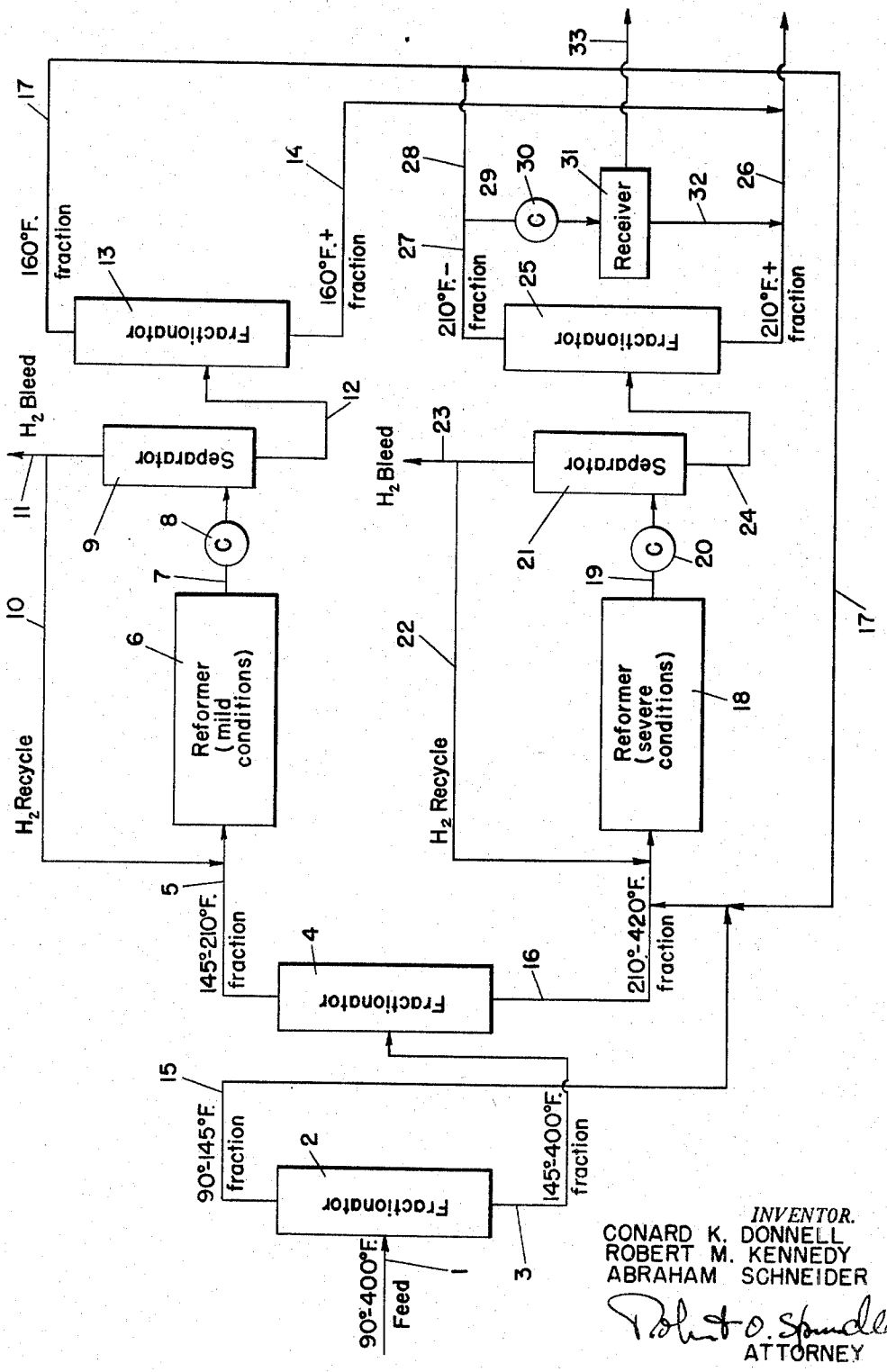
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CATALYTIC REFORMING PROCESS OF SELECTIVE FRACTIONS

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CATALYTIC REFORMING PROCES OF SELECTIVE FRACTIONS

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This invention relates to the catalytic reforming of straight-run naphthas boiling over the gasoline boiling range and relates more particularly to a combination process in which selected fractions of the naphtha are subjected to reforming under selected conditions, the lower boiling fraction of the naphtha being subjected to less severe reforming conditions than the higher boiling fraction, and in which a normally liquid low boiling paraffinic fraction is admixed with the higher boiling fraction prior to reforming.

