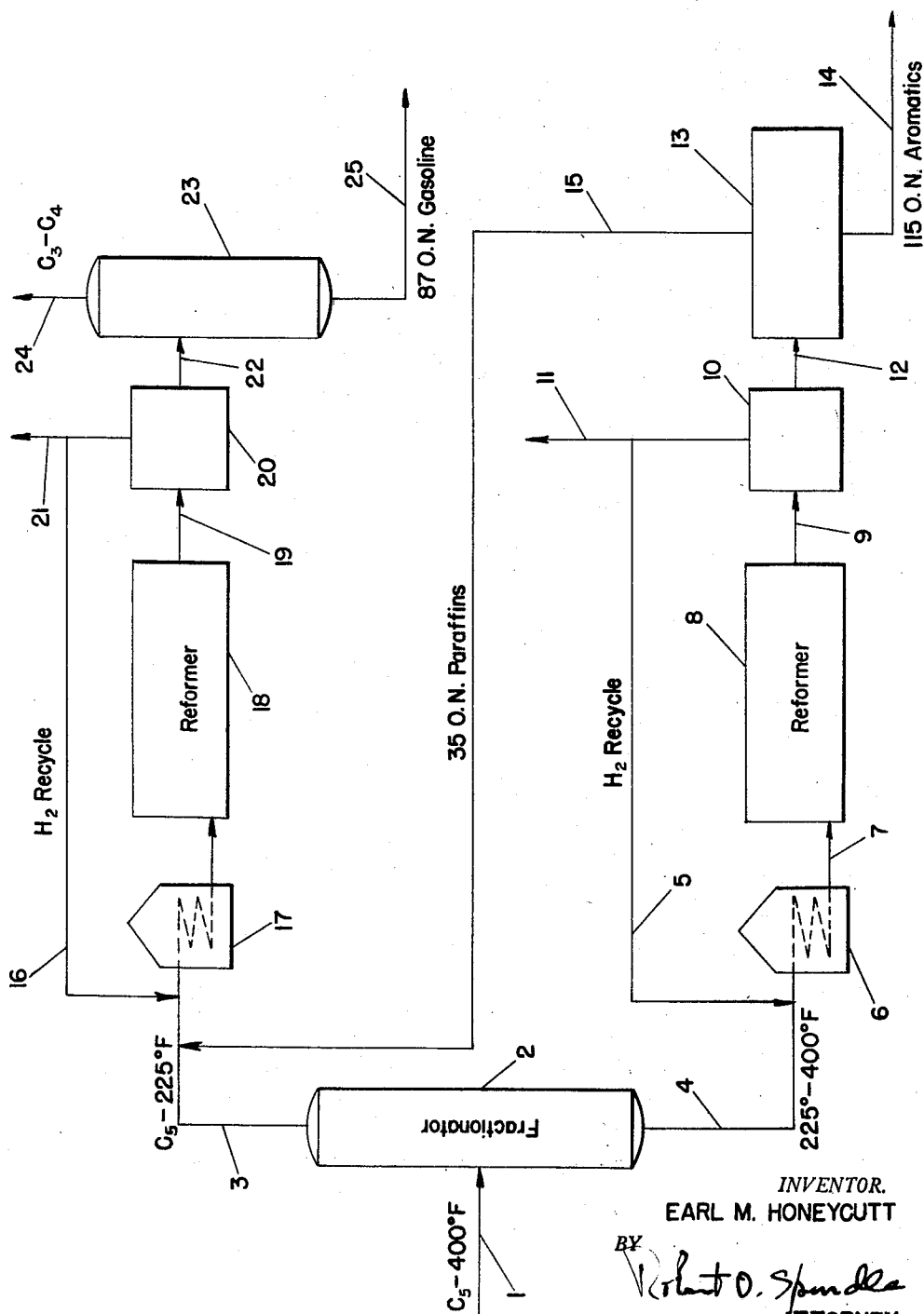


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E. M. HONEYCUTT
REFORMING STRAIGHT-RUN NAPHTHA
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REFORMING STRAIGHT-RUN NAPHTHA

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6 Claims. (Cl. 208—65)

This invention relates to the production of high octane gasoline, and more particularly relates to a process for the catalytic reforming of a naphtha boiling over the full gasoline boiling range wherein the process conditions for treating various fractions are so selected as to insure the maximum isomerization and aromatization of all components of the naphtha to yield a gasoline blend having a very high octane number, while at the same time deactivation of catalyst is minimized.

