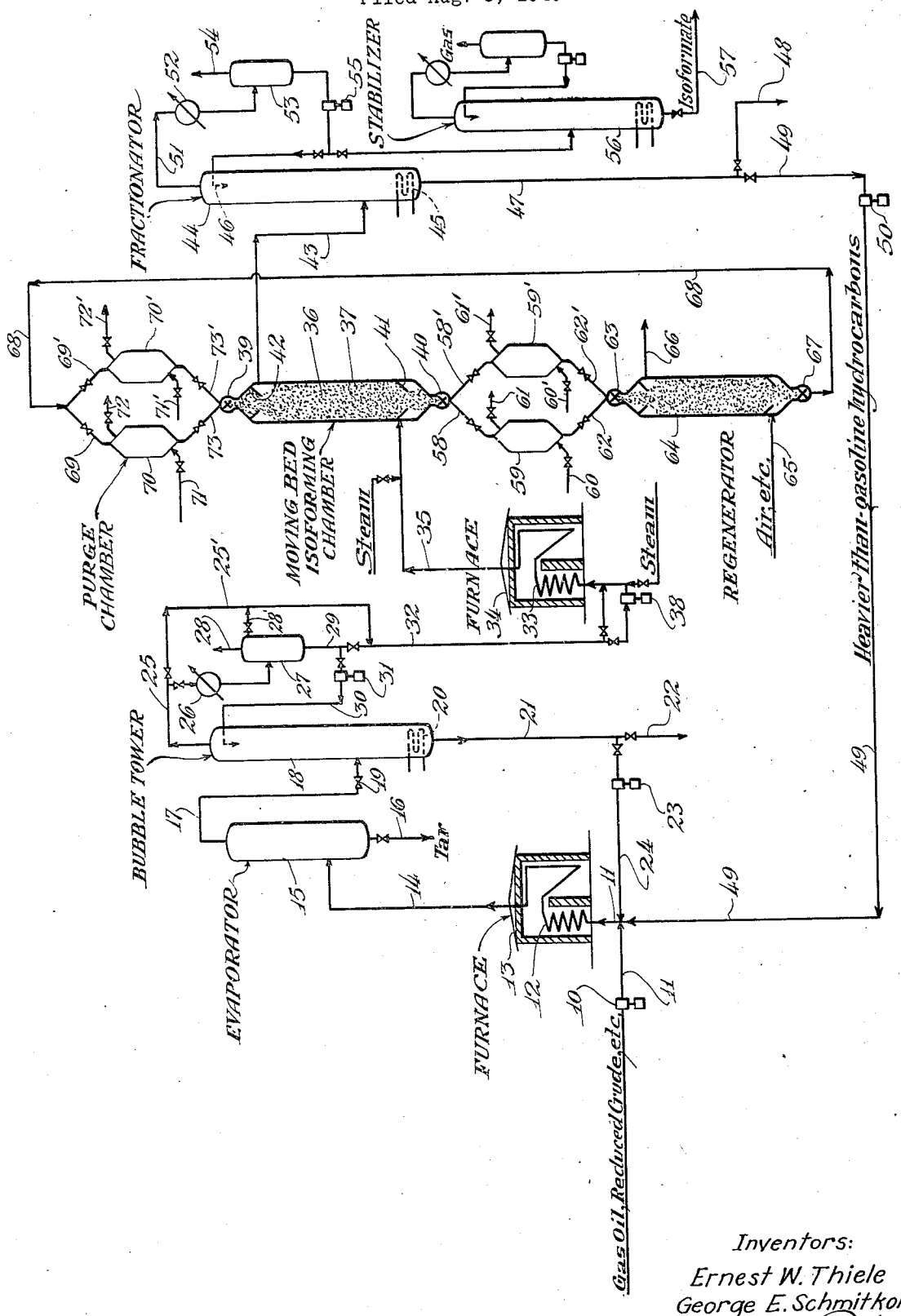
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ISOFORMING

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ISOFORMING

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This invention relates to an improved method of making high antiknock motor fuels from charging stocks consisting essentially of gas oils and heavier hydrocarbons.

