

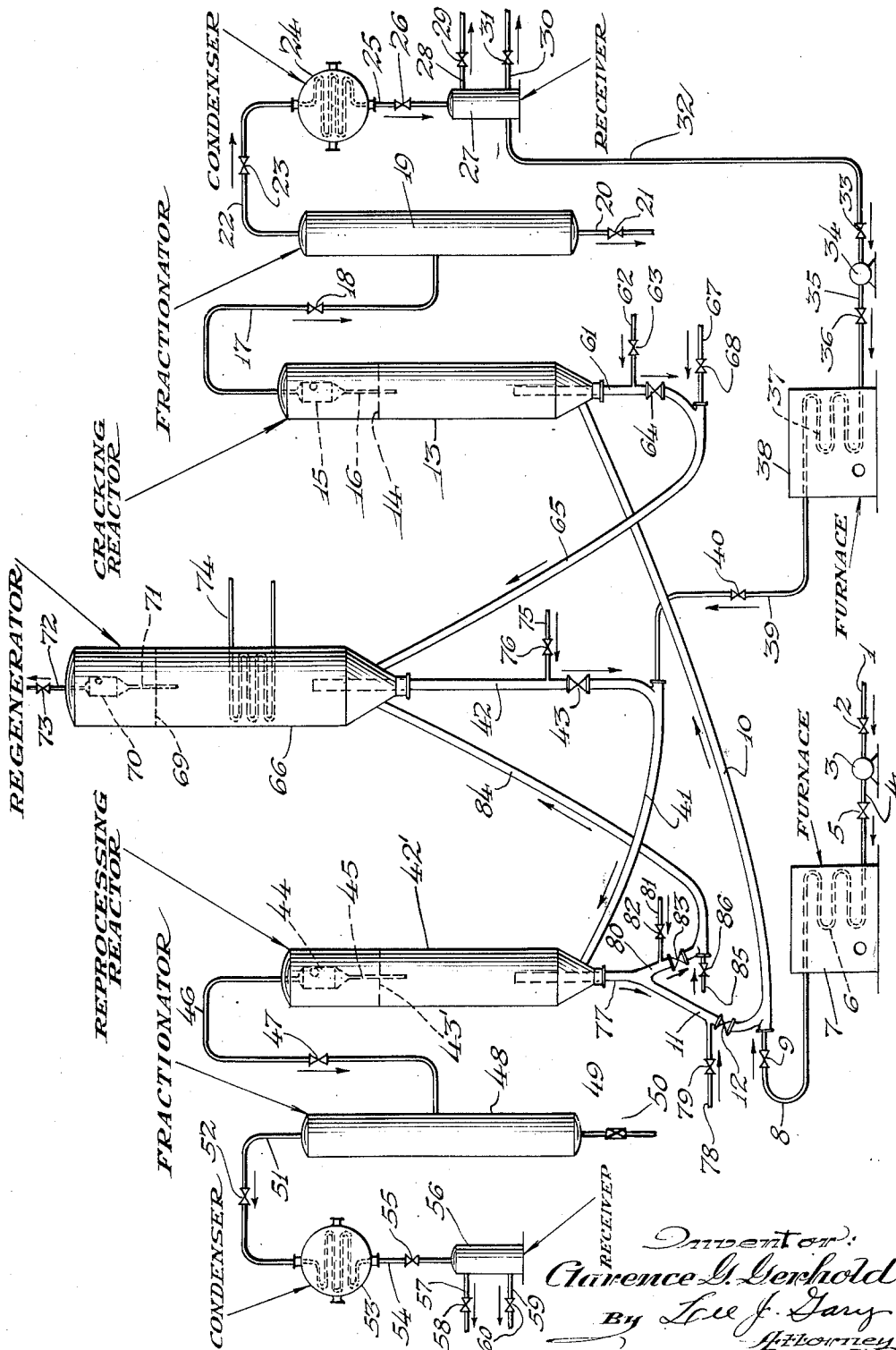
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HYDROCARBON CONVERSION

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HYDROCARBON CONVERSION

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This invention relates to a method for the conversion of hydrocarbons boiling higher than gasoline into gasoline boiling range fractions. More specifically it is concerned with a method for the preparation of gasoline having not only a high initial octane number but also a high lead susceptibility.

