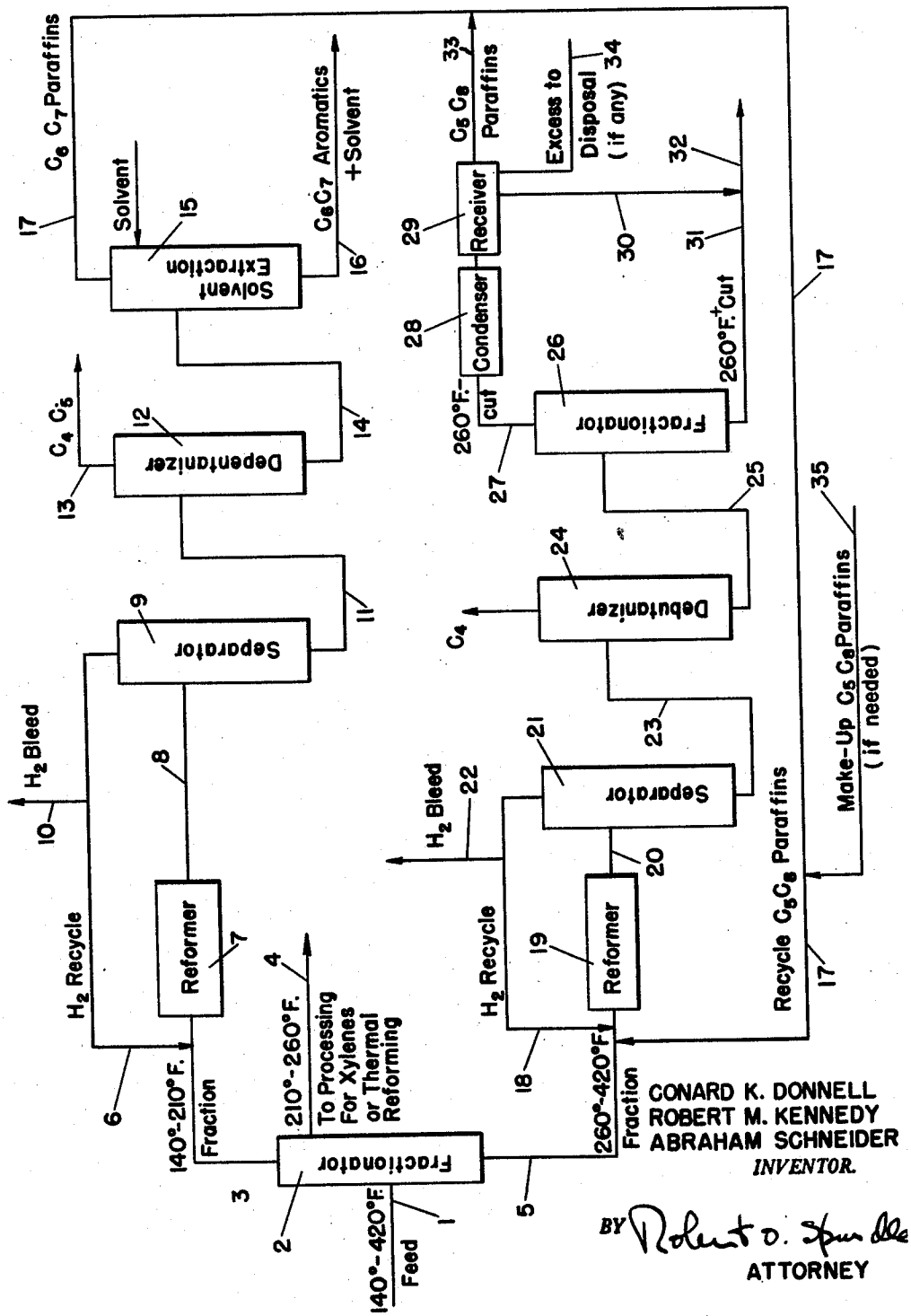
April 19, 1960 C. K. DONNELL ET AL 2,933,445

CATALYTIC REFORMING PROCESS EMPLOYING A BLEND OF SELECTED HYDROCARBON FRACTIONS

Filed April 8, 1955



CONARD K. DONNELL
ROBERT M. KENNEDY
ABRAHAM SCHNEIDER
INVENTOR.