Heretofore, most motor fuel has been produced by thermal cracking and most refineries are, therefore, equipped with thermal cracking systems. Demands for higher octane number gasoline have given rise to a new problem because the maximum octane number obtainable by commercial thermal cracking is about 65 to 74 CFR—M. Furthermore, thermally cracked naphtha is not sufficiently responsive to tetraethyl lead to make it commercially feasible to obtain the desired higher octane numbers by this route. Hence refiners have turned to expensive and complicated processes of catalytic cracking, destructive hydrogenation, hydroforming, aromatization, alkylation, isomerization, polymerization, etc. We have discovered that the problem can be solved most advantageously and economically by subjecting thermally cracked naphtha to a simple high temperature contacting with a catalyst to effect what we term "isoforming."

In catalytic reforming and cracking processes the yield-octane curve tends to flatten out, but it does not bend backwards; in isoforming we have found that yield-octane curve actually does bend backwards, showing a definite optimum octane number with a yield of 94 to 99%, the maximum in most cases being with a yield of about 96% to 97%. Also in catalytic reforming and cracking the octane number is gradually lower with increasing space velocities, while in the isoforming reaction there is a definite peak in the curve. At atmospheric or low pressures and with active catalysts this peak usually is within the range of 4 to 12 volumes of liquid thermally cracked naphtha per volume of catalyst space per hour. At high pressures of the order of 125 pounds per square inch the peak is usually within a space velocity range of 20 to 40.

Isoforming is distinctly different from all prior art processes in that it employs thermally cracked naphtha as its charging stock and in that it produces almost 100% yields based on this charging stock as the result of surprisingly low losses to gas, coke and heavier-than-gasoline hydrocarbons.

Thermally cracked naphtha has been contacted with clay for improving its stability against gum formation, for lowering its sulphur content, etc. but the conditions of these clay contacting processes have been such that very little if any improvement in octane numbers was accomplished. Both thermal and catalytic reforming or isomerization have been applied to virgin naphtha, but always with yields considerably below 100% and with considerable losses to gas, coke and heavier-than-gasoline hydrocarbons. Hydrogenation, aromatization and hydroforming have been proposed for increasing the octane number of thermally cracked naphtha but experience has shown that thermally cracked naphtha is not particularly responsive to such processes, that only a very small improvement is obtained in octane number and that losses are much higher than those obtainable by isoforming. Innumerable complicated and expensive processes have been proposed in an effort to solve this problem and since it appeared to be practically unsolvable, many refiners are electing to change their refining processes to substitute catalytic cracking, destructive hydrogenation, etc. in order to meet the demands for higher octane number gasoline. Our isoforming process makes it possible to utilize existing thermal cracking equipment and to meet the demands for higher octane number gasoline. Our isoforming process makes it possible to utilize existing thermal cracking equipment and to meet octane requirements with minimum losses to gas and carbon and with a catalyst holding time, i. e. time that the catalyst is on stream in the reactor, which far exceeds the catalyst holding time possible in catalytic cracking processes. An important feature of the isoforming process is the fact that it markedly increases the susceptibility of the finished gasoline, which we call isoformate, to tetraethyl lead. In addition to obtaining increases of 5 to 15 octane numbers at a relatively high octane number level, we obtain the advantage of increased responsiveness to lead tetraethyl.