A recent development in the reforming art has been the so called "iso-forming" process in which an olefinic gasoline is contacted with a cracking catalyst at temperatures usually of the order of 950 to 1050° F., at high space velocities ranging from 5 to 50, and at low catalyst to oil ratios of less than about .05, to increase the octane number of the gasoline fraction. In such process, apparently the olefins contained in the gasoline are isomerized into olefins of a higher antiknock value resulting in an increase in the octane number of the entire gasoline amounting to from 3 to 8 points. However, the olefin content of the naphtha fraction is substantially unchanged by the process.

In contrast to that operation a process has also been developed for drastically reducing the olefin content of an olefinic gasoline by contacting the gasoline with a cracking catalyst of the same type at temperatures usually ranging from 700 to 900° F. and at relatively low space velocities ranging from .05 to 2. In the latter saturation operation apparently some of the olefins are cyclicized and dehydrogenated, the resulting free hydrogen then serving to hydrogenate other olefin molecules. In this manner the olefin content of the naphtha fraction is greatly reduced, while the paraffin and aromatic content of the fraction is considerably increased. By such low temperature operation, however, little if any increase in octane number is obtained and a slight decrease in octane number is the general rule.

The present invention provides a method not only for drastically reducing the olefinic content of an olefinic hydrocarbon fraction but also for increasing the octane number of the fraction treated in this processing operation. These advantages result when the operating conditions in the reprocessing step, particularly temperature and catalyst-to-oil ratio, are carefully controlled.

It is an object of this invention, therefore, to increase the octane number and reduce the olefinic content of an olefin-containing naphtha fraction by contacting said fraction with a cracking catalyst at a temperature of from about 900 to about 1050° F. while employing a catalyst to oil ratio of from about 5:1 to about 30:1.

A combination process involving a catalytic cracking step to produce an olefinic naphtha from a higher boiling oil and a reprocessing step such as that just described, possesses many advantages since, according to this process, an aviation gasoline may be readily produced from a heavy oil such as gas oil or topped crude. In the reprocessing step a highly active catalyst is required to bring about the saturation reaction to any great extent, whereas in the cracking step a somewhat less active catalyst is desirable since less gas is produced thereby.

Therefore another object of this invention is to provide for a combination operation in which partially spent catalyst obtained from the processing step is used in the cracking step, the catalyst thereafter being regenerated and returned to the reprocessing step for further use.

In one specific embodiment the present invention comprises a process for the production of a gasoline of low olefin content and high octane number from a hydrocarbon oil heavier than gasoline which comprises cracking said oil in the presence of a partially spent catalyst obtained as hereinafter set forth to produce an olefinic naphtha fraction, contacting said naphtha fraction at a temperature of from 900 to 1050° F. with a freshly regenerated catalyst obtained as hereinafter set forth while employing weight ratios of catalyst to oil ranging from about 5:1 to about 30:1, thereby reducing the olefin content of said naphtha fraction, regenerating the spent catalyst removed from the cracking step, contacting the regenerated catalyst with said naphtha fraction as hereinbefore set forth, and supplying the partially spent catalyst so obtained to the cracking step as hereinbefore set forth.

The accompanying drawing illustrates diagrammatically in side elevation one specific form of the apparatus that may be employed in conducting the process of this invention.

