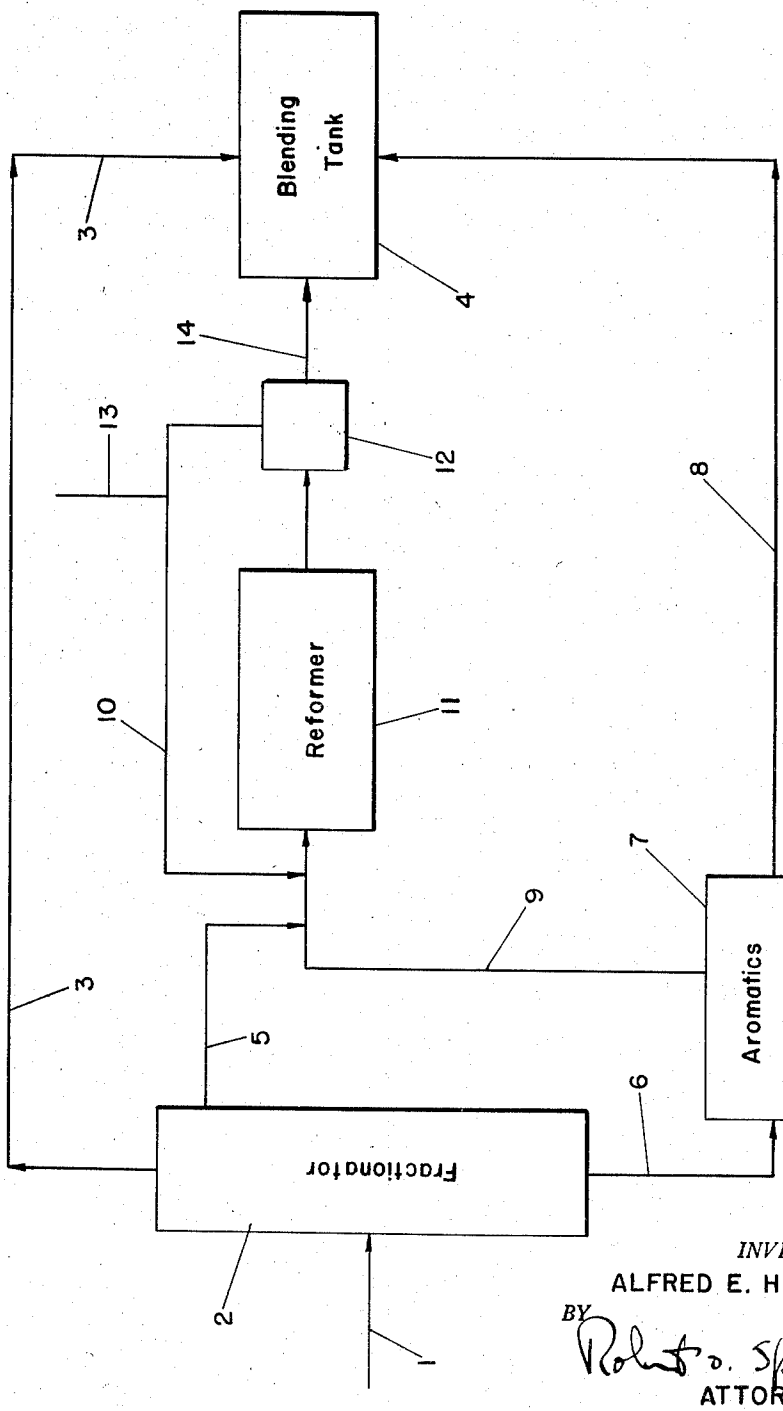
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PROCESS FOR IMPROVING THE QUALITY OF CATALYTIC GASOLINE

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INVENTOR.
ALFRED E. HIRSCHLER
BY Robert O. Spindle
ATTORNEY

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PROCESS FOR IMPROVING THE QUALITY OF CATALYTIC GASOLINE

Alfred E. Hirschler, Springfield, Pa., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

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This invention relates to the up-grading of catalytically cracked gasoline and is concerned more particularly with a combination process in which the gasoline is separated into high and low octane fractions, the low octane fraction is treated to increase its octane number and the fractions are then combined to form a product of very high octane number.