Isoforming has practically no effect on catalytically cracked naphtha. We have discovered, however, that the gas oil from a catalytic cracking process may be thermally cracked to give a thermally cracked naphtha which does respond to the isoforming treatment. Thermal cracking evidently ruptures the molecules to form a different type of naphtha than is formed by catalytic processes. The initial thermal cracking step is thus an essential element of our combined process. The thermal cracking should preferably be effected at relatively high temperatures and low pressures, i. e. at about 900° to 1050° F. and about atmospheric to 200 pounds per square inch, although pressures of 300 pounds or even

higher pressures may be advantageously used. Thermally cracked naphtha produced at high temperature and low pressure gives much greater octane improvement by isoforming than is given by naphthas from low pressure-low temperature thermal cracking or high pressure-high temperature thermal cracking. The coking process described in our co-pending application No. 311,778 is a very special type of thermal cracking and while coker naphtha is, generally speaking, in a class by itself, it is one species of thermally cracked naphtha. Our present invention is applicable to all types of thermally cracked naphtha. The expression "thermally cracked naphtha" as used in this specification refers only to naphtha produced by the thermal cracking of gas oil and other hydrocarbon charging stocks which boil above the gasoline boiling range. The species of the invention hereinafter described will be the isoforming of naphthas from conventional thermal processes, referred to as continuous pressure stills and as "combination" cracking which latter includes a mixture of thermally cracked naphthas from various parts of the combination unit.

A particular feature of the present invention is the use of a moving bed catalyst system preferably at high temperatures. In catalytic cracking pressures must be below 50 pounds per square inch in order to obtain the desired yields, product distribution, octane number, etc. In our isoforminb process either low or high pressures may be used, from atmospheric up to about 200 pounds per square inch. At the higher pressures higher space velocities will be required, and the sizes of equipment, lines, etc., will be reduced. In catalytic cracking there is an increase in yield and lowering in octane number with increased space velocities. In our isoforming process both yield and octane numbers will be an optimum at the same space velocity, which will depend on the conditions of operation as to pressure, temperature, catalyst, and feed.

In catalytic cracking approximately the same results are obtained on fixed bed units as are obtained on moving bed units. The moving bed operation in the isoforming process results in a greater octane number improvement than could be obtained in a fixed bed with any possible combination of space velocity and time between regenerations. Furthermore, in the isoforming process less catalyst will have to be regenerated for a given amount of naphtha treated in moving bed operation than in fixed bed operation.

In fixed bed isoforming operation the quality and yield of the isoformate vary continuously during the whole period on stream for naphtha conversion between regenerations whereas in moving bed operation the quality and yield of the isoformate do not vary with time (when other conditions are held constant) and by proper selection of space velocity are substantially the same as the best instantaneous results obtained in fixed bed operation. Hence a better yield and octane number can be obtained with moving bed operation than for any space velocity in fixed bed operation at the same holding time, temperature, etc.

In catalytic cracking processes it is desirable to employ as short a catalyst holding time as possible and to employ space velocities of the order of one or two volumes of liquid feed per volume of catalyst space per hour. In our isoforming process the optimum catalyst holding time is much longer, even in fixed bed operation. As noted above, it may be extended even further in moving bed operation. The circulation of the catalyst is one of the objectionable points in moving bed operation, involving danger of catalyst crushing, and complicated machinery. However, this low rate of circulation in isoforming makes the moving bed process particularly advantageous. The temperatures for the isoforming step may range from 850 to 1150° F. but optimum results are obtained at a temperature of about 900 to 975° F.

A feature of our process is the direct combination of thermal cracking with moving bed isoforming wherein the products of the thermal process, which have been separated from gas oil, may be directly utilized in the isoforming process without stabilization and without loss of substantial pressure. We thus provide a unitary high pressure system wherein at least a substantial part of the pressure employed in the thermal cracking step is carried forward and utilized in the isoforming step.

The invention will be more clearly understood from the following detailed description and from the accompanying drawing which forms a part of this specification and which is a diagrammatic flow sheet of our process.

The charging stock to our system may be a Mid-Continent gas oil although it may comprise a gas oil from any other source and it may include any hydrocarbons heavier than gasoline, i. e. reduced crudes, residual stocks, etc. Any conventional thermal cracking process may be employed for preparing the feed stock for isoforming, but a thermal cracking pressure is preferred which is sufficient to supply the necessary pressure in the isoforming step. The temperatures and pressures of thermal cracking may vary throughout a wide range and "once through" thermal cracking as distinguished from recycling processes may be used.