When hydrocarbons boiling in the gasoline boiling range are reformed in the presence of a hydrogenation-dehydrogenation catalyst, a number of reactions take place, including dehydrogenation of naphthenes to the corresponding aromatics, dehydrocyclization of paraffins to aromatics, isomerization, hydrocracking of saturates to lower molecular weight products, and, when the reforming conditions are severe enough, coke formation, with consequent deactivation of the catalyst. With the exception of coke formation, all of the above reactions are desirable, since the reaction products are all of higher octane rating than the corresponding components of the feed. Dehydrocyclization of paraffins to aromatics is however, more desirable than any of the other reactions since this reaction gives the greatest increase in octane number.

It has been observed that, as the end boiling point of the feed to a reforming process is increased, coke formation increases rapidly, due probably to the presence of bicyclic compounds, or feed impurities that are unstable at reforming temperatures and pressures. When treating a naphtha having a final boiling point of 400° F. to 425° F. it is necessary, therefore, to operate under conditions mild enough to avoid excessive coke formation, the reforming severity being limited by the coke-forming characteristics of the feed. Under these conditions the naphthenes will be dehydrogenated to aromatics in good yield, but very little dehydrocyclization of low octane paraffins to aromatics will take place, and the reformate will not have an octane number as high as could be obtained if the reformer conditions could be made more severe.

In order to obtain a gasoline of higher octane rating than can be obtained by one-pass reforming of a wide-cut naphtha in its entirety, it has heretofore been proposed to separate the naphtha into a higher boiling and a lower boiling cut, and to reform the cuts separately, the lower boiling cut being subjected to more severe reforming conditions than the higher boiling cut. By operating in this manner it is possible to up-grade the lower boiling hydrocarbons to a greater extent and the blended reformates form a gasoline of higher octane number than would be obtained if all fractions were reformed together. For example, Haensel et al. in U. S. Patent 2,659,692 divide a 100–400° F. naphtha into a 100°–200° F. cut and a 200°–400° F. cut and separately reform these fractions, the severity of the operating conditions to which the lower boiling fraction is subjected being at least twice that to which the higher boiling fraction is

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subjected. While an improvement is obtained by so operating, the milder conditions to which the higher boiling fraction is subjected precludes any substantial dehydrocyclization of the low octane paraffins therein contained. Murray et al. in U. S. Patent 2,689,208 disclose a similar process, in which a higher boiling cut is processed at greater hydrogen to hydrocarbon ratio and higher pressure than the lower boiling cut. Here the high hydrogen pressure used in processing the higher boiling cut inhibits dehydrocyclization of low octane, high boiling paraffins, conversion of paraffins being chiefly hydrocracking. Haensel in U. S. Patent 2,698,829 proposes a process in which a high boiling straight run naphtha fraction is reformed under high pressure, the effluent is mixed with a low boiling fraction, and the combined fractions are subjected to a second reforming stage at lower pressures. While the lower pressure in the second reforming stage is conducive to paraffin dehydrocyclization, the large proportion of aromatics in the feed to the second stage, derived from dehydrogenation of naphthenes in the first stage, inhibits any extensive dehydrocyclization of paraffins, due to thermodynamic equilibrium considerations.

Another approach to the problem has been to separate the effluent from a reforming operation into a fraction comprising aromatics and lower boiling non-aromatic hydrocarbons, and a higher boiling, low octane saturate fraction, and to recycle the saturate fraction to the reformer in admixture with fresh feed, as in the Rexforming process described in the April 1955 issue of "Petroleum Processing." By so proceeding the high-boiling saturates may be hydrocracked to higher octane products, but conditions in the reformer must be maintained at a mild enough value to avoid deactivation of the catalyst by coking of the fresh feed components. Under such conditions very little dehydrocyclization of the high-boiling paraffins to super-octane aromatics takes place.

It is an object of this invention to provide a process for reforming a full gasoline boiling range naphtha in which a maximum degree of dehydrocyclization of high-boiling paraffins is obtained, while minimizing catalyst deactivation by coke formation.