Commercial catalytic gasolines usually have an F–1 clear octane number of from about 88 to 91, which may be improved by the addition of suitable amounts of tetra ethyl lead to octane numbers of about 95 to 98. Such gasoline is satisfactory for use in almost all present-day automobiles, but, with the trend towards higher compression engines, it appears that in the near future gasolines of 100 octane number or higher will be required. Processes have been developed for making 100 octane gasoline from straight run naphthas such as the Rexforming process described in Petroleum Processing for April 1955. Since, however, the straight run naphtha fraction forms only a small part of refinery production in the gasoline boiling range, 100 octane gasoline from this source alone will be insufficient to supply the demand. So far as I am aware, no processes have yet been proposed for up-grading catalytic gasoline, which is the largest volume component in commercial motor gasolines, to 100 octane number. In order to meet the demand for 100 octane gasoline in the future it will be necessary to up-grade catalytic gasolines to this extent. The purpose of this invention is to provide a process for so doing.

The hydrocarbon type composition of catalytic gasoline varies over its boiling range, although the octane number for each fraction is relatively constant. The lower boiling portions of catalytic gasoline may be predominantly olefinic, depending on the catalytic process used, with very little aromatics, while the higher boiling portions of the gasoline such as the fraction boiling over 260° F. may contain from about 40% up to over 90% aromatics. The total aromatics in the gasoline will depend in large part upon the cracking temperatures employed, high temperature cracking for example at 950°–975° F. yielding a gasoline far richer in aromatics than when cracking at 850°–900° F. Proposals have heretofore been made to increase the octane number of this higher boiling fraction by reforming in the presence of added hydrogen, but while some improvement in the octane number is obtained, due to dehydrogenation of the naphthenes present and by isomerization of the paraffins to more highly branched structures, very little improvement due to dehydrocyclization of low octane paraffins to aromatics is obtained, since the presence of such a large amount of aromatics in the fraction tends to inhibit this reaction. So far as I am aware, no proposals have been made for up-grading the fraction boiling below about 260° F.

It is an object of this invention to secure a maximum up-grading of the total catalytic gasoline.

It is a further object of this invention to provide a flexible process for raising the octane number of catalytic

gasoline to any extent desired up to the maximum obtainable.

In accordance with the preferred form of my invention the catalytic gasoline, or the total catalytic crude product, is fractionated to obtain a low boiling fraction, an intermediate boiling fraction, and a high boiling fraction. The cut point between the low boiling fraction and the intermediate boiling fraction is selected to limit the amount of olefins in the non-aromatic portion of the intermediate and higher boiling fractions to that amount for which sufficient hydrogen is available for saturation thereof. Preferably the ratio of olefin to naphthenes and cycloolefins in the intermediate and higher boiling fractions is such that when these hydrocarbons are combined and subjected to a reforming operation there will be a net production of hydrogen resulting from dehydrogenation of naphthenes and cycloolefins to aromatics. While the cut point between the low-boiling fraction and the intermediate fraction will vary to some extent, depending upon the olefin content of the catalytic gasoline treated, it will generally be in the neighborhood of 145 to 170° F.

The lower boiling fraction will contain C_5 hydrocarbons and branched chain C_6 hydrocarbons. Since this fraction will ordinarily contain a large proportion of isopentane and isopentenes, no substantial improvement can be obtained by further treating to isomerize the normal pentane and pentene, so this fraction is segregated and set aside for blending into the finished gasoline without further treatment.

The intermediate fraction, which normally will have an end boiling point of about 260° F. contains very little aromatics, but contains naphthenes and cycloolefins capable of being dehydrogenated to aromatics and paraffins capable of being dehydrocyclized to aromatics or isomerized to higher octane number more highly branched compounds. It also may contain up to 50% non-cyclic olefins. It has heretofore been deemed impracticable from a cost standpoint, to further treat this fraction by reforming, since there are insufficient naphthenes in the fraction to provide, by dehydrogenation thereof, sufficient hydrogen for hydrogenation of the non-cyclic olefins present, resulting in a net consumption of hydrogen and excessive deposition of coke on the catalyst.