In the drawing we have diagrammatically illustrated thermal cracking of the continuous pressure still type wherein gas oil is forced by pump 10 through line 11 to coils 12 of pipe still furnace 13 under a pressure of about 300 pounds per square inch and a temperature of about 925° F. The thermally cracked products are then introduced by transfer line 14 either directly or through a conventional soaking drum (not shown) to evaporator 15 which is provided with a tar draw-off line 16 at the bottom. Cracked naphtha gas oil and gases are taken overhead through line 17 leading to a bubble tower 18. A pressure reducing valve 19 may be employed in line 17 if it is desired to obtain the fractionation in the bubble tower at lower than reaction pressures.

A reboiler 20 at the base of the bubble tower insures the removal of all of the naphtha from the gas oil which gas oil is withdrawn from the base of the tower through line 21 and which may be withdrawn from the system through line 22 or recycled by pump 23 and line 24 to line 11 for further cracking.

The naphthas and lighter hydrocarbons are taken overhead through line 25 through cooler 26 and then introduced into a gas separator or receiver tank 27 from which gases are vented through line 28 and liquid naphtha is withdrawn through line 29. A portion of the naphtha is recycled through line 30 by pump 31 for reflux in top of bubble tower 18. The remainder of the naphtha is introduced through line 32 to the isoforming step of our process. A feature of our invention is the fact that the thermally cracked naphtha does not have to be stabilized before it is

introduced to the isoforming system. In fact the total overhead products from tower 18 may be introduced directly to line 32 through line 25' when no part of it is required for reflux in tower 18. Alternatively, cooler 26 may condense only the liquid required for reflux and naphtha and vapors may pass through lines 28' and 25' to line 32 for charging to the isoforming process.

The thermally cracked naphtha for our isoforming process should have an end point of about 400° to 450° F. It should be substantially free from gas oil since such material tends to foul the catalyst and to interfere with the proper operation of the isoforming process. The boiling range of the thermally cracked naphtha may be relatively wide, but the greatest improvement is effected in the high boiling portions. The lower limit of this boiling range may be lower than 100° F. and in fact normally gaseous hydrocarbons may be beneficial in reducing the partial pressure of the thermally cracked naphtha undergoing the isoforming treatment. In other words, when normally gaseous hydrocarbons are employed with the naphtha the overall pressures may be superatmospheric while the effective pressure is only atmospheric or even sub-atmospheric.

The thermally cracked naphtha produced as hereinabove described may have an olefin content of about 25–70%, an octane number of about 60 to 70 CFR–M and an A. P. I. gravity of about 50–60. A feature of our process is the octane improvement obtained at this relatively high octane level.

This thermally cracked naphtha is passed through coils 33 of pipe still furnace 34 and thence through transfer line 35 into moving catalyst bed 36 in chamber 37. The pressure may be from atmospheric to 200 pounds per square inch or more but is preferably about atmospheric to 50 pounds per square inch. If necessary a pump 38 may be employed in line 32 for obtaining this desired pressure.

The temperatures employed for isoforming may range from about 850 to 1150° F. and beneficial results may even be obtained at lower temperatures. Our preferred temperature is about 925° F. and we have found that temperatures of about this order of magnitude, i. e., about 900 to 975° F. or even higher offer extremely important and wholly unexpected advantages in the amount of charging stock which can be treated by a given amount of catalyst. In previous catalytic processes, catalyst life was prolonged by the use of relatively low temperatures but in the isoforming process the catalyst may treat about ten to fifteen times as much feed stock between regeneration of the catalyst without loss of yield or octane number in the finished product when operating at 925° F. as could be obtained by operating at 850° F. The distribution of by-products is not the same for 50 barrels per ton at 850° F. as for 720 barrels per ton at 925° F. but since the amount of by-products is so extremely small in the isoforming process this matter is not of great importance. The important fact is that about ten to fifteen times as many regenerations would have to be performed for a process at 850° F. as for a process at 925° F. when operated at the same space velocity. Only about one-sixth as much coke would have to be burned off per regeneration at the lower temperature but about 2.6 times the total coke would have to be burned per barrel of feed. Our invention contemplates the use of a relatively wide temperature range but the extremely important and unexpected advantages of the high temperature isoforming, i. e. temperatures of about 900 to 975° F., makes this feature one of particular importance.