Referring now to the drawing, the charging oil for this process which may comprise any hydrocarbon oil heavier than gasoline, such as kerosene, gas oil, topped crude or the like, is supplied through line 1 and valve 2, pump 3, line 4 and valve 5 to heating coil 6 disposed in furnace 7, wherein the charge is heated to a temperature such that on subsequent contact with a cracking catalyst the mixture will be at reaction temperature. The hydrocarbons from coil 6 are supplied through line 8 and valve 9 into transfer line 10, in which they are commingled with a partially spent catalyst obtained as hereinafter set forth

and supplied through line 11 and valve 12. At this point the weight ratio of catalyst to oil is in the range of from about 1:1 to 8:1. The suspension of catalyst in oil vapor is supplied through transfer line 10 to the cracking reactor 13 wherein the hydrocarbons are bubbled upward through a turbulent mass of powdered catalyst. In the cracking reactor a sufficient amount of catalyst is maintained in suspension so that the ratio of the weight of oil charged per hour to the weight of catalyst in the reactor (weight space velocity) is usually maintained in the approximate range of from 1 to 6, the temperatures in this zone usually ranging from about 850 to 1100° F., and as a rule the higher temperatures are employed with the higher space velocities. Low pressures, usually less than 50 pounds gage, are preferred in the reactor.

In reactor 13 a separation of the catalyst into two "phases" is the usual occurrence, the lower phase, having a very high catalyst concentration ranging from 10 to 25 pounds per cubic foot, and the upper phase which is separated from the lower phase by a "meniscus" 14, having a low catalyst concentration which decreases as the vertical distance above the "meniscus" increases. Hydrocarbon vapors are withdrawn from the upper phase through cyclone separator 15 wherein entrained catalyst is separated from the vapors and returned to the dense phase by means of line 16. The vapors are then withdrawn through line 17 and valve 18 and supplied to fractionator 19 wherein a vapor of the desired end point is separated from higher boiling products, the latter being removed through line 20 and valve 21. The vapor, which may have an end point range from 300 to 500° F. is withdrawn through line 22 and valve 23, cooled in condenser 24, and supplied through line 25 and valve 26 to receiver 27 wherein the condensed liquid is separated from the uncondensed gas. The gases are withdrawn through line 28 and valve 29, while a portion of the liquid may if desired be withdrawn through line 30 and valve 31.

All or a portion of the distillate is supplied through line 32 and valve 33, pump 34, line 35 and valve 36 into heating coil 37, disposed in furnace 38, wherein it is heated to a temperature of such degree that on subsequent contact with hot regenerated catalyst the mixture will be at reaction temperature. The heated hydrocarbons are then supplied through line 39 and valve 40 into catalyst transfer line 41 wherein they are contacted with hot regenerated catalyst supplied through catalyst stand pipe 42 and valve 43. The heat content of the catalyst serves to vaporize the hydrocarbons, if vaporization was not effected in coil 6, so that the material flowing through line 41 usually has the properties of a vapor or gas of relatively low viscosity carrying a high concentration of catalyst dust.

The relative weight of the catalyst and the oil commingled in line 41 is of the utmost importance in establishing the type of reaction which is likely to predominate in the reaction zone to which this catalyst-oil mixture is supplied. As previously noted, in order to effect reduction of olefin content, the weight ratio of catalyst to oil at this point should range from about 5 to 1 to about 30 to 1. Ordinarily when the catalyst to oil weight ratio is less than the lower limited mentioned above, the desired reduction in the olefin content is not effected, although a very slight reduction may occur. On the other hand if the weight ratio of catalyst to oil is substantial-

ly higher than the above mentioned upper limit, difficulties in operation are encountered in transporting a fluid containing such a high catalyst concentration.

The suspension of catalyst in oil vapor is supplied to reprocessing reactor 42', wherein the catalyst is added to a bed of powdered catalyst maintained in a turbulent state by the upward passage of hydrocarbon vapors therethrough. In reactor 42' the temperature is maintained within range of 900 to 1050° F. and the pressure is usually less than about 50 pounds. A weight space velocity ranging from 1 to 8 is employed, the higher weight space velocity being employed at the higher temperature to prevent excessive cracking of the naphtha charge.

In reactor 42' as in reactor 13, a separation of the catalyst into two "phases" separated by a "meniscus" 43' occurs. The hydrocarbon vapors containing entrained catalyst are separated therefrom in cyclone separator 44, the catalyst being returned to the dense phase by means of line 45. The hydrocarbon vapors are withdrawn through line 46 and valve 47 and supplied to fractionator 48, wherein a distillate of the desired end point is separated from the higher boiling bottoms the latter being withdrawn through line 49 and valve 50. The vapor is supplied through line 51, valve 52, condenser 53, line 54 and valve 55 to receiver 56 wherein uncondensed gases are separated from the distillate. The gases are withdrawn through line 57 and valve 58 and the distillate through line 59 and valve 60. The distillate may be stabilized and subjected to any further desired treatment. When this process is operated according to the specified conditions a highly suitable aviation blending stock is obtained after stabilization of the distillate.