As stated above, hydroforming of the total 260° F. plus fraction will result in a mild improvement of octane number but not sufficient to produce a 100 octane gasoline. I have now found that if this higher boiling fraction is separated into two fractions, one containing the aromatics present, preferably together with some or all the olefins, and the other predominately saturated, the saturate fraction may be combined with the intermediate fraction, and the combined fractions will contain enough naphthenes and cycloolefins to yield, when they are subjected to a reforming step, a net production of hydrogen. Since the combined fraction contains very little aromatics, dehydrocyclization will not be inhibited and the reformate will contain a large proportion of high octane aromatics formed from low octane paraffins. The lower boiling fraction, the hydroformate and the aromatic fraction are then combined to form a finished gasoline having an octane number which may be 100 or over, depending on the severity of the conditions in the hydroforming step.

The foregoing procedure is adopted when it is desired to raise the octane number of the gasoline to a maximum. However, it is conceivable that it may be desired to effect only a moderate improvement of octane number. In this case the low boiling fraction and intermediate fraction would be taken as a single cut and passed directly to the finished gasoline, and only the saturate fraction from the higher boiling fraction would

be reformed. This, of course, would reduce the size of the reactor required to effect reforming and reduce capital investment while still permitting a substantial increase in octane number of the final blend over that of the feed. The size of the equipment required for both reforming and aromatics separation may be still further reduced by increasing the cut point between the intermediate fraction and the higher boiling fraction so as to reduce the total amount to be treated, and give the most improvement per dollar of cost. For example, the cut point may be raised to about 300 to 320° F.

In order that those skilled in the art may more fully appreciate the nature of my invention and the method for carrying it out it will be more fully described in connection with the accompanying drawing which is a diagrammatic flow sheet of one form of my new process.

As illustrated in the drawing, a catalytically cracked gasoline which may boil between about 90° F. and about 420° F. is taken through line **1** and is passed to a fractional distillation unit **2** from which a lower boiling fraction is taken overhead through line **3** and is passed to gasoline blending tank **4**. The end point of the lower boiling fraction may vary considerably depending on the olefinic content of the catalytic gasoline. For example, when treating a highly olefinic gasoline such as that described in Industrial and Engineering Chemistry, vol. 44, p. 1142 (1952), the end point will preferably be about 170° F., while when treating a catalytic gasoline low in olefins, such as that described in Industrial and Engineering Chemistry, vol. 41, p. 2292 (1949), the end point may be as low as 145° F. An intermediate fraction having an end boiling point of about 260° F. is taken off as a side stream through line **5** while a fraction boiling above 260° F. is taken off through line **6** as bottoms. The end point of the higher boiling fraction will vary with the catalyst used in the susequent reforming step. If a non-regenerative catalyst such as platinum is used, the end point should be about 390° F., whereas if a regenerative catalyst, such as molybdenum oxide is used, an end point as high as 425° F. may be tolerated. The 260° F. plus fraction which contains 80 to 90% of the aromatics in the total gasoline, is then passed to an aromatics recovery unit **7**, which may be an adsorption unit such as the "Arosorb" unit described in Petroleum Refiner, volue 31, number 5, pages 109 to 113 (May 1952 issue), or may be a solvent extraction unit using known solvents such as ethylene glycol, furfural, or phenol. An aromatic extract containing substantially all the aromatics in the fraction and having an octane number in excess of 100 is recovered from the adsorbent or solvent and is sent to gasoline blending tank **4** through line **8**. A low octane raffinate fraction, which consists chiefly of saturates, is recovered through line **9** and is blended with the intermediate fraction. The blended fractions will be a mixture of paraffins, naphthenes, and olefins, together with a small amount of benzene and toluene. A typical analysis for the 170° F. and higher blend from a highly olefinic gasoline, would be paraffins 30%, olefins 30%, cycloparaffins 20.5%, cycloolefins 13.3,%, and aromatics 6.7%; whereas a typical analysis of the 145° F.+ blend from a low-olefin catalytic gasoline migh be 48% paraffins, 7% olefins, 28% cycloparaffins, and 17% aromatics.