BY Robert O. Stumbles
ATTORNEY

United States Patent Office 2,933,445 Patented Apr. 19, 1960

2,933,445

CATALYTIC REFORMING PROCESS EMPLOYING A BLEND OF SELECTED HYDROCARBON FRACTIONS

Conard K. Donnell, Springfield, Robert M. Kennedy, Newtown Square, and Abraham Schneider, Overbrook Hills, Pa., assignors to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

Application April 8, 1955, Serial No. 500,084

4 Claims. (Cl. 208—64)

This invention relates to the catalytic reforming of gasoline fractions, and more particularly to the reforming of a hydrocarbon feed boiling over the gasoline range, in which that portion of the feed boiling in the C_5–C_8 range contains less than about 10% naphthenes, and contains at least 80% or more C_5–C_8 paraffins.

In the past a great deal of work has been done on processes for upgrading low octane number straight-run naphtha by contact with an appropriate hydrogenation-dehydrogenation catalyst in the presence of added hydrogen, under conditions such that there is no net consumption of hydrogen, to produce a product having a considerably higher octane number than the original feed. Such processes have become known to the art as "Hydroforming," "Platforming," "Houdriforming," or "Catforming," depending on the particular catalyst used. Catalysts particularly suitable for such processes are platinum supported on alumina, platinum on alumina containing 0.1 to 8% combined halogen, and molybdena or chromia on alumina or other supports such as synthetic alumina-silica cracking catalyst, naturally occurring clay, bauxite, and the like. Process conditions usually are temperature—750°–1000° F.; pressure—250–700 p.s.i.g.; H_2/hydrocarbon ratio—0.5:1 to 10:1; and liquid hourly space velocity 0.5 to 5. Reactions taking place under these conditions include dehydrogenation of naphthenes to aromatics, isomerization of paraffins to more highly branched structures, isomerization of cyclopentanes to cyclohexanes, dehydrocyclization of paraffins, and hydrocracking.

In commercial plants using reforming processes of the type described above, the virgin naphtha feed, boiling say from 140° F. to 420° F., may be fractionated into two streams, for example a light naphtha cut boiling from about 140° F. to 260° F., which is separately processed to convert the naphthenes contained therein to benzene, toluene, and xylenes, which are recovered by solvent extraction or adsorption for use as chemical intermediates, and a heavy naphtha cut boiling from about 260° F. to about 420° F., which is separately processed to yield a high octane gasoline. The light naphtha cut may be further divided into a 140° F.–210° F. cut, which is processed to yield benzene and toluene, and a 210–260° F. cut, which may be processed to yield xylenes, or which may be thermally reformed to yield a gasoline blending stream.

The raffinate separated from the aromatics is a highly paraffinic stream with a low octane number, in the range of 50 to 60 (F–1 clear), depending on the chemical composition of the charge, which can be upgraded by further reforming to some extent, but only in the range of 10 octane numbers or so without excessive loss to hydrocracking reactions. With the advent of high compression automobiles, with high octane demands, disposal of this stream presents quite a problem, since, although a portion of it may be blended with high octane cracked gasoline or alkylate, the quantity so used is

necessarily limited by the octane number desired in the blend.

The reformate from reforming the 260°–420° F. naphtha has generally an octane number of 90–100 (F–1 clear) but octane numbers above 90 are only obtainable when operating under severe conditions so that a considerable loss to hydrocracking reactions and coke formation is encountered. Normally, when operating under conditions such that the reformate has an octane number of 90, about 10% of the feed is lost, while, when operating under conditions such that the octane number is raised to a higher value, losses may run to 20% to 25%.

We have now discovered that if a highly paraffinic C_5–C_8 fraction, such as the raffinate from the previously described separation of aromatics, is added to the 260°–420° F. feed prior to reforming, in amounts such that the paraffinic fraction comprises from about 20% to about 80% of the total feed, the following unexpected advantages are obtained:

(1) The total reformate has a much higher yield-octane relationship than when the two streams are reformed separately under the same conditions.

(2) The aromatic content of the 260° F.+ fraction of the reformate is considerably higher than that of the 260° F.+ fraction recovered from the reformate obtained by processing a 260°–420° F. feed without the addition of low-boiling paraffins, and the blending octane number is also considerably higher.

(3) The reformate can be fractionated and blended to yield a 100 blending octane number (F–1 clear) gasoline in yield of better than 100% based on the heavy naphtha charged to the process, whereas a heavy naphtha processed without the addition of light paraffins will, on fractionation, yield 80% or less of 100 blending octane gasoline, based on the naphtha charged.