The spent catalyst from reactor 13 is withdrawn from the reactor through catalyst stand pipe 61, wherein it is contacted with an upwardly rising stream of inert gas such as steam supplied through line 62 and valve 63, the purpose of this gas being to fluidize the catalyst so that a smooth continuous flow will result and to remove volatilizable hydrocarbons from the surface of the catalyst. The spent catalyst is then supplied through valve 64 into catalyst transfer line 65 through which it is "lifted" to regenerator 66 by means of oxygen containing gases supplied through line 67 and valve 68. In the regenerator as in the reactors, a bed of powdered catalyst is maintained in a state of turbulence by an upwardly rising stream of oxygen containing gas which serves to remove carbonaceous deposits from the surface of the catalyst by combustion, thereby restoring its activity. Again a separation of the catalyst into two "phases" occurs, the "meniscus" separating the "phases" being denoted by line 69. Spent regenerating gas containing entrained catalyst is supplied to cyclone separator 70, wherein the entrained catalyst is separated and returned to the dense "phase" by means of line 71. Vent gases are then removed through line 72 and valve 73. It should be noted at this point that additional separation equipment may be provided to separate the entrained catalyst from the vapors leaving either of the reactors or from the vent gases leaving the regenerator if more complete separation of the catalyst is required.

It is usually necessary to provide a method for cooling the catalyst bed in the regenerator since if temperatures are allowed to get out of control

damage to the catalyst may result. For this reason a cooling coil 74 may be supplied in the regenerator to control the temperature of the dense "phase." Alternatively, by means not shown, a portion of the dense "phase" may be withdrawn from the regenerator, passed through a cooler, and returned to the regenerator thereby cooling the entire mass of catalyst undergoing regeneration.

Hot regenerated catalyst, usually at a temperature in the range of from 1000 to 1200° F. is withdrawn through stand pipe 42 wherein it is "fluidized" and stripped of oxygen containing gas by an inert gas such as steam supplied through line 75 and valve 76. The regenerated catalyst is, as previously noted, then combined with hydrocarbons in line 41 and supplied to reprocessing reactor 42'.

Partially spent catalyst from the reprocessing reactor is withdrawn through stand pipe 77 wherefrom all or a portion of the catalyst is supplied through stand pipe 11 and valve 12 into line 10 for use in cracking reactor 13. A fluidizing and stripping medium such as steam is supplied through line 78 and valve 79 to the catalyst being withdrawn through stand pipe 11.

In some cases the catalyst withdrawal rate from reactor 42' is greater than the catalyst supply rate required in reactor 13. When this situation exists a portion of the partially spent catalyst withdrawn from reactor 42' through stand pipe 77 is directed through stand pipe 80, wherein it is "fluidized" and stripped by inert gas added through line 81 and valve 82. The stripped catalyst is passed through valve 83 and supplied by means of line 84 to regenerator 66, an oxidizing gas such as air being added to the stream of catalyst through line 85 and valve 86. It is seen, therefore, that the rate at which catalysts are supplied to and withdrawn from reactor 42' may be made equal to or greater than the rate at which catalyst is supplied to and withdrawn from reactor 13, such a method providing for extreme flexibility of operation.

The following example is intended to illustrate operating conditions that are employed in this process and the effect of these operating conditions on the quality of the product.

A heated gas oil having an A. P. I. gravity of 35° is contacted with a partially spent silica-alumina cracking catalyst at a weight ratio of catalyst to oil of 3 to 1 and the resultant suspension is supplied to the cracking reactor wherein the catalyst is kept in "fluidized" state by the hydrocarbon vapors passing upward therethrough. In the reactor an average temperature of about 925° F. and an average pressure of about 10 pounds gage is employed. A weight space velocity of 2 is maintained, the catalyst being continuously withdrawn from the dense "phase" at the same rate as that at which it is supplied. The hydrocarbon vapors are separated from entrained catalyst and fractionated to remove a distillate having a 325° F. end point.