The combined fractions are then mixed with recycle hydrogen from line **10** and passed to a reformer **11** which is packed with a hydrogenation-dehydrogenation catalyst such as platinum, molybdena, or chromia supported on alumina or other suitable base. The support preferably also contains an isomerization component such as silica or a halogen.

Conditions in the reformer, preferably a temperature of 750° F. to 1000° F., pressure of from about 200 p.s.i.g. to about 600 p.s.i.g., and space velocity (vol. liquid feed/vol. catalyst/hour) of from 0.5 to 5, are such as to promote formation of aromatics by dehydrocyclization of the paraffins contained therein, although many other reactions may take place. For example, the paraffins may undergo dehydrogenation to form olefins, or isomerization to isoparaffins, or cracking. The naphthenes may undergo isomerization from alkyl C_5 rings to C_6 rings and dehydrogenation to form aromatics. The olefins may be hydrogenated to paraffins which may be subsequently dehydrocyclized, or dehydrogenated to diolefins; they may transfer hydrogen by disproportionation producing molecules of more or less saturation; or they may be isomerized, cyclized, polymerized, alkylated, or cracked. In any event, the overall reaction will proceed in such a manner that a considerable amount of aromatics and branched chain compounds of high octane number will be produced to raise the octane number of the combined fractions by a considerable amount. Under severe conditions, such as low space velocity or high temperatures within the preferred ranges, the octane number of the reformate may be as high as 95 or 100.

From the reformer **11** the products are passed to separator **12** from which hydrogen is removed from line **10** for recycle to the reformer. The amount of hydrogen so recycled should be from about 1 to about 10 moles per mole of feed, excess hydrogen produced being bled from the system through line **13**. The liquid products from the reformer are then passed through line **14** to gasoline blending tank **4** in which they are mixed with the aromatic fraction recovered from the aromatic separation unit and with the low boiling fraction from fractionator **2** to form a finished gasoline of greatly improved octane number as compared to the feed.

As previously pointed out, the intermediate cut is hydroformed only when a maximum increase in octane number is required. If it is desired to increase the octane number only moderately, the side stream taken off through line **5** may be dispensed with, and a fraction boiling up to 260° F. or over may be taken overhead through line **3** and passed directly to blending tank **4**. In operating in this manner, the feed to reformer **11** will consist only of the raffinate from aromatics separation unit **7**, and recycle hydrogen, thus reducing the size of the equipment required in the reforming step. By proper selection of the cut point, the amount of feed to the reformer **11** may be varied over wide limits, and the octane number of the finished blend may thereby be tailored to fit current requirements.

I claim:

1. A process for improving the octane number of catalytically cracked gasoline which comprises distilling a catalytically cracked gasoline comprising olefins to recover a low-boiling fraction, an intermediate fraction poor in aromatics, and a higher boiling fraction rich in aromatics, said higher boiling fraction boiling above about 260° F., the cut point between the low-boiling fraction and the intermediate fraction being so selected that the ratio of olefins to naphthenes and cycloolefins in the intermediate fraction and the higher boiling fraction is such that when the intermediate fraction and an aromatics-lean portion of the higher boiling fraction are combined and subjected to reforming there will be a net production of hydrogen; separating the higher boiling fraction into an aromatics-rich portion and an aromatics-lean portion; mixing the aromatics-lean portion with the intermediate fraction; passing the mixture to a reformer and therein contacting it with a catalyst comprising a hydrogenation-dehydrogenation component, in the presence of added hydrogen, at a temperature of from about 750° F. to about 1000° F., and at a pressure of from about 200 p.s.i.g. to about 600 p.s.i.g.; said pressures and temperatures being correlated to produce an environment in the reactor favoring dehydrocyclization of paraffins; recovering from the reformer a reformate of higher octane number than the feed thereto;

and combining the low-boiling fraction, the reformate, and the aromatics-rich portion of the higher boiling fraction.

2. The process according to claim 1 in which the catalyst also comprises an isomerization component.

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