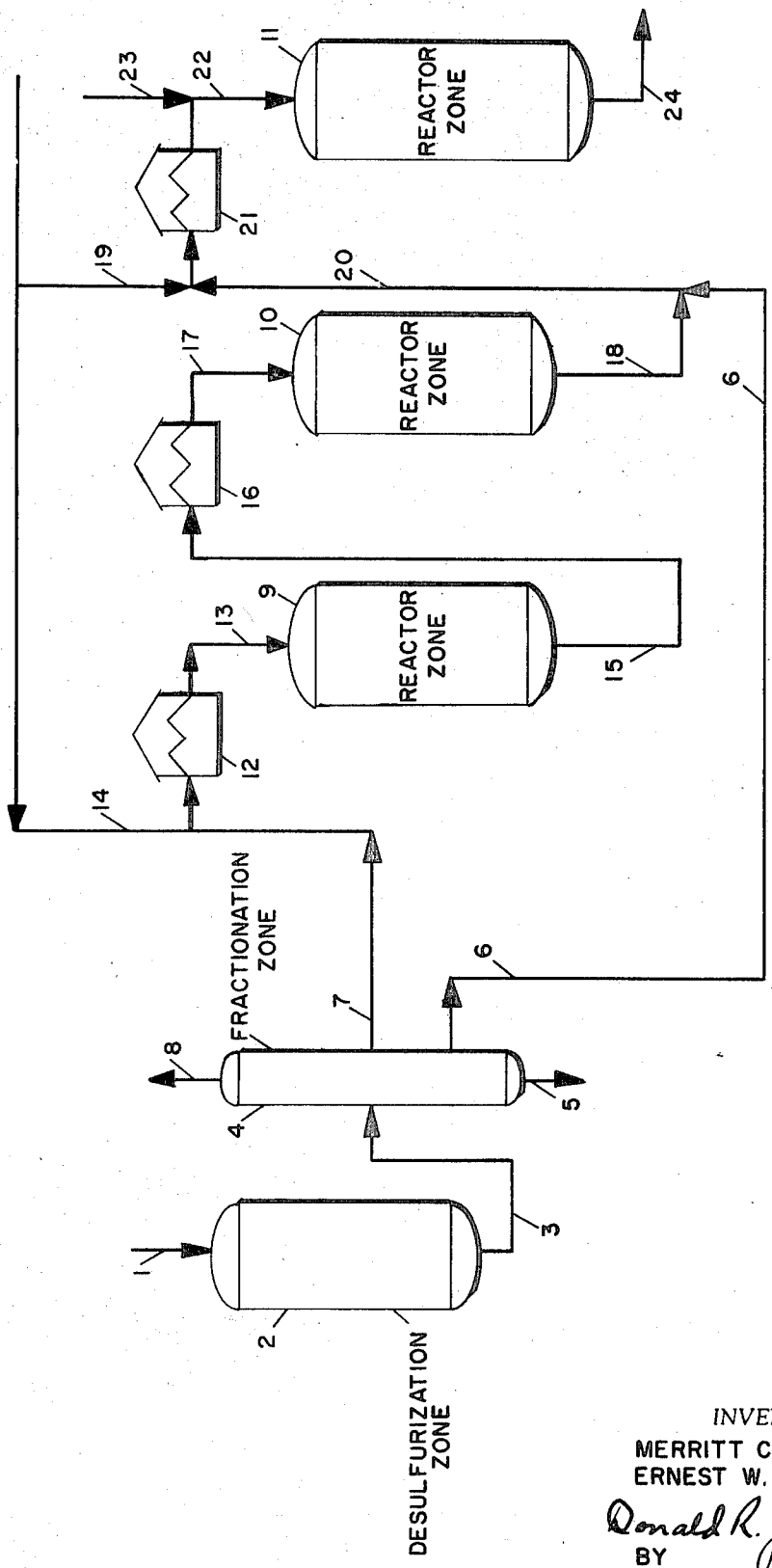
March 7, 1972 M. C. KIRK, JR., ET AL 3,647,679

PROCESS FOR REFORMING HEAVY NAPHTHA

Filed June 25, 1970



INVENTORS
MERRITT C. KIRK JR.
ERNEST W. DOBSON
Donald R. Johnson
BY
ATTORNEY

United States Patent Office 3,647,679
Patented Mar. 7, 1972

3,647,679

PROCESS FOR REFORMING HEAVY NAPHTHA

Merritt C. Kirk, Jr., Thornton, and Ernest W. Dobson, Westtown Township, Chester County, Pa., assignors to Sun Oil Company, Philadelphia, Pa.

Filed June 25, 1970, Ser. No. 49,606
Int. Cl. C10g 39/00
U.S. Cl. 208—63 2 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a process for reforming heavy naphtha wherein a naphtha feed boiling in the range of below about 390° F. is reformed in a series of reactors while a naphtha fraction boiling between about 390° to 415° F. is added to the feed into the last reactors of the series. The last reactors are provided with an excess of hydrogen. The invention provides an increased amount of reformate of increased octane. The invention also provides for the upgrading of a heavy naphtha fraction without excessive coke formation.