The accompanying drawing is a flow sheet of a process in which a full boiling range naphtha is processed for aromatic production and for the production of a high octane motor fuel according to the present invention.

A feed in the 140°–420° F. boiling range is introduced through line 1 to a fractionator 2, from which a 140°–210° F. fraction is taken overhead through line 3, an intermediate fraction boiling from about 210° F. to about 260° F. is withdrawn through line 4, and from which a fraction boiling above 260° F. is recovered through line 5.

It will be realized, of course, that the boiling point of these particular fractions are merely selected for illustration, and that the initial boiling point of the heavy naphtha fraction might be considerably lower if desired, for instance, about 230° F. or 240° F. or the intermediate stream may be eliminated, and all constituents of the feed boiling below 260° F. may be taken off overhead.

The light fraction is mixed with hydrogen introduced through hydrogen recycle line 6 and is passed to reformer 7 which contains a hydrogenation-dehydrogenation catalyst such as platinum, molybdena, or chromia, supported on alumina, naturally occurring clay, bauxite or other suitable support. Reaction conditions in the reformer may be as follows:

Temperature 750° to 1000° F., preferably 925° to 975° F.,

Pressure 250 to 700 p.s.i.g., preferably 300 to 400 p.s.i.g.,

Mol ratio of hydrogen to hydrocarbon 1:1 to 10:1, preferably about 5:1 and space rate (liquid volume of feed/volume of reactor/hour) from 1 to 5, and preferably about 3.

From reformer 7 the products are taken off through line 8 to separator 9 in which hydrogen and any non-condensable hydrocarbons produced in the reaction are taken

off through line 6 for recycle, any excess hydrogen produced being removed from the system through hydrogen bleed line 10. The C_4+ hydrocarbons are removed from separator 9 through line 11 and are taken to dependanizer 12 in which C_4 and C_5 hydrocarbons are taken overhead through line 13. The bottoms from dependanizer 12 are passed through line 14 to solvent extraction tower 15 in which the hydrocarbons are contacted with a suitable solvent such as ethylene glycol-water or phenol. While the aromatics-paraffin separation system is illustrated as a solvent-extraction process, it will, of course, be understood that any equivalent process may be used, such as adsorption. A C_6–C_7 aromatic and solvent stream is removed through line 16 for further processing to recover pure aromatics and solvent for recycle, while a saturated C_6–C_7 stream is removed through line 17. The C_6–C_7 fraction consists mainly of paraffins, although up to about 5 to 8% naphthenes, chiefly methyl cyclopentane, may be present. This stream is passed through line 17 and is mixed with the heavy naphtha in line 5. Hydrogen is added through hydrogen recycle line 18 and the mixture is passed to reformer 19 which contains a hydrogenation-dehydrogenation catalyst similar to that in reformer 7. Reaction conditions in reformer 19 may correspond to the conditions in reformer 7, but preferably the temperature is from about 875° F. to 925° F., pressure from 400 to 600 p.s.i.g., hydrogen recycle 5 to 1, and space rate 0.5 to 3.

Reaction products are removed from reformer 19 through line 20 and are taken to separator 21 in which hydrogen is removed overhead for recycle to reformer 19, any excess hydrogen produced being taken off through hydrogen bleed line 22. The liquid reaction products are then taken through line 23 to debutanizer 24 in which a C_4 fraction is removed overhead. The balance, consisting of C_5+ gasoline, is then passed through line 25 to fractionator 26 in which the products are fractionated to take overhead a stream boiling below 260° F., while a stream boiling above 260° F. is taken off as bottoms. The overhead fraction is passed through line 27 to condenser 28 and the liquid products are passed to receiver 29. A portion of the liquid products from receiver 29, sufficient to make a 100 blending octane number gasoline blend with the bottoms from fractionator 26 is passed through line 30 to line 31 where it is mixed with the fractionator bottoms. The blend is then passed through line 32 to storage.

As has been previously pointed out the C_6–C_7 paraffins from the solvent extraction tower are mixed with the heavy naphtha feed prior to reforming. It is desirable that these light paraffins should make up from 20 to 80% of the total feed to reformer 19. Since ordinarily insufficient paraffins will be recovered from the solvent extraction tower to make up this concentration of paraffins in the feed, a portion of the overhead from fractionator 26 is removed from receiver 29 and is passed through line 33 for admixture with the C_6–C_7 paraffins in line 17, in an amount sufficient to make up the desired proportion of low blending constituents in the feed. Any excess over and above that required for balancing the feed is taken off for disposal from receiver 29 through line 34. In the event that the total amount of light paraffins available from receiver 29 and from the solvent extraction tower is insufficient, make up C_6–C_7 paraffins may be added from an extraneous source through line 35. It is also contemplated that all of the light paraffins added to the heavy naphtha may be recycled from receiver 29.

In order that those skilled in the art may more fully understand the invention and the results produced thereby, the following examples are given:

Example I

In this run a 260° to 375° F. straight run naphtha having an octane number of 39.2 was diluted with a 57.7 octane number C_6–C_7 paraffin stream recovered from a solvent extraction process for the production of benzene and toluene in the proportion of 30 volumes of naphtha to 70 volumes of paraffins. This mixture was reformed over a platinum catalyst, supported on alumina, at a temperature of 896° F., pressure of 400 p.s.i.g., space velocity of 3, and a 5 molar ratio of hydrogen to oil. 91.5 volumes of C_5+ reformate with 74.7 octane number (F–1 clear) were recovered. This product was fractionated to give 72.2 volumes of a C_5 to 260° F. fraction with 66.2 octane number and 19.3 volumes of a 260° F.+ fraction with a blending octane number of 119. When "blending octane numbers" are referred to, it should be understood to mean the value determined by testing a blend of 20% reformate and 80% of a 60 octane number reference fuel composed of n-heptane and isooctane. "Octane number" refers to the value determined by testing the material unblended with reference fuel. The latter fraction amounted to 64.3% of the original naphtha. 10.9 volumes of the below 260° F. fraction was then combined with the heavier fraction to give 30.2 volumes of 100 blending octane number gasoline, a yield of 100.7% based on the original naphtha charge.

Example II

In this run the same reforming conditions and catalyst were used as in Example I, but the feed to the reformer was 60 volumes of 260°–375° F. naphtha and 40 volumes of C_6–C_7 paraffins. 90.5 volumes of reformate of 85 octane number were recovered. This reformate was fractionated into 51.9 volumes of a C_5 to 260° F. gasoline having an octane number of 67, and 38.6 volumes of a 260° F.+ cut having a blending octane number of 120. This heavy fraction contained 88% by volume aromatics. 23.1 volumes of the lighter cut was then blended with the heavy fraction to yield 61.7 volumes of 100 blending octane number gasoline, a yield of 106% based on the heavy naphtha charge.

Example III

This run was made under the same conditions as Examples I and II, except that the feed was 80% naphtha and 20% C_6–C_7 paraffins. It was found that a yield of 102% of 100 blending octane number gasoline, based on the heavy naphtha charged could be recovered by fractionating and blending as described above.

Example IV

A further run under the same conditions was made charging 100 volumes of 260°–375° F. naphtha alone. 89.8 volumes of 89.8 octane number gasoline were recovered which, on fractionation, gave 20.6 volumes of C_5 to 260° F. reformate with a 67.8 octane number and 69.2 volumes of heavy reformate with 105 blending octane number and containing 75% aromatics. By combining the cuts a yield of 80 volumes of 100 blending octane number gasoline was obtained, a yield of 80% on the naphtha charged.

Example V

100 volumes of C_6–C_7 paraffins having an octane number of 57.7 were reformed under the same conditions as above. A yield of 80.3% of a product having an octane number of 67.4 was recovered. No 100 blending octane number gasoline could be produced from this product.

As may be observed from the foregoing, when low-boiling paraffins are added to the feed, the blending octane number of the 260° F.+ fraction is greatly increased, 119 O.N. for the product from the 70 paraffin/30 naphtha blend, and 120 O.N. for the 40 paraffin/60 naphtha blend, as compared to only 105 blending octane number for the 260° F.+ fraction obtained from the heavy naphtha alone.

The yield-octane relationship is also favored by inclusion of low boiling paraffins in the feed. Thus, as may be observed from Examples IV and V, reforming of

heavy naphtha alone will given an 89.8% yield of 89.8 octane number gasoline, while reforming of the C_6–C_7 paraffin fraction will give a yield of 80.5% of 67.4 octane number product. It may be calculated that if 70 volumes of C_6–C_7 paraffins are reformed separately, 30 volumes of 260° F.+ naphtha are reformed separately, and the products are combined, a yield of only 83.2 volumes of 75.7 octane number product will be obtained, as compared to the yield shown in Example I of 91.5 volumes of 74.4 octane number product.