In accordance with my invention, naphtha boiling below about 425° F. is fractionated into a lower boiling cut and a higher boiling cut. The final boiling point of the lower boiling cut may vary from about 200° F. to about 275° F., but preferably is in the vicinity of 225° F. The higher boiling cut is reformed in the presence of added hydrogen, and in the presence of a hydrogenation-dehydrogenation catalyst, at a temperature of from about 850°–950° F., and at a pressure of from about 300 p. s. i. g. to about 600 p. s. i. g. The pressure and temperature will be so coordinated that excessive lay-down of coke on the catalyst is avoided. That is, when operating at temperatures in the upper end of the permissible range, higher pressures will be used, while when operating at lower temperatures, lower pressures may be used. Any of the well known hydrogenation-dehydrogenation catalysts such as molybdena, or chromia, or combinations thereof may be used, but I prefer to use a catalyst comprising alumina containing from 0.15 to 2 percent platinum. An acidic component such as a halogen or silica, may also be present in small amount. The hydrogen/hydrocarbon ratio may vary from about 0.5/1 to about 10/1, but generally hydrogen/hydrocarbon ratios of from 2/1 to 6/1 are preferred.

Under these conditions dehydrogenation of naphthenes to the corresponding aromatics will be the predominant reaction, together with some hydrocracking of high boiling paraffins to lower boiling products. A large part of the low octane paraffins present in the feed will, however, pass through the reformer unchanged, since conditions therein will not be severe enough to promote

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any considerable amount of dehydrocyclization. The liquid reformat, after separation therefrom of hydrogen-containing gases, is then passed to an aromatics-separation process in which it is separated into an aromatic fraction, which will usually have a blending octane number of 115 or more, and a paraffinic fraction, of octane number in the order of 35. The aromatic separation process is preferably an adsorption process such as the "Arosorb" process described in "Petroleum Refiner," volume 31, number 5, pages 109-113, or it may be a solvent extraction process using known solvents such as ethylene glycol, phenol, or furfural. Such aromatic separation processes are well known to the art, and need not be further described herein.

The low octane paraffinic fraction is then blended with the lower boiling naphtha fraction and the blend is reformed in the presence of added hydrogen, and in the presence of a hydrogenation-dehydrogenation catalyst, which may or may not be the same type employed in reforming the high-boiling naphtha fraction, at a temperature of from about 875-975° F., and at a pressure of from about 100 p. s. i. g. to about 400 p. s. i. g. The temperature should be at least 20° F. higher, and the pressure should be at least 100 p. s. i. g. lower than when reforming the higher boiling naphtha fractions. The hydrogen/hydrocarbon ratio may be the same as when reforming the higher boiling fraction, but is preferably lower. Since the feed to this reforming stage does not contain as many carbon-forming constituents as the high-boiling naphtha, these relatively more severe operating conditions may be used without danger of excessive coke formation and consequent catalyst deactivation. Under these conditions the naphthenes derived from the low-boiling naphtha will be dehydrogenated to aromatics, and a very considerable amount of paraffins will be dehydrocyclized to aromatics, such dehydrocyclization being induced by the severe reforming conditions. In addition, the very low concentration of aromatics in the feed to this reforming step favors the thermodynamics of dehydrocyclization. The liquid reformat from this reforming stage will have an octane number of from about 85 to 95, depending on the severity of the conditions to which the feed is subjected, and it may be blended with the heavy aromatic fraction previously recovered to yield a gasoline having an octane number in the vicinity of 100.

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

Referring now to the drawing, a C₅-400° F. straight-run naphthenic petroleum fraction is introduced through line 1 into distillation tower 2, from which a fraction boiling to 225° F. is recovered overhead through line 3, while a fraction boiling from 225°-400° F. is recovered as bottoms through line 4. The 225°-400° F. fraction is mixed with recycle hydrogen from line 5, in a molecular proportion of hydrogen to feed of 5:1, and is then passed through furnace 6, in which it is heated to a temperature of 900° F. under a pressure of 500 p. s. i. g. The mixture is then passed through line 7 to reformer 8, in which it is contacted with a catalyst comprising alumina on which has been deposited about 0.3% platinum, under the influence of which naphthenes are dehydrogenated to aromatics and some hydrocracking of paraffins takes place, at a liquid hourly space velocity (vol. feed/vol. catalyst/hr.) of 3. After contact with the catalyst, the products are cooled and passed through line 9 to high pressure separator 10, from which a hydrogen-containing gas is removed through line 5 for recycle, excess hydrogen being bled off through line 11.