The distillate is heated and commingled with a freshly regenerated silica-alumina catalyst obtained as hereinafter set forth, a catalyst to oil weight ratio of about 15:1 being employed. The suspension of catalyst in oil vapor is supplied to the reprocessing reactor wherein the vaporous hydrocarbons are bubbled upward through a turbulent mass of powdered catalyst. In this reactor a temperature of 970° F. and a pressure of about 10 pounds gage are employed, while a weight space velocity of 2.5 is maintained. Entrained

catalyst is separated from the product vapors and the latter are fractionated to separate a 300° F. end point distillate from the bottoms. This distillate, which is then stabilized to a 7 pound Reid vapor pressure is suitable as an aviation fuel blending stock, and possesses properties which will be described later.

The spent catalyst from the cracking reactor is regenerated in a vessel in which the catalyst is maintained in a fluid state by upwardly rising oxygen containing gases. The temperature in this vessel is maintained at about 1100° F. by heat exchange with a suitable fluid. Hot regenerated catalyst is then contacted with the distillate produced in the cracking step and supplied to the reprocessing reactor as previously described. Catalyst is continuously withdrawn from the reprocessing reactor at substantially the same rate as that at which it is supplied to the reactor and is combined with the fresh charging oil as previously set forth to be supplied to the cracking reactor.

When operating in this manner one may obtain from the reprocessing step a 300° F. end point gasoline having a bromine number of 19, an octane number of 80, and an octane number of 94 on the addition of 4 cc. of tetra ethyl lead per gallon of gasoline. Such a gasoline is highly suitable as an aviation fuel blending stock since it not only has a high initial octane number but also a high lead susceptibility as a result of its low olefin content.

In contrast to the above operation, when a catalyst to oil ratio of less than about 5:1 is employed in the reprocessing step the product is generally unsuitable for use as an aviation fuel because of its high olefin content and relatively low lead susceptibility.

For example, if the reprocessing zone is operated separately on an olefinic gasoline such as that produced by the cracking zone in this operation, while employing a catalyst to oil ratio of only 2:1 (the temperature and space velocity being the same as the previous operation) a 300° F. end point distillate having a bromine number of 48, a clear octane number of 80 and an octane number of 87 on the addition of 4 cc. of tetra ethyl lead per gallon is obtained.

I claim as my invention:

1. A process for producing gasoline of low bromine number and high octane number which comprises cracking hydrocarbon oil heavier than gasoline in the presence of a used cracking catalyst, thereby forming olefinic gasoline, separating the catalyst and regenerating the same, commingling freshly regenerated catalyst from the regenerating step and olefinic gasoline products of the cracking step and subjecting the resultant mixture to a temperature of from about 900° F. to about 1050° F. while maintaining a catalyst-to-oil weight ratio of from about 5:1 to about 30:1, then separating the catalyst from the treated gasoline products and supplying at least a portion thereof to the heavy oil cracking step as said used catalyst.

2. A process for producing gasoline of low bromine number and high octane number which comprises cracking hydrocarbon oil heavier than gasoline in the presence of a used cracking catalyst, thereby forming olefinic gasoline, separating the catalyst and regenerating the same, commingling freshly regenerated catalyst from the regenerating step and olefinic gasoline products of the cracking step and subjecting the resultant mixture to a temperature of from about 900° F.

to about 1050° F. while maintaining a catalyst-to-oil weight ratio of from about 5:1 to about 30:1 and a weight space velocity of from about 1 to about 8, then separating the catalyst from the treated gasoline products and supplying at least a portion thereof to the heavy oil cracking step as said used catalyst.

3. The process as defined in claim 1 further characterized in that said catalyst comprises silica and alumina.

4. The process as defined in claim 2 further characterized in that said catalyst comprises silica and alumina.

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