It will be appreciated that, while in the foregoing description the source of the low-boiling paraffins used to dilute the 260° F.+ naphtha is the raffinate from a solvent extraction process for the recovery of benzene and toluene, the invention is not so limited, and the paraffin fraction may be obtained from any source, the essence of the invention being the discovery that the production of high blending octane fractions, can, in a reforming operation, be substantially increased if the heavy naphtha feed to such a process is diluted with paraffins boiling below the boiling range of the naphtha treated. Thus, the paraffins may be obtained as selected fractions from highly paraffinic crudes, such as Pennsylvania and Kuwait crudes, or they may be obtained by the solvent extraction of other crude fractions to remove aromatics and naphthenes therefrom. It is importan only that the paraffinic diluent should contain less than about 10% naphthenes, and should contain at least 80% paraffins. In the specification and claims, whenever the term "paraffinic fraction" is used it means a hydrocarbon fraction containing at least 80% paraffins.

We claim:

1. A catalytic reforming process which comprises blending a straight run naphtha having a boiling range of from about 260° F. to about 420° F. with a normally liquid hydrocarbon fraction boiling entirely below 260° F. and comprising at least 80 percent paraffins by volume in such proportions that the naphtha forms from 20 percent to 80 percent by volume of the blend, subjecting the blend together with added hydrogen to the action of a refroming catalyst under reforming conditions of temperature and pressure conducive to naphthene dehydrogenation, and recovering and a liquid product having an octane number higher than the blend.

2. The process according to claim 1 in which the catalyst comprises platinum, the reforming temperature is from 750° F. to 1000° F., and the reforming pressure is from about 250 p.s.i.g. to about 700 p.s.i.g.

3. A catalytic reforming process which comprises fractionating a full boiling range straight run naphtha to recover a fraction boiling from about 140° F. to about 210° F. and a fraction boiling between 260° F. and 420° F., subjecting the lower boiling fraction in the presence of added hydrogen to the action of a reforming catalyst under conditions such that the naphthene content thereof will be converted to benzene and toluene,

recovering a liquid reformate, treating the reformate to recover an aromatic extract and a raffinate comprising at least 80 percent by volume of paraffins, blending the raffinate with the naphtha fraction boiling between 260° F. and 420° F., subjecting the blend together with added hydrogen to the action of a reforming catalyst under reforming conditions of temperature and pressure, and recovering a liquid product having a higher octane number than the blend.

4. A catalytic reforming process which comprises fractionating a full boiling range straight run naphtha, recovering a fraction boiling from about 140° F. to about 210° F. and a fraction boiling between 260° F. and 420° F., subjecting the lower boiling fraction in the presence of added hydrogen to the action of a reforming catalyst under reforming conditions of temperature and pressure, recovering a liquid reformate containing benzene and toluene, treating the reformate to recover a fraction rich in aromatics and a fraction comprising at least 80 percent by volume of paraffins, blending at least a part of the paraffinic fraction with the naphtha fraction boiling between 260° F. and 420° F., and with a paraffinic hydrocarbon recycle stream, subjecting the blend to the action of a reforming catalyst under reforming conditions of temperature and pressure conducive to naphthene dehydrogenation, recovering a liquid product, separating the product into a fraction boiling below 260° F. and a higher boiling fraction, recycling at least a part of the fraction boiling below 260° F. to admixture with the naphtha fraction boiling between 260° F. and 420° F. and with the paraffinic fraction from the aromatic separation treatment, the quantity so recycled being such that the naphtha will comprise from about 20 percent to about 80 percent by volume of the blend.

References Cited in the file of this patent

UNITED STATES PATENTS

2,241,430	Snow	May 13, 1941
2,653,175	Davis	Sept. 22, 1953
2,697,684	Hemminger et al.	Dec. 21, 1954
2,740,751	Haensel et al.	Apr. 3, 1956
2,767,124	Myers	Oct. 16, 1956
2,768,126	Haensel et al.	Oct. 23, 1956
2,877,173	Thorne et al.	Mar. 10, 1959
2,880,164	Viland	Mar. 31, 1959

FOREIGN PATENTS

720,388	Great Britain	Dec. 15, 1954

OTHER REFERENCES

Fulton: "Petroleum Refiner," vol. 29, No. 12 (1950), pp. 109–112.

Resen: "Oil and Gas Journal," June 16, 1952, pp. 313–316.

Haensel: "Petroleum Processing," February 1953, pp. 236–239.