The products are then passed through line 12 to an Arosorb unit 13, in which they are separated into an aromatic

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fraction and a paraffinic fraction. The aromatic fraction, which has a blending octane number of 115, is taken off to storage through line 14, while the paraffinic fraction, which has an octane number of 35, is taken through line 15 and is blended with the C₅-225° F. naphtha recovered from distillation tower 2. The blend is then admixed with hydrogen introduced through line 16, in a molar proportion of hydrogen to blend of 3:1. The mixture is passed through furnace 17, in which it is heated to a temperature of 930° F., and is then passed, at a pressure of 300 p. s. i. g., and liquid hourly space velocity of 3, to reformer 18, in which it is contacted with a catalyst comprising alumina and platinum. Under these conditions naphthenes in the C₅-225° F. naphtha component of the feed are dehydrogenated to aromatics, while a considerable proportion of the 35 O. N. paraffinic components of the feed are dehydrocyclized to aromatics. Some hydrocracking and isomerization of the paraffins also takes place.

From reformer 18 the products are cooled and taken through line 19 to high pressure separator 20, from which hydrogen is removed through recycle line 16, excess hydrogen produced in the reaction being bled off through line 21. The products are then passed through line 22 to stabilizer 23, from which C₄ and lower hydrocarbons are removed overhead, and a gasoline product of 87 O. N. is recovered as bottoms and passed to storage through line 25. When blended with the aromatic fraction recovered through line 14, a gasoline blend with an octane number of 98 will result.

As may be seen from the foregoing, I have devised a process in which the higher boiling naphthenes of a full gasoline boiling range naphtha may be upgraded by dehydrogenation to the maximum extent permitted by thermodynamic considerations, while avoiding excessive coke formation, and in which the higher boiling paraffins are upgraded by dehydrocyclization to a great extent, also without excessive coke formation, while simultaneously subjecting the lower boiling fraction to conditions conducive to maximum octane increase. As a result a high yield of very high octane gasoline is obtained.

I claim:

1. A reforming process which comprises distilling a petroleum fraction containing naphthenes and boiling below about 425° F. into a higher and a lower boiling fraction, reforming said higher boiling fraction in the presence of hydrogen and a hydrogenation-dehydrogenation catalyst in a first reforming zone at a temperature between about 850° F. and 950° F., and at a pressure of from about 300 p. s. i. g. to about 600 p. s. i. g., recovering a first reformat from said first reforming zone, separating the first reformat into an aromatic fraction and a paraffinic fraction, admixing the paraffinic fraction with the said lower boiling petroleum fraction, and reforming the mixture in the presence of hydrogen and a hydrogenation-dehydrogenation catalyst in a second reforming zone at a temperature between about 875° F. and 975° F. and at a pressure of from about 100 p. s. i. g. to about 500 p. s. i. g., reforming conditions in the second reforming zone being more severe than in the first reforming zone.

2. The process according to claim 1 in which the temperature in the second reforming zone is at least 20° F. higher than in the first reforming zone, and in which the pressure in the second reforming zone is at least 100 p. s. i. g. lower than the pressure in the first reforming zone.

3. The process according to claim 2 in which the catalyst in both zones comprises platinum and alumina.

4. A reforming process which comprises distilling a naphthenic petroleum fraction boiling between about 90° F. and 425° F. into a higher boiling fraction and a lower boiling fraction, said higher boiling fraction having an initial boiling point between about 200° F. and 275° F., reforming said higher boiling fraction in the presence of

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added hydrogen and a hydrogenation-dehydrogenation catalyst at a temperature between about 850° F. and 950° F., and at a pressure of from about 300 p. s. i. g. to about 600 p. s. i. g., recovering a first reformat 5 from said first reforming zone, separating the first reformat into an aromatic fraction and a paraffinic fraction, admixing the paraffinic fraction with the said lower boiling petroleum fraction, and reforming the mixture in the presence of hydrogen and a hydrogenation-dehydrogena- 10 tion catalyst in a second reforming zone at a temperature between about 875° F. and 975° F. and at a pressure of from about 100 p. s. i. g. to about 500 p. s. i. g., and correlating the temperature and pressure in each reform- 15 ing zone in a manner to obtain maximum octane increase while avoiding deactivation of the catalyst by coke formation.

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5. The process according to claim 4 in which the temperature in the second reforming zone is at least 20° F. higher than in the first reforming zone, and in which the pressure in the second reforming zone is at least 100 p. s. i. g. lower than the pressure in the first reforming zone.

6. The process according to claim 5 in which the catalyst in both zones comprises platinum and alumina.

References Cited in the file of this patent

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2,304,183	Layng et al.	Dec. 8, 1942
2,698,829	Haensel	Jan. 4, 1955