This application is a continuation in part of our co-pending application, Serial No. 500,084, filed April 8, 1955. In that application we disclosed that higher yields of high octane gasoline might be obtained, in reforming a naphtha boiling between 260° F. and 420° F., if the feed, prior to reforming, were diluted with a paraffinic hydrocarbon boiling below the initial point of the feed, conveniently obtained from the raffinate of an aromatics recovery process. The present invention makes use of the principles disclosed in the said co-pending application, but provides a process for the upgrading of a straight-run naphtha, boiling over the full gasoline boiling range, to a high octane gasoline, without the necessity of including a solvent extraction or other aromatic separation step in the process.

Our invention contemplates fractionating a straight-run naphtha boiling over the entire gasoline range, say from 90° F. to about 400° F. into three fractions, the first boiling from about 90° F., to about 145° F., the second boiling from about 145° F. to about 210° F., and a third boiling above 210° F. The second fraction is subjected to mild reforming conditions in the presence of a platinum catalyst deposited on an acidic base, and in the presence of added hydrogen, in order to isomerize the normal paraffins contained therein to higher octane number branched chain paraffins, the conditions being selected so that hydrocracking is substantially eliminated and there is a minimum conversion of naphthenes to aromatics. The reformate from this reforming step is fractionated to take overhead an essentially paraffinic fraction boiling below 160° F., and to recover as bottoms a higher octane gasoline rich in branched chain paraffins, together with some aromatics and unconverted high octane naphthenes. The first naphtha fraction, the fraction of the first reformate boiling below 160° F., and the third naphtha fraction are combined, and the mixture is then subjected to the action of a hydrogenation-dehydrogenation catalyst under severe reforming conditions, in the presence of added hydrogen, in order to dehydrocyclize the high boiling paraffins in the feed, to isomerize and dehydrogenate the naphthenes to aromatics, and to isomerize or hydrocrack those higher boiling paraffins which are not cyclized, to paraffins of higher octane number. Since the paraffins boiling below 160° F. are very resistant to dehydrocylization, and will pass through the reactor virtually unchanged, except for some isomerization or hydrocracking to still lower boiling paraffins, the paraffinic content of the reaction mixture

will always be high enough so that an equilibrium between aromatics and paraffins will not be reached, thus insuring a maximum dehydrocylization of the high boiling, low octane, paraffins to the corresponding aromatics of high octane number.

The reformate from this second reforming stage is distilled to recover an aromatic-rich fraction of very high octane number boiling above 210° F., and a paraffinic fraction consisting largely of branched chain paraffins boiling below 210° F. The 210° F.+ fraction and the 160° F.+ fraction from the first reforming step are blended, and sufficient amounts of the 210° F.— fraction and extraneous butanes are added to produce a high octane finished gasoline of balanced volatility.

In order that those skilled in the art may more fully appreciate our invention, and the manner in which it is carried out it will be further described in connection with the accompanying drawing, which is a diagrammatic flow sheet of the process.

As illustrated in the drawing, a hydrocarbon feed boiling from 90° to 400° F. is introduced through the line **1** to fractionator **2**, in which a fraction boiling from 90° F. to 145° F. is taken overhead. This fraction consists of branched chain hexanes and normal and branched chain pentanes.

A fraction boiling from 145° to 400° F. is taken off as bottoms from fractionator **2** and is passed through line **3** to a second fractionator **4** in which a stream boiling from 145° to 210° F. is removed overhead. This stream, which consists of normal hexane, heptanes, cyclohexane, and methylcyclopentanes is taken through line **5** to reformer **6** in which it is contacted with platinum catalyst deposited on an acidic base, such as alumina containing from about 0.3 to 3% combined fluorine. The conditions in reformer **6** are relatively mild, temperature being from about 850° to about 875° F., pressure being from about 300 to about 500 p.s.i.g., and preferably in the vicinity of 400 lbs. p.s.i.g., and liquid hourly space velocity being about 3. Hydrogen is added to the the feed in such amount that the hydrogen to hydrocarbon ratio is from about 5 to 1 to about 10 to 1. Under these conditions isomerization of the straight chain paraffins to branched chain paraffins will take place to a considerable degree. In addition a portion of the naphthenes will be converted to the corresponding aromatics, while essentially no hydrocracking will take place. Since in the boiling range the naphthenes have about the same octane numbers as the corresponding aromatics, dehydrogenation, with attendant shrinkage in volume, is not desired, and consequently incomplete conversion of the naphthenes is an asset, rather than a liability.

The reaction products are taken from reformer **6** through line **7** and are passed through condenser **8** and thence to separator **9** in which hydrogen is removed overhead and recycled to the process through line **10**, any excess hydrogen being bled from the system through line **11**. The liquid products from separation **9** are taken through line **12**, to fractionator **13**, in which a fraction boiling below 160° F. is taken overhead, while a high octane gasoline fraction boiling over 160° F. is removed as bottoms through line **14** for blending with other products of the present process.

The 90° to 145° F. overhead fraction from fractionator **2** is taken through line **15** and is blended with the 210° to 400° F. fraction removed as bottoms from fractionator **4** through line **16**. The fraction boiling below 160° F. taken overhead from fractionator **13** is passed through line **17** and is mixed with the 210° to 400° F. fraction and the 90° to 145° F. fraction. Preferably, these light paraffinic fractions will make up at least from 20% to 30% of the mixture, and if the composition of

the initial naphtha feed is such that the 90°–145° F. fraction and the 160° F.— fraction together, are insufficient to bring the light paraffinic content of the mixture up to this percentage, a sufficient quantity of a paraffinic fraction boiling under 210° F., obtained from a later stage of the process, may also be added. Similarly, if the 90°–145° F. fraction is large enough, the 160° F.— fraction may be omitted from the mixture.

The combined fractions are then passed to reformer **18**, in which they are contacted with a hydrogenation-dehydrogenation catalyst under relatively severe conditions. The catalyst in reformer **18** may be the same catalyst as is used in reformer **6**, but may also be a platinum catalyst deposited on alumina containing no fluorine or a metal oxide catalyst such as molybdena or chromia. If the catalyst contains fluorine, the temperature is preferably from about 900° to 950° F.; while if no fluorine is contained in the catalyst, the temperature should be about 20 degrees higher. In the event a metal oxide catalyst is used, the temperature is preferably from about 950° to 1000° F. The pressure will range from about 500 to about 700 lbs. p.s.i.g. when using a platinum catalyst, or from 100 to 300 p.s.i.g. when using a metal oxide catalyst, the liquid hourly space velocity will be from about 1 to 4 and the hydrogen to hydrocarbon ratio should be from about 3 to 1 to from about 5 to 1. Under these conditions the naphthenes contained in the feed are essentially completely dehydrogenated to the corresponding aromatic, while the high boiling paraffins will be almost completely dehydrocyclized to aromatics, or hydrocracked to lower boiling high octane paraffins. The effluent from reformer **18** is taken off through line **19** and passed through condenser **20** and thence to separator **21**. Hydrogen is taken from separator **21** through line **22** for recycle to the process while excess hydrogen produced in reactor **18** is bled from the system through line **23**. Liquid products from separator **21** are passed through line **24** to a fractionator **25**, from which a bottoms product boiling above 210° F. is removed through line **26** and is blended with the fraction boiling above 160° F. recovered from fractionator **13**.

A fraction boiling below 210° F., which is essentially paraffinic, is removed from fractionator **25** overhead through line **27**. A portion of this product may be taken through line **28** and mixed with the below 160° F. fraction in line **17**. This will be done, however, only when the combined fractions passing through lines **15** and **17** are less than about 30% of the feed to reformer **18**. If these fractions make up about 30% or more of the feed, the entire below 210° F. fraction removed from fractionator **25** through line **27** will be passed through line **29** and condenser **30** to receiver **31**. From receiver **31** a portion of the product may be removed through line **32** for blending with the bottoms from fractionators **13** and **25**, while another portion of the product may be removed through line **33** for further processing, or for blending with other gasoline fractions, such as a higher boiling catalytically cracked gasoline.

As may be appreciated from the foregoing, we have invented a process for the upgrading of a straight-run naphtha in which there is minimum degradation of low boiling, high octane naphthenes to aromatics of similar octane number but smaller volume; in which there is maximum dehydrocyclization of high boiling, low octane paraffins to form aromatics of high octane number; and in which all fractions of a full gasoline boiling range straight-run naphtha are utilized to greatest advantage to produce a final gasoline product of superior octane number in high yield.

We claim:

1. A reforming process for the upgrading of a straight-run naphtha boiling in the full gasoline boiling range which comprises fractionating a straight-run naphtha boiling between about 90° F. and about 400° F. into a fraction boiling below about 145° F., a fraction boiling between about 145° F. and about 210° F., and a fraction boiling from about 210° F. to about 400° F., contacting the 145°–210° F. fraction in a first reforming zone, in the presence of added hydrogen, with a catalyst comprising platinum, alumina, and fluorine under relatively mild reforming conditions of temperature, pressure, and space rate such that isomerization of paraffins is promoted and dehydrogenation of naphthenes and hydrocracking is minimized; recovering a first reformate, fractionating the first reformate, recovering a paraffinic fraction boiling below about 160° F. and a fraction of enhanced octane number boiling above about 160° F.; mixing the naphtha fraction boiling below about 145° F., the naphtha fraction boiling from about 210° F. to about 400° F., and the fraction of the first reformate boiling below about 160° F., contacting the mixture in a second reforming zone, in the presence of added hydrogen, with a hydrogenation-dehydrogenation catalyst under relatively severe reforming conditions of temperature, pressure, and space rate such that dehydrocyclization and hydrocracking of C_8+ paraffins and dehydrogenation of naphthenes is promoted, and fractionating the effluent from the second reforming zone to recover a paraffinic fraction boiling below about 210° F., and an aromatic-containing fraction boiling above about 210° F.

2. A gasoline reforming process which comprises fractionating a straight-run naphtha boiling in the full gasoline boiling range into a paraffinic fraction boiling below about 145° F., a fraction boiling between about 145° F. and about 210° F., and a fraction boiling above about 210° F.; contacting the 145°–210° F. fraction in a first reforming zone, in the presence of added hydrogen, with a catalyst comprising platinum, alumina, and fluorine, at a temperature of from about 850° F. to about 875° F., and at a pressure of from about 300 to about 500 p.s.i.g.; recovering a first reformate, fractionating the first reformate to recover a paraffinic fraction boiling below about 160° F. and a fraction of enhanced octane number boiling above about 160° F.; mixing the naphtha fraction boiling above 210° F. with at least a part of the fraction boiling below about 145° F. and with the first reformate fraction boiling below about 160° F.; contacting the mixture, in a second reforming zone, in the presence of added hydrogen, with a hydrogenation-dehydrogenation catalyst, at a temperature of from about 900° to about 1000° F. and at a pressure of from about 500 p.s.i.g. to about 700 p.s.i.g.; and recovering a second reformate of enhanced octane number; and blending the fraction of the first reformate boiling above about 160° F. with the second reformate.

3. A gasoline reforming process which comprises fractionating a straight-run naphtha boiling in the full gasoline boiling range into a paraffinic fraction boiling below about 145° F., a fraction boiling between about 145° F. and about 210° F., and a fraction boiling above about 210° F.; contacting the 145–210° F. fraction in a first reforming zone, in the presence of added hydrogen, with a catalyst comprising platinum, alumina, and fluorine, under isomerizing conditions of temperature and pressure, recovering a first reformate, fractionating the first reformate to recover a paraffinic fraction boiling below about 160° F., and a fraction of enhanced octane number boiling above 160° F., blending, with the naphtha fraction boiling above 210° F., a lower boiling paraffinic fraction selected from the naphtha fraction boiling below 145° F., and admixtures thereof with the first reformate fraction boiling below about 160° F., and the hereinafter specified paraffinic fraction boiling below 210° F., in such proportions that at least 20% of the blend will boil below 210° F., contacting the blend in a second reforming zone, in the presence of added hydrogen, with a hydrogenation-dehydrogenation catalyst under dehydrocyclization conditions of temperature and pressure, recovering a second reformate, and fractionating the second reformate to recover said paraffinic fraction boil-

ing below about 210° F., and a fraction rich in aromatics boiling above about 210° F.; and blending the fraction of the first reformate boiling above about 160° F. with the fraction of the second reformate boiling above about 210° F. and with a sufficient quantity of the fraction of the second reformate boiling below 210° F. to yield a gasoline of balanced volatility.

4. The process according to claim 3 in which the temperature in the first reforming zone is from about 850° F. to about 875° F., and in which the temperature in the second reforming zone is from about 900° F. to about 1000° F.

5. The process according to claim 4 in which the pressure in the first reforming zone is from about 300 to about 500 p.s.i.g., and in which the pressure in the second reforming zone is from about 500 p.s.i.g. to about 700 p.s.i.g.

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