock value.

It is well known that naphthas used in the blending of high grade motor fuels and particularly aviation gasoline must have a high anti-knock value, must be free of gum-forming components and must maintain their anti-knock properties, under severe engine conditions, i. e. high temperature, high compression and rich mixture. For these reasons naphthas, rich in aromatic hydrocarbons and substantially free from olefins, are preferred. Aromatics are known to have excellent anti-knock properties which do not decrease under severe operating conditions and have no tendency to form gums or to deteriorate otherwise during storage. Olefins, on the contrary, frequently oxidize and polymerize during storage, forming gums, and thus render a motor fuel less desirable for airplane engines.

It is well known that, by cracking, i. e. by thermal treatment resulting in carbon-carbon scission and dehydrogenation or isomerization or polymerization or a combination of these reactions it is possible to increase the octane number of hydrocarbons whose boiling range is not substantially changed by the cracking or reforming operation, and also to increase their content of aromatics. "Thermal" means non-catalytic or in the absence of a catalyst as understood in the conventional sense, in accordance with the accepted usage in the prior art as exemplified by the definition found on page 37 of "The Chemistry of Petroleum Derivatives" by Carlton Ellis, published in 1934. Such thermal operations when conducted by conventional methods cause however at the same time the formation of large amounts of olefins. This drawback has heretofore precluded the use of cracked products, particularly of higher boiling cracked naphthas in aviation gasolines, despite their relatively high octane number and aromaticity.

It is also known that for any given hydrocarbon feed the improvement in octane number of products whole boiling range is not substantially changed increases as the severity of cracking conditions is raised. This may be effected by increasing the temperature or the residence time of the hydrocarbons in the cracking furnace or both of these factors. However, coking of the furnace places a strict practical limit upon the improvement which may thus be obtained in that there is a certain severity of cracking above which coking becomes so rapid that it precludes commercial operation. This critical value may, to some extent, depend on the design of the furnace in which cracking is conducted, but for a given furnace it is primarily a function of the nature of the feed. Since a furnace requires shutting-down and cleaning as soon as deposition of coke begins to plug it, it is obvious that only processes in which coking is relatively slow are economically practical.

It has been proposed that more severe cracking conditions can be maintained without objectionable coking by introducing into the cracking zone, together with the naphtha, gaseous hydrocarbons such as those having one to five carbon atoms in the molecule. Such processes are described, for example, in U. S. Patents 2,135,-014 to Ostergaard or 2,220,699 to Angell. The introduction of these gases raises very appreciably the cost of heating, fractionation, compressing and pumping. Moreover, such light hydrocarbons and particularly the light olefins contained therein, or which are formed by dehydrogenation of the paraffins, tend to form unsaturated polymers which find their way into the cracked products, particularly in the naphtha fractions, thereby increasing their unsaturation.

It is an object of the present invention to provide a cracking process capable of producing naphthas having a high aromatic content and unusually low olefin content. It is another object to produce naphtha having excellent anti-knock and storage properties, and a still further object is to provide an improved method for making aviation blending stock and aviation gasoline. Further objects will be found in the improvements hereinafter disclosed.

According to this invention a straight-run petroleum is fractionated and a selected naphtha fraction is cracked. From the cracked products a selected naphtha fraction is separated which is recracked and a naphtha of improved octane number is recovered from the recracked products to serve as aviation gasoline base.

The success of the present invention and particularly of the recracking depends upon the proper selection of both the straight-run and the cracked naphtha fraction. It is only when both these fractions are properly chosen and cracked under proper conditions that the full benefits of my invention are obtained.

The nature of the invention will be better understood from the following detailed description,

taken together with the drawing forming a part of this specification, which drawing is a flow diagram illustrating both a general and a particularly preferred form of the improved process.

For simplicity the drawing does not show pumps, heat exchangers, valves, by-passes, vents, reboilers, condensers, and other auxiliaries, the proper placement of which will be at once evident to those skilled in the art.

The hydrocarbon oil which forms the starting material of the present process may be of any origin, though naphthenic oils are preferred to paraffinic ones.

In the first step of my process a suitable hydrocarbon oil such as a naphthenic crude oil is introduced from storage not shown through line 1 into fractional distillation zone 2, wherein it is fractionally distilled to produce a gaseous fraction consisting essentionally of gases having 3 or less carbon atoms in the molecule which are withdrawn through line 3. Fractions consisting essentially of hydrocarbons having 4 and 5 carbon atoms respectively are withdrawn through lines 4 and 5 to be used, preferably, in the process as will be hereinafter described. A naphtha fraction substantially free of C_4 hydrocarbon, and preferably free of C_5 and lighter hydrocarbon, is withdrawn through line 6 which leads to cracking zone 7. This naphtha fraction has an end point below about 500° F. and preferably below 450° F. Higher boiling products if included in this naphtha yield olefins in the product and tend to cause rapid coking in cracking zone 7 and prevent the attainment of sufficiently severe cracking conditions, and are therefore unsuitable for the objects of this process. Components of the crude oil boiling above the naphtha fraction are withdrawn through line 8.

This selected naphtha fraction should have a U. O. P. characterization factor below 11.6 and preferably below 11.4, i. e. it should not be paraffinic in nature. The U. O. P. characterization factor is a measure of paraffinicity of an oil. A highly paraffinic oil has a factor of about 12.5 and a highly aromatic and naphthenic oil has a lower factor approaching 10 as a minimum. (See "Characterization of Petroleum Fractions" by Watson, Nelson and Murphy of U. O. P., Industrial and Engineering Chemistry, volume 27, No. 12, 1460.) Higher boiling paraffinic components crack easily with the formation of olefins and often subsequent coking, and thus are not desirable in the practice of this invention.

In the second step of this process the selected naphtha is cracked in cracking zone 7 under conditions as severe as is practical without excessive coking, i. e. conditions which permit a furnace to operate for at least 3 or 4 weeks without necessitating a shut-down. Such conditions correspond, for example, to inlet pressures of 600 to 1500 p. s. i. and outlet temperatures slightly above 1000° F., preferably from about 1010° F. to 1040° F., e. g. a pressure of 1,255 lbs. and a temperature of 1015° F. The pressure drop across the cracking coil is, in general, of the order of 200 to 400 p. s. i. If desired, the time of cracking may be extended and controlled with the aid of a reaction chamber not shown.

The cracking operation is thus conducted in the "pseudo liquid phase" as opposed to "vapor phase" cracking in which lower pressures are maintained and larger proportions of olefins are formed. Actually the naphtha is above its critical temperature so that these terms do not have the conventional meaning, but indicate that the pressure is above or below the critical pressure of the naphtha respectively.

In the third step of my process the cracked products thus obtained pass through line 9 and are quenched and fractionally distilled in zone 10 to separate therefrom: a light gaseous fraction consisting essentially of hydrocarbons having 3 or less carbon atoms and withdrawn through line 11; a C_4–C_5 fraction rich in olefin and substantially free of higher and lower hydrocarbons which is obtained through line 12 to be used in the preferred embodiment of this process as hereinafter described; a heavy oil fraction comprising residue which is withdrawn through line 13; and the middle naphtha fraction which is the selected feed for the recracking step process. This selected naphtha fraction has a final boiling point between about 400° F. and 450° F., preferably about 425° F.

This fraction is characterized by relatively high content of monocyclic aromatics and naphthenes as opposed to hydrocarbons boiling above about 450° F. which contains a relatively large amount of polycyclic aromatics and naphthenes and are preferably not included in my selected fraction because upon cracking under severe conditions they tend to promote coke formation and lower the quality of the final product.

The selected naphtha fraction has a high octane number of the order of 72 and could normally be used with advantage as a motor fuel but not as aviation fuel. I have discovered, however, that by further treating this particular fraction, as described below, its octane number can be greatly improved, its aromatic content increased, and its olefin content decreased so that it may be used for aviation fuel.

The fourth step of my process comprises subjecting the selected fraction to severe cracking conditions in recracking zone 15 to perform the above-mentioned changes. This may be performed immediately or after prolonged storage.

The recracking operation should be conducted under the most severe conditions which can be tolerated without excessive coking. These conditions may be more severe than those of the first cracking operation, because many components of the original fluid which tend to decompose readily and to cause coking have been cracked in the first cracking step and eliminated in fractional distillation zone 10.

I prefer to use pressures just sufficient to maintain the hydrocarbons in a pseudo liquid phase, i. e. pressures above the critical for the cracking mixture, ranging from about 500 to 2,000 p. s. i., while maintaining high temperatures in the range of 1020° F. to 1100° F., or higher, preferably about 1050° F. and 1000 p. s. i.

The severity of the cracking may be defined either by the cracking conditions or by the changes brought about by these cracking conditions in the properties of the hydrocarbon, and particularly in its boiling range. The latter method is particularly applicable when the feed stock has a relatively narrow boiling range, as is the case in the present process, because in such a case, portions whose boiling ranges are changed are most likely to boil outside the boiling limits of the feed. When defined according to this method, the cracking conditions which I prefer for this process are such that a cracked fraction having the same boiling range as the naphtha feed amounts to about 60% to 90% of the cracked products in each cracking operation, and

preferably about 80% in the first operation and about 70% in the second operation.

Another easily measured change effected by cracking is a change in octane rating. It is, in general, convenient to measure the octane number of a debutanized gasoline having an end point of 400° F. For the purpose of this invention, it is preferred that such a gasoline separated from the first cracking condition have an octane number of 72 to 78 by the CFR "Motor Method," and one separated from the products of the second cracking step have an octane number at least 4 points higher i. e. of 76 to 82.

It is essential that the cracking and recracking operation of this process be carried out as separate steps. If it were attempted to maintain cracking conditions sufficiently severe to produce the desired result in one operation without intermediate separation of light and heavy components, heavy and tarry components produced in the initial stages would cause rapid coking in the subsequent stages. Moreover, the light unsaturated components formed at the beginning would be present in a large concentration, would polymerize to form olefins boiling within the naphtha range, and thus produce finally a more unsaturated naphtha.

The recracked products are obtained through line 16 and in the fifth step of the process are rapidly quenched and fractionally distilled in zone 17 to produce two fractions particularly useful in the practice of this invention. One such fraction is a C_4–C_5 fraction substantially free of higher and lower boiling hydrocarbons which is withdrawn through line 19 to be used as hereinafter described. The other is a middle naphtha fraction withdrawn through line 21 to be further treated in zone 23 and blended in zone 25 into an aviation gasoline. This middle naphtha fraction has an octane number of at least 81 and preferably above 83. Its olefin content is much lower and the aromatic content is much higher than that of the corresponding fraction obtained from the products of the first cracking operation.

Besides these two fractions which are used in the present process three other fractions are obtained, namely: fraction containing C_3 and lighter hydrocarbons; a light naphtha fraction intermediate between the C_4–C_5 fraction and the middle naphtha fraction; and a heavy oil containing tars. These fractions are withdrawn respectively through lines 18, 20, and 22.

The light fraction withdrawn through line 20 is highly olefinic and has a lower octane number than the middle fraction. It is worth noting that, if successive narrow boiling fractions are separated from the recracked products, and the olefin content of these narrow fractions is plotted against their boiling range, a very distinct temperature will be found at which the olefin content decreases abruptly, while the octane number increases at the same time. This temperature at which separation between the light and middle naphtha fraction should be effected lies in general between 240° F. and 270° F., usually at about 255° F. The separating point between the middle naphtha and the heavy fractions will depend to a large extent upon the volatility requirements of the final product and will in general be at about 340° F., for example, between 325° F. and 375° F. Thus, for best results, the middle fraction should have a boiling range between 240° F. and 375° F., preferably from about 255° F. to 340° F. The light fraction has, however, a high toluene content which may be extracted with phenol, aniline, furfural, SO_2, etc.

It may be noted that the fractionation zones, 10 and 17, must be separate and distinct and may not be combined for the success of my process, since otherwise the naphtha fractions which boil over substantially the same range could not be separated and part of the straight-run product and of once recracked naphtha would be found in the final product which thus would not be sufficiently improved, while part of the recracked middle fraction would unnecessarily be cracked a third time, etc.

As just cited, the middle naphtha from the second cracking obtained through line 21 from fractional distillation zone 17, has an octane number of at least 81 and a bromine value below 20. It may be subjected to well known refining treatments in treating zone 23 to improve further its quality, reduce its gum-forming components, improve its color, odor, stability, etc.

Such treatments may include, for example, passing over adsorption agents such as clay, bauxite, fuller's earth, diatomaceous earth, silica gel, etc., preferably at elevated temperatures below incipient cracking; contacting with sulfuric acid, phosphoric acid of suitable concentrations to produce a sludge containing the undesirable constituents which can be separated; hydrogenation in the presence of a suitable hydrogenation catalyst, such as finely divided nickel, chromium oxide, molybdenum or tungsten sulfide or a combination of these, etc.; treatment with catalyst of the clay type under conditions which do not cause substantial cracking; destruction or removal of harmful sulfur compound by doctor treatment, extraction with alkaline solution in the presence of a solutizer for mercaptans, or oxidation in the presence of copper catalysts, etc.

A particular advantage of my process is that these treatments may be relatively light, i. e. much lighter than treatments which would have to be applied to conventionally cracked naphthas or to the naphtha obtained in the first cracking step of this process in order to obtain a product having the same color, stability, low degree of unsaturation and low mercaptan content. Furthermore, sulfuric acid treatment, which is known ordinarily to reduce octane number of cracked gasolines, does, on the contrary, further raise the octane number of the special naphtha prepared according to the invention.

The treated naphthas may be redistilled to remove higher boiling constituents formed during the treating operations.

The finished naphtha is highly aromatic and therefore has very high anti-knock value when tested by the 3–C or other methods which emphasize rich mixture or highly supercharged operation. Naphthas of still further improved anti-knock properties, having octane numbers up to 93–94, may be obtained by extraction of this naphtha fraction by means of selective solvents, having greater solvent power for aromatic than for paraffinic hydrocarbons, such as SO_2, nitrobenzene, furfural, acetone, aniline, phenol, methyl acetate, ethyl cellosolve, etc., and separation of the extract from the solvent.

The specific conditions involved in the treating processes abovementioned may be readily obtained from the book "Chemical Refining of Petroleum," Kalichevsky and Stagner, published by Reinhold Publishing Corporation, 1942. In this book are descriptions of processes for the treat-

ment of hydrocarbons with sulfuric acid (see Chapter II), with alkaline reagents (see Chapter IV), sweetening processes (see Chapter V), refining by adsorption (see Chapter VI) and refining with a solvent (see Chapter VII).

The treated naphtha obtained from zone 23 through line 24 may then be blended in zone 25 with suitable blending agents to produce a finished aviation gasoline withdrawn through line 26. Suitable blending agents include light straight-run gasolines, isopentane, cyclopentane, neohexane, 2,3-dimethyl butane, di-isopropyl ether, triptane, iso-octane, alkylation gasoline produced by reacting isobutane with C_5 and lower olefins, etc. These blending agents give the proper boiling range to the final blend, and its octane number may be further improved by the addition of tetra-ethyl lead.

In a preferred form of the present process at least a part of the blending agents necessary for the production of aviation gasoline from the highly aromatic middle naphtha is obtained by treatment of the lighter fractions obtained in the process.

Thus, the C_5 fraction obtained through line 5 from zone 2 is fractionally distilled in column 27 to separate the isopentane contained therein which is withdrawn through overhead line 28 and led into blending zone 25. The normal pentane is withdrawn through line 29.

The straight-run C_4 fraction obtained through line 4 contains large amounts of isobutane. Considerable amounts of this isoparaffin are also contained in both cracked C_4–C_5 fractions obtained through lines 12 and 19. This isobutane may be advantageously alkylated by the olefins contained in the two C_4–C_5 fractions in alkylation zone 30.

The normal butane contained in the straight-run C_4 fraction and in the two cracked C_4–C_5 fractions as well as small amounts of normal pentane obtained in cracking may be withdrawn from the alkylation zone 30 through line 31.

The isopentane obtained in cracking passes unchanged through the alkylation treatment and may be withdrawn together with the alkylate through line 32 and conveyed to blending zone 25.

Alkylating zone 30 comprises the fractioning equipment necessary to separate isobutane from the feed and from the alkylate and to maintain a constant large excess of this isoparaffin over the olefins in the presence of alkylation catalyts. Suitable alkylation catalysts compose strong mineral acids such as phosphoric, hydrofluoric or sulfuric acids. The latter is particularly suitable when used at a relatively low temperature of the order of 30 to 40° F.

It may be noted that the preferred embodiment of this process permits the best utilization of a given petroleum crude oil for the manufacture of aviation fuel in that both the high boiling naphtha components are improved to give a highly aromatic aviation gasoline base and that C_4 and C_5 gases obtained both from the crude and in the cracking operation are utilized to further improve the octane number and add susceptibility of this base and to give the finished aviation gasoline the proper boiling range.

I claim as my invention:

1. In a process for manufacturing naphthas having improved anti-knock rating and low unsaturation and being suitable for aviation gasoline, the steps comprising: cracking at a temperature between about 1100° F. and 1400° F. and at a pressure between 600 and 1500 p. s. i. in a first non-catalytic cracking operation, a straight-run naphtha having a Watson characterization factor below 11.6, being substantially free of C_4 and lighter hydrocarbons, and having an end boiling point below about 500° F.; separating from the resulting cracked products a second naphtha fraction free from C_5 and lighter hydrocarbons, boiling below about 425° F., and having an octane number above about 72; recracking at a temperature between 1020° F. and 1100° F. and at a pressure between 500 and 2000 p. s. i. in a second non-catalytic cracking operation said second naphtha fraction by itself; and separating from the resulting cracked products a third naptha fraction boiling substantially between about 225° F. and about 340° F. and having an octane number at least 4 units higher and a bromine value lower than that of said second naphtha fraction.

2. In a process for manufacturing naphthas having improved anti-knock rating and low unsaturation and being suitable for aviation gasoline, the steps comprising: non-catalytic cracking at a temperature between about 1100° F. and 1400° F. and at a pressure between 600 and 1500 p. s. i. in a first cracking operation, a straight run naphtha having a Watson Characterization Factor below 11.6, being substantially free of C_4 and lighter hydrocarbons, and having an end boiling point below about 500° F.; separating from the resulting cracked products a second naphtha fraction free from C_5 and lighter hydrocarbons, boiling below 425° F. and having an octane number above about 72; re-cracking at a temperature between 1020° F. and 1100° F. and at a pressure between about 500 and 2000 p. s. i. in a second non-catalytic cracking operation said second naphtha fraction by itself; separating from the resulting re-cracked product a third naphtha fraction boiling between about 250° F. and about 340° F. and having an octane number of at least about 81 and having a bromine value lower than that of said second naphtha fraction; and further treating said third naphtha fraction to improve its stability.

HAROLD GERSHINOWITZ.