This invention relates to a process for reforming heavy naptha. Generally, naphtha fractions boiling in the range of about 200° to 390° F. are used as charge feed to reformers. The feed is prepared by desulfurization and prefractionation of a 200° to 440° F. naphtha. The desulfurized fraction boiling above about 390° F. is normally used in jet fuel or kerosene. The latter fraction is undesirable reformer feed because it contains dicyclic naphthenes and Tetralins which dehydrogenate to dicyclic aromatics which are high boiling coke formers of low octane number.

The present invention relates to a modified reforming process which permits the reforming of feed stocks boiling up to about the 415° F. range. In the process, desulfurized naphtha feed is separated into a fraction with a boiling range below about 390° F., a fraction boiling in the approximate range of 390° to 415° F. and a fraction boiling above 415° F. The fraction of boiling range below about 390° F. is charged into a multiple reactor reformer and is reformed in the conventional manner. The 390° to 415° F. fraction is charged along with excess hydrogen into the last reactors in the reformer. The excess hydrogen minimizes coking from the increased hydrocracking in the last reactors which might have occurred on account of the presence of the 390° to 415° F. feed material. The present proposal takes advantage of the predominance of this hydrocracking reaction in later reforming stages which reaction is predominant over the dehydrogenation of naphthenes which takes place, for the most part, in the first reforming stages. The promotion of the hydrocracking of the Tetralins and naphthenes in the heavy naptha to alkyl aromatic in preference to their conversion to naphthalenes results in the production of high octane low boiling gasoline components.

The invention is describable as an improvement to a process for reforming naptha in a multiple reactor reformer in which the process comprises charging a naptha feed boiling below about 390° F. sequentially into each reactor of the reformer to reform the feed, and recovering a product of increased octane number. The improvement comprises feeding a naphtha fraction boiling in the range of about 390° to 415° F. into later reactors of the reformer in the presence of excess hydrogen to thereby increase the amount of product of increased octane.

The present invention can be thought of as a reforming process characterized by altered conditions in its later stages as described above or the invention can be thought of as an integrated process characterized by a combination of two steps wherein the first step comprises dehydrogenation under reforming conditions and the second step comprises hydrocracking.

Angell, U.S. Patent No. 2,333,625 which issued Nov. 9, 1943, teaches thermal reforming a naphtha and hydrogenating the reformate in the presence of a naphthenic oil hydrogen donor. Olefins of the reformate are saturated by the hydrogenation step. The objects of the Angell patent are the reduction of the olefinic nature of reformate by a conversion which does not materially decrease the reformate anti-knock value and the provisions of an inexpensive hydrogen source to effect this conversion. The Angell process does not seek to upgrade the added hydrogen donor as a gasoline component.

Hemminger, U.S. Patent No. 2,696,460 which issued Dec. 7, 1954, discloses a combination process for making gasoline in which a heavy naphtha is split into two streams. One stream is reformed and the other stream (the heavier fraction) is subjected to thermal cracking and hydrogenation. Preferably, the cracking and hydrogenation processes are performed in the same zone. By the invention, the tendency of heavier fraction to form coke in reforming is avoided. The lighter fraction, which is conventionally reformed is a 175° to 320° or 350° F. fraction. The heavier fraction boiling from about 350° up to 450° F. is cracked and reformed in combination with the lighter stream. The cracked heavier stream may be hydrogenated before being charged into the reforming zone. In the present invention, the heavier fraction need not be preliminarily cracked because its boiling range has been selectively chosen to eliminate that portion of the fraction which would need to be cracked to high octane gasoline precursors. The heavier fraction of the present invention can be charged directly into the latter stages of the reforming process thus taking advantage of predominating reactions which take place in these later stages to upgrade the heavier fraction without producing excessive coking and without the requisite cracking of the fraction preliminary to charge to the reforming zone. The advantages obtained by this combined process in simplicity of equipment and processing steps reflect the significant improvements obtained by the present invention.

M. Oblad, U.S. Pat. No. 2,703,308, Mar. 1, 1955, teaches a heavy naphtha fraction hydrocracked to produce a high octane light gasoline fraction and a naphtha fraction of relatively poor octane quality which is reformed. Reformate from this latter step boiling below 400° F. is added to the high octane fraction produced in the hydrocracking step. Reformate boiling above 400° F. is added to the feed to the cracking zone. This process requires a fractionation of the product from the reforming zone, to reform a fraction boiling up to 400° F., prior to hydrocracking in combination with the complete feed. The patent process effects conversion of substantially the entire feed of a hydrocarbon charge stock of above gasoline boiling range to gasoline of high octane rating. The present invention preliminarily divides a heavy naphtha into two streams. The two streams can be then converted under conditions most responsive to their respective processing requirements.

Scott, U.S. Pat. No. 3,124,523, Mar. 10, 1964, proposes subjecting a heavy fraction boiling in the range of 180° to 550° F. or 250° to 450° F. to reforming followed by treatment with hydrogen in a cracking isomerization zone. The present invention, by subjecting only the lower boiling portion of the heavy naphtha fraction to reforming, reduces the problem of heavy coke formation which problem must inherently accompany the reforming of the high range of the heavy naphtha fraction as proