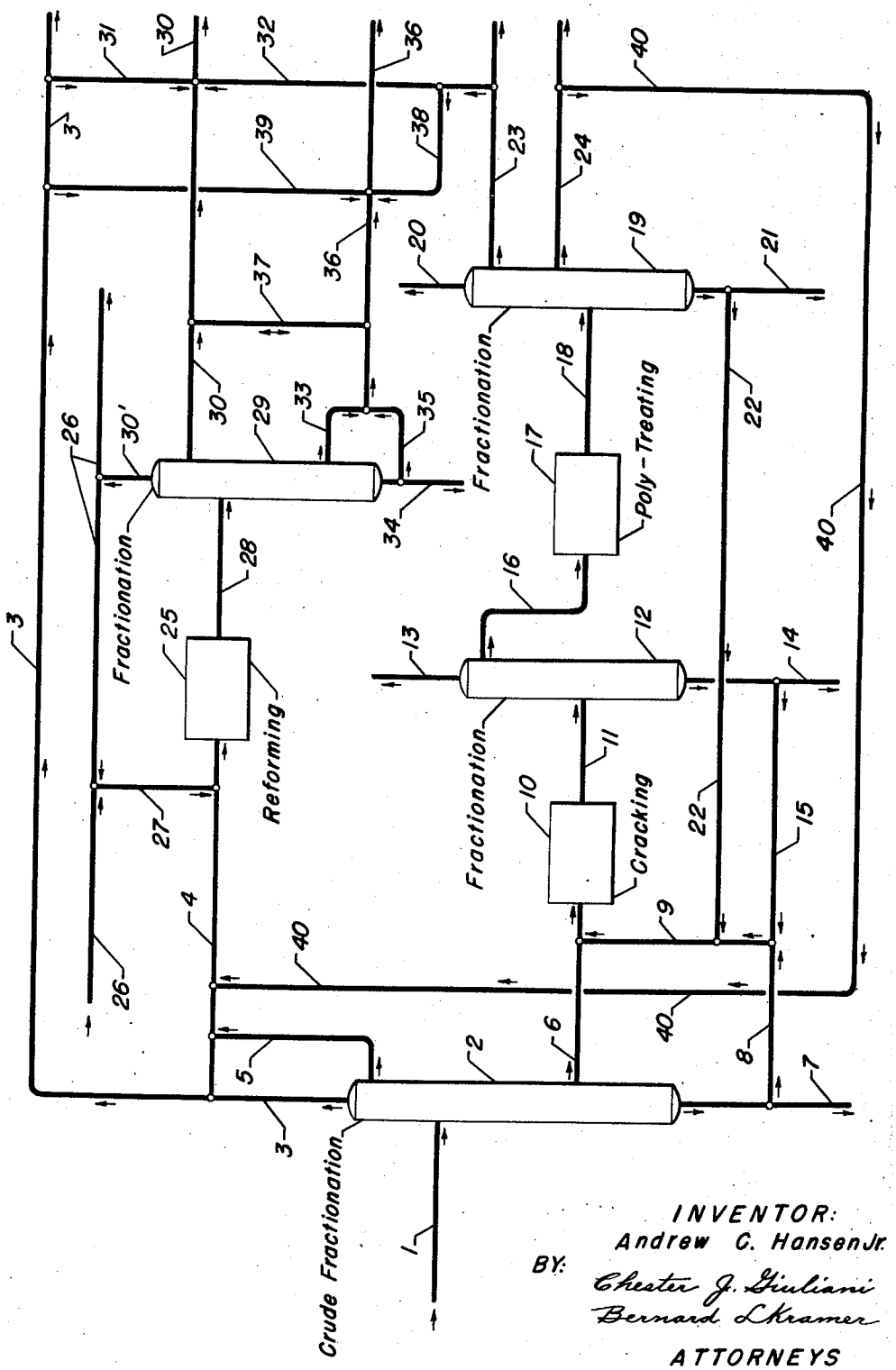
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PRODUCTION OF HIGH OCTANE GASOLINE

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PRODUCTION OF HIGH OCTANE GASOLINE

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The present invention relates to a novel process for the production of high octane gasoline and comprises a combination of mutually related and interdependent steps.

At the present time, high octane gasoline is obtained in one method by blending catalytically reformed gasoline and catalytically cracked gasoline, with or without light straight run fractions, and adding lead tetraethyl (TEL) to the blend. As the demand for higher octane gasoline increases, it is necessary to increase the severity employed in the catalytic reforming process and also to increase the concentration of TEL added to the gasoline blend. The increase in reforming severity results in decreased yields and shortened catalyst life. The increase in the concentration of TEL adds considerably to the cost of the gasoline. The present invention provides a novel combination process wherein the higher octane gasoline is obtained without imposing excessive severity to the catalytic reforming process and without increasing the concentration of TEL beyond economical limits.

In one embodiment the present invention relates to a combination process for producing high octane gasoline which comprises fractionating crude oil to separate a gasoline fraction from a higher boiling fraction, reforming said gasoline fraction in the presence of hydrogen to produce a high octane gasoline fraction substantially free of olefinic constituents, cracking said higher boiling fraction to produce a gasoline fraction containing olefinic constituents, separating the last-mentioned gasoline fraction and poly-treating the same to produce a gasoline fraction of reduced olefin content and of improved TEL susceptibility, and blending at least a portion of the last-mentioned gasoline fraction with the high octane gasoline fraction produced by said reforming.

The invention will be explained further with reference to the accompanying flow diagrammatic drawing which illustrates several specific embodiments thereof.

Referring to the drawing, crude oil is introduced to the process through line 1 and is supplied to crude fractionation zone 2. In the interest of simplicity, zone 2 is illustrated as a single column, although it is understood that it may comprise two or more separate fractionating zones, which may be operated at atmospheric, subatmospheric and/or superatmospheric pressures. The exact conditions of operation of the crude fractionation will depend upon the particular crude oil charged and the particular products desired. These conditions are well-known in the art and need not be described in detail in the present application. Regardless of the particular method employed, the crude oil is separated into a gasoline fraction and a higher boiling fraction, along with whatever other fractions are desired. In one embodiment, the gasoline fraction comprises a full boiling range gasoline, including components having an initial boiling point of from about 60° to about 120° F. and an end boiling point of from about 350° to about 450° F. The gasoline fraction is withdrawn from zone 2 through line 3 and is supplied through line 4 to reforming in the manner to be hereinafter set forth. In another embodiment the gasoline fraction comprises a selected higher boiling cut, generally referred to as naphtha and having an initial boiling point within the range of from about 150° to about 300° F. and an end boiling point within the range of from about 350° F. to about 450° F. In this embodiment a light gasoline fraction is withdrawn from the upper portion of zone 2 through line 3 and is directed through a continuation of this line for blending in the manner to be hereinafter set forth, while the high boiling gasoline fraction or so-called naphtha is withdrawn from zone 2 through line 5 and is passed through line 4 for reforming in the manner to be hereinafter described.

In the embodiment illustrated in the drawing, a gas oil fraction is separated in zone 2 and withdrawn therefrom through line 6 and sent to cracking zone 10, while a higher boiling fraction is withdrawn from the lower portion of zone 2 through line 7. The composition of the fraction withdrawn through line 6 will vary with the particular refinery operation and may comprise components boiling as low as kerosene or heavy naphtha and as high as reduced crude. When it is desired to charge a bottoms product from zone 2 to cracking, this may be accomplished by withdrawing the bottoms product through line 7 from zone 2 and passing the same by way of lines 8, 9 and 6 to cracking zone 10. As hereinbefore set forth, it is understood that selected fractions desired for other purposes may be withdrawn from zone 2 in any suitable manner, not illustrated, and these fractions may, for example, be of the nature of kerosene, specialty products, diesel fuel, lube oil, or asphalt.

In zone 10 the fraction to be cracked is subjected to contact with a cracking catalyst at cracking conditions. The cracking conditions include a temperature of from about 800° to about 1200° F. and a pressure of from atmospheric to about 200 pounds per square inch. Any suitable catalytic cracking process may be employed and preferably comprises the type now known in the art as fluidized catalytic cracking, in which process the charge and catalyst are maintained in a state of turbulence under hindered settling conditions in a reaction zone. In this process the catalyst is continuously supplied to a regeneration zone, wherein carbonaceous deposits are burned from the catalyst by contact with an oxidizing gas, for example air, and the regenerated catalyst is continuously returned to the reaction zone. Examples of other suitable cracking processes which may be employed are the fixed bed type, the moving bed type and the suspensoid type of operation.

Any suitable cracking catalyst may be employed in zone 10 and preferably comprises a composite of silica and alumina, the alumina comprising from about 5 to about 40% by weight of the catalyst composite and the remainder comprising silica. Examples of other suitable cracking catalysts are composites of silica-zirconia, silica-alumina-zirconia, silica-thoria, silica-alumina-thoria, silica-magnesia, silica-alumina-magnesia and alumina-boria. These catalysts may be synthetically prepared or naturally occurring, and the latter preferably are treated, for example with acid, to improve their activity. The synthetic catalyst may be prepared in any suitable manner.

The cracking products are directed from zone 10 through line 11 to fractionation zone 12. Here again, zone 12 may comprise two or more suitable separation zones. In the case illustrated, normally gaseous products are withdrawn from zone 12 through line 13, and heavy products are withdrawn therefrom through line 14. When desired, all or a portion of the heavy products may be recycled by way of lines 15, 9 and 6 to cracking zone 10 for further conversion therein. Specialty products, kerosene, diesel oil, fuel oil, or other selected product frac-

tions may be withdrawn from fractionating zone 12 in any suitable manner not illustrated.

Cracked gasoline is withdrawn from zone 12 through line 16 and is directed to poly-treating zone 17. In zone 17 the cracked gasoline is subjected at elevated temperature to contact with a catalyst which reduces the olefinic content of the gasoline.

In a preferred embodiment, the catalyst employed in zone 17 is a composite of phosphoric acid and kieselguhr, such a composite being available commercially under the name of "solid phosphoric acid." This catalyst contains about 65–70% of higher H_2O content than the meta acid phosphoric acid and the remainder is kieselguhr. It is understood that any other suitable phosphoric acid catalyst may be employed in this step of the process. When using the solid phosphoric acid catalyst, the temperature employed is within the range of from about 350° to about 750° F. and preferably from about 400° to about 600° F. and the pressure is from about 100 to about 2000 pounds or more per square inch and preferably from about 500 to about 1500 pounds per square inch, utilizing a liquid hourly space velocity (defined as the volume of charge per hour per volume of catalyst in the reaction zone) of from about 0.1 to about 10 and preferably from about 0.5 to about 5. With this catalyst, it is believed that the reactions which occur include those of conjunct polymerization. This conjunct polymerization involves a plurality of reactions including the polymerization of olefins to higher olefins, cyclization of higher olefins to naphthenes, dehydrogenation of the naphthenes to aromatics, and hydrogenation of olefins present in the original gasoline to paraffins by the hydrogen formed in the aforesaid dehydrogenation. The net result of this operation is that a gasoline fraction of reduced olefin content is obtained since the polymerization, aromatization and hydrogenation all decrease olefin content.

In another embodiment, a catalyst of the same composition as that described above for use in the cracking step of the process is utilized in zone 17. This catalyst and particularly silica-alumina, silica-alumina-zirconia, silica-magnesia, or silica-alumina-magnesia, serves to reduce the olefin content of the gasoline. In this embodiment, the temperature employed is below that used in the cracking operation and will range from about 500° to about 800° F. and preferably from about 650° to about 750° F., and the pressure will range from atmospheric to 1500 pounds per square inch or more, and preferably from about 50 to about 500 pounds per square inch, while using a liquid hourly space velocity of from about 0.1 to about 10 and preferably from about 0.5 to about 5.

It is understood that reference to poly-treating and poly-treating catalyst includes the two embodiments hereinbefore set forth. The range of operating conditions thus includes a temperature from about 350° to 800° F., a pressure from atmospheric to 2000 pounds per square inch or more, and a liquid hourly space velocity of from about 0.1 to about 10, the specific conditions being dependent upon the particular catalyst employed.

The poly-treated gasoline has a reduced olefin content. In some cases, the poly-treated gasoline will be of higher octane number than the cracked gasoline prior to poly-treating. In other cases, the octane number of the poly-treated gasoline may be substantially the same as the untreated cracked gasoline but, in any event, the gasoline will be of improved susceptibility to tetraethyl lead and, therefore, will result in a higher octane number product upon the addition of the same concentration of tetraethyl lead than is obtained with the untreated cracked naphtha. This, in turn, means that the reforming step of the process, to be hereinafter described, may be operated at lower severity and, therefore, with longer catalyst life, and also that a lower concentration of tetraethyl lead is required to obtain the high octane gasoline product.

The poly-treated products are directed from zone 17 through line 18 into fractionation zone 19. Here again, it is understood that zone 19 may comprise two or more separation zones but, in the interest of simplicity, it is illustrated as a single zone. The separation effected in zone 19 will depend upon the particular refinery operation but, in general, will comprise separating normally gaseous components, gasoline boiling range components and higher boiling material. The gasoline components may be separated either as a single fraction or as a light gasoline and a heavy gasoline or naphtha fraction. The normally gaseous components are withdrawn from zone 19 through line 20 and may be supplied to any desired use. The heavier components are withdrawn from zone 19 through line 21 and may be withdrawn from the process or recycled, all or in part, by way of lines 22, 9 and 6 to cracking zone 10 for conversion therein into lower boiling material.

In the case illustrated in the drawing, a light gasoline fraction is withdrawn from zone 19 through line 23 and a heavy gasoline fraction is withdrawn therefrom through line 24. The specific split between the light and heavy gasolines may vary with the particular refinery operation. Generally the end boiling point of the light fraction and accordingly the initial boiling point of the heavy fraction will be within the range of from about 150° to about 250° F. At least a portion of the poly-treated gasoline is blended with the reformed products in the manner to be hereinafter set forth.

The full boiling range gasoline or the naphtha fraction withdrawn from crude fractionation zone 2 by way of line 4 is subjected to reforming in zone 25. The reforming is effected in the presence of hydrogen introduced to the process through line 26 and supplied to zone 25 through lines 27 and 4 and/or hydrogen recycled within the process in the manner to be hereinafter described.

The reforming is effected at a temperature of from about 800° to about 1100° F. and preferably from about 900° to about 1000° F. and a pressure of from about 100 to about 2000 pounds per square inch and preferably from about 500 to about 1000 pounds per square inch, utilizing a space velocity of from about 0.1 to about 10 and preferably from about 1 to about 5. Any suitable reforming catalyst may be employed and preferably a platinum-containing catalyst is used. A particularly desirable reforming process is the "platforming" process which utilizes a catalyst comprising a composite of alumina, platinum in a concentration of from about 0.1 to about 3% by weight and combined halogen in a concentration of from about 0.2 to about 8% by weight. Other platinum-containing catalysts comprise composites of platinum with silica-alumina, silica-zirconia, silica-magnesia, or the like, preferably treated to reduce cracking activity, or platinum composited with alumina, silica or other suitable carriers. In some cases, catalysts comprising composites of alumina-molybdenum oxide, alumina-molybdenum oxide-cobalt oxide, alumina-vanadium oxide, or the like, which composites also may contain silica, may be used in the reforming step of the present process, but generally these catalysts are not as effective as the platinum-containing catalysts for producing high octane gasoline.

Regardless of the particular reforming process employed, more severe operation is required to obtain higher octane products. As the severity, including increased temperature and pressure and decreased space velocity, is increased, the activity of the catalyst is adversely affected. One explanation is that the use of more severe conditions results in the simultaneous production of by-products which deactivate the catalyst. The "platforming" process is flexible and can withstand high severity, but even in this process there is a point where the increased severity does impair the catalyst life. Therefore, it is advantageous to operate the reforming process at the lowest severity which will produce a gasoline of satisfactory

octane number upon blending with other gasoline fractions. For example, it generally is necessary to produce a reformed gasoline of higher octane number than the final blended product because the reformed gasoline is blended with lower octane gasoline and the final blend possesses an octane number intermediate the two.

The reformed products are withdrawn from zone 25 through line 28 and are subjected to separation in fractionation zone 29. Here again, only one zone is illustrated in the drawing, although two or more separation zones may be employed. In the case here illustrated, hydrogen is withdrawn from the upper portion of zone 29 through line 30 and, while a portion may be withdrawn through an extension of line 26, at least a portion of the hydrogen preferably is recycled by way of lines 26, 27 and 4 to reforming zone 25. The particular separation of the reformed gasoline in zone 29 will depend upon the refinery market conditions and these include both aviation gasoline and motor gasoline. In one embodiment, aviation gasoline or high octane motor gasoline is formed by separating the reformate into a light fraction and a heavy fraction in zone 29, the light fraction being withdrawn through line 30 and blended with all or a portion of the light straight run fraction separated in zone 2 and passed by way of lines 3 and 31 to commingle with the light reformate in line 30. When desired, poly-treated gasoline, and particularly the light fraction thereof, may be directed by way of lines 23 and 32 to blend with the gasoline in line 30. Also, when desired, all or a portion of the heavy reformate separated in fractionation zone 29 may be withdrawn through lines 33 or lines 34 and 35 and directed through lines 36 and 37 to blend with the gasoline in line 30. In another embodiment, two separate blends of gasolines are produced, one blend comprising the light gasoline fraction separated in zone 2 with the low boiling reformate as hereinbefore described, and the other comprising a blend of heavy reformate and the poly-treated gasoline. In this embodiment, the poly-treated gasoline, either full boiling range or a light fraction thereof, is withdrawn from zone 19 through line 23 and directed through lines 32 and 38 to line 36, where it blends with heavy reformate withdrawn from zone 29 through lines 33 or 35. In some cases, depending upon the particular refinery operation, a portion of the light gasoline fraction separated in zone 2 is directed through lines 3 and 39 to commingle with the blend in line 36. It will be seen from the above description that the present process provides great flexibility in permitting the refiner to prepare different blends to meet the market demands.

As hereinbefore set forth, fractionation in zone 29 will depend upon the particular operation desired and, in some cases, means may be provided for the withdrawal of a heavy reformate bottoms through line 34 for other uses. Similarly, in some cases, the poly-treated gasoline is separated in zone 19 into a light and heavy fraction and only the light fraction is used for blending. The heavy fraction then is supplied by way of lines 24 and 40 into line 4 to be subjected to reforming in zone 25 for the production of high octane gasoline components to be used in the blend or otherwise as desired.

From the above description, it is seen that an improved process for the production of high octane gasoline is presented. The poly-treating step of the process permits lower severity operation in the reforming zone and this results in longer on-stream times with the concomitant increased efficiency thereof. The cracking step of the process furnishes the cracked gasoline as charge to the poly-treating step of the process.

In the interest of simplicity, valves, pumps, heaters and similar appurtenances have been omitted from the drawing. It is understood that these will be provided as required.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

A Kuwait crude oil is subjected to atmospheric and vacuum distillation in a series of zones to separate about 10% by volume of a light gasoline fraction having an end boiling point of 200° F., about 13% by volume of a naphtha fraction having a boiling range of from about 200° to about 400° F., and about 15% by weight of gas oil, in addition to other fractions desired for other uses, including kerosenes, diesel fuel and asphalt. The gas oil fraction is subjected to catalytic cracking in a fluidized operation, utilizing a silica-alumina catalyst, at a temperature of about 900° F. and a superatmospheric pressure of about 10 pounds per square inch. This results in the production of about 50% by volume of cracked gasoline. This cracked gasoline is subjected to poly-treating in the presence of a solid phosphoric acid catalyst at a temperature of 500° F. and a pressure of 1000 pounds per square inch, utilizing a liquid hourly space velocity of about 3. The poly-treated gasoline is fractionated to separate a light fraction having an end boiling point of about 200° F. and a heavy gasoline fraction having an end boiling point of about 400° F. The bromine number of the cracked gasoline is reduced from about 50 to less than about 20.

The naphtha originally separated from the crude oil is subjected to reforming in the presence of hydrogen in a mol ratio to hydrocarbon of 10:1, at a temperature of 1000° F. and a pressure of 500 pounds per square inch in the presence of a catalyst comprising alumina, about 0.4% by weight of platinum and about 0.4% by weight of combined halogen, the latter comprising a mixture of combined fluorine and combined chlorine. The reformed products are fractionated to separate a gasoline fraction having a clear octane number of about 95. Hydrogen separated from the reformed products is recycled within the process.

The reformed gasoline of 95 clear octane number is blended with the light poly-treated fraction and with the light straight run gasoline previously separated in the first fractionation. Tetraethyl lead is added in a concentration to produce a final blend of 100 leaded octane number. In addition to being of this high octane number, the blend is a full boiling range gasoline and is readily marketable as premium motor fuel.

When it is desired to also produce aviation gasoline, the different streams are blended to produce the aviation gasoline, to which tetraethyl lead is added to obtain the required octane number, and the remaining products are blended to produce only premium motor fuel or a mixture of premium and regular motor fuel as desired. From the above, it is apparent that considerable benefits are obtained by the novel combination process herein set forth.

Example II

In another operation similar to that described in Example I, the catalyst employed in the poly-treating step is a composite of silica and 10% by weight of alumina. The cracked gasoline is subjected to poly-treating at 735° F. and a pressure of 920 pounds per square inch. The bromine number of the gasoline is reduced to less than 20, and the leaded octane number of the gasoline is increased about 7 numbers over that obtained with the untreated cracked gasoline.

I claim as my invention:

1. A combination process for producing high octane gasoline which comprises fractionating crude oil to separate a gasoline fraction and a higher boiling fraction, reforming said gasoline fraction in the presence of hydrogen to produce a high octane gasoline fraction substantially free of olefinic constituents, cracking said

higher boiling fraction to produce a gasoline fraction containing olefinic constituents, separating the last mentioned gasoline fraction and poly-treating the same to produce a gasoline fraction of reduced olefin content and of improved TEL susceptibility, and blending at least a portion of the last mentioned gasoline fraction with the high octane gasoline fraction produced by said reforming.

2. The process of claim 1 further characterized in that said reforming is effected in the presence of a catalyst comprising alumina and platinum.

3. The process of claim 2 further characterized in that said catalyst also contains combined halogen.

4. The process of claim 1 further characterized in that said poly-treating is effected in the presence of a solid catalyst containing phosphoric acid, at a temperature of from about 350° to about 750° F. and a pressure of from about 100 to about 2000 pounds per square inch.

5. The process of claim 1 further characterized in that said poly-treating is effected in the presence of a catalyst comprising silica and alumina, at a temperature of from about 500° to about 800° F. and a pressure of from about atmospheric to about 1500 pounds per square inch.

6. The process of claim 1 further characterized in that said first-mentioned gasoline fraction comprises a heavy gasoline fraction which is subjected to reforming, a light gasoline fraction also is separated by fractionation of said crude oil, and a portion of the light gasoline fraction is blended with the reformed gasoline and poly-treated gasoline fractions.

7. The process of claim 1 further characterized in that the gasoline fraction from said poly-treating is seperated into light and heavy fractions, the light fraction being blended with at least a portion of the reformed gasoline fraction, and the heavy fraction is subjected to reforming in commingled state with said first-mentioned gasoline fraction.

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