The catalyst employed in bed 36 is preferably of the type generally employed for cracking virgin gas oils and heavier hydrocarbons for obtaining gasoline of high octane number. Activated hydrosilicate of alumina has been found to give excellent results. Such catalysts may be prepared from acid treated bentonite by making a dough of such bentonite and water, forming pellets, and thoroughly drying said pellets by heating to a temperature of about 850 to 1000° F. The catalyst may also be prepared by depositing alumina or other metal oxides on silica gel by impregnation with appropriate salts of the metals. Examples of such other metal oxides are copper, magnesium, beryllium, and thorium. Cadmium, titanium, manganese, zirconium, vanadium and cerium have shown slight activity in particular catalysts tested. A ball-milled 50–50 mixture of magnesium oxide and silica gave less coke and less gas than the preferred alumina-on-silica-gel catalyst, but it likewise gave less octane number improvement. Catalysts of the natural or synthetic zeolite type may be employed, preferably after sodium is displaced or leached out of the catalyst. Catalyst may be obtained by the treatment of blast furnace slag with hydrochloric acid followed by coagulation of the acid solution, washing and drying. Acid treated clay commonly marketed as Super Filtrol can be formed into catalyst pellets of high activity and long life. Applicants are not herein claiming any novelty in the catalyst per se but they do not employ catalysts of the dehydrogenation, hydroforming or aromatization type. Generally speaking, catalysts of the dehydrogenation or aromatizing type, such as bauxite, activated alumina, or oxides of certain metals, (such as those of chromium, tungsten, nickel, or molybdenum) on alumina, are inferior and may be detrimental. Likewise, ordinary untreated clays are inferior in the isoforming process.

The holding time in chamber 37 is the amount of time required for any particle of catalyst to pass through the chamber or the time required for discharging one reactor volume and simultaneously charging with fresh or regenerated catalyst. We may use holding times of the order of 3 to 60 hours, preferably about 6 to 30 hours, the lower holding times being employed with higher space velocities and pressures. With a temperature of 925° F. and a pressure of 25 pounds per square inch and a space velocity of 8 to 20 volumes of liquid feed per volume of catalyst space per hour, the optimum holding time may be from 24 to 48 hours. The holding time will, of course, depend on the activity of the particular catalyst and on the nature of the charging stock as well as on temperature, pressure and space velocity. Space velocity may range from 4 to 60 volumes of liquid charging stock per volume of catalyst space per hour, a preferred range being about 6 to 20.

Fresh or regenerated catalyst may be continuously or intermittently introduced into chamber 37 through vapor sealed catalyst charging means 39 and spent catalyst may be withdrawn at the same rate through vapor sealed catalyst discharge means 40. Either concurrent or countercurrent catalyst to vapor flow may be employed. In the drawing, countercurrent flow is illustrated, the hot cracked naphtha vapors being introduced into the space underneath inclined

baffle plate 41 and the products of the isoforming being withdrawn from the space below inclined baffle 42. These products may be introduced by line 43 into any suitable fractionation system which is diagrammatically illustrated in the drawing as a fractionating tower 44 containing reboiler means 45 and reflux means 46. The small amount of heavy products may be continuously or intermittently withdrawn through lines 47 and 48 or may be recycled through line 49 by pump 50 to the thermal cracking step. Isoformate and gases may be taken overhead through line 51, cooled in cooler 52 and introduced into accumulator or separator tank 53 from which uncondensed gases may be vented through line 54. A part of the condensate is recycled by pump 55 to reflux means 46. The remainder of the condensate passes to stabilizer 56 from which stabilized isoformate is withdrawn through line 57.

The spent catalyst from chamber 37 may be discharged through valved line 58 or 58' into stripping chamber 59 or 59', an inert stripping gas being introduced through line 60 or 60', withdrawn through line 61 or 61'.

The stripped catalyst is then introduced through line 62 or 62' by catalyst transfer means 63 into regeneration chamber 64 which may be similar in type to chamber 37 or which may be a rotary kiln or any other system commonly employed for revivifying catalyst or burning carbonaceous material from clay under carefully controlled temperature conditions. Oxygen containing regeneration gases may be introduced through line 65 and combustion products withdrawn through line 66. The regenerated catalyst may then be discharged from chamber 64 by means of feeder 67 and returned by line 68 through line 69 or 69' to stripper 70 or 70'. Inert stripping gas may be introduced through line 71 or 71' and withdrawn through line 72 or 72'. The stripped regenerated catalyst may be returned to chamber 37 through line 73 or 73'. Steam may be used as the stripping gas and steam, in amounts of 1 to 15% by weight, may be admixed with the thermally cracked naphtha during the isoforming step.

While we have described in detail a preferred embodiment of our invention, it should be understood that the invention is applicable to a fairly wide range of operating conditions and procedural steps but is limited to thermally cracked naphtha charging stocks in the isoforming step.

We claim:

1. The method of improving the knock rating of thermally cracked naphtha which method comprises contacting said thermally cracked naphtha with a moving bed of a catalyst comprising silica and a metal oxide at a pressure of from about atmospheric to 50 pounds per square inch and a temperature of about 875 to 1150° F., retaining the catalyst in the contacting zone for about three to sixty hours and maintaining a space velocity in the contacting zone within the appropriate range of four to sixty volumes of liquid cracked naphtha feed per volume of catalyst space per hour and sufficient to give a liquid yield within the approximate range of 94 to 99 weight per cent and an octane number improvement of at least about 5 A. S. T. M. octane number units.

2. The method of claim 1 wherein the catalyst contains thoria.

3. The method of claim 1 wherein the thermally cracked naphtha is produced by the thermal cracking of heavy hydrocarbons at a temperature of about 900 to 1050° F., and at a pressure not higher than about 300 pounds per square inch.

4. The method of improving the knock rating of a thermally cracked naphtha which comprises contacting said thermally cracked naphtha with a moving bed of a catalyst of which a major part is silica and a minor part is a metal oxide, maintaining the temperature in the contacting step at about 900 to 975° F., maintaining the pressure in the contacting step at about 5 to 25 pounds per square inch, maintaining the catalyst in the contacting zone for a period of about twelve to forty-eight hours, and maintaining a space velocity in the contacting step within the approximate range of six to twenty volumes of liquid thermally cracked naphtha feed per volume of catalyst space per hour and sufficient to give a liquid yield within the approximate range of 94 to 99 weight per cent and an octane number improvement of at least about 5 A. S. T. M. octane number units.

5. The method of claim 4 wherein the metal oxide is alumina.

6. The method of claim 4 wherein the metal oxide is magnesia.

7. The method of claim 4 wherein the metal oxide is thoria.

8. The method of claim 4 wherein the thermally cracked naphtha is produced from the thermal cracking of heavy hydrocarbons at a temperature of about 900 to 1050° F. and a pressure not substantially higher than about 300 pounds per square inch.

9. The method of improving the knock rating of a thermally cracked naphtha which comprises contacting said naphtha with a moving bed of a silica-alumina catalyst at a temperature of about 875 to 1150° F., a pressure of about atmospheric to 25 pounds per square inch and a space velocity within the approximate range of six to twenty volumes of liquid thermally cracked naphtha feed per volume of catalyst space per hour and sufficient to give a liquid yield within the approximate range of 94 to 99 weight per cent and an octane number improvement of at least about 5 A. S. T. M. octane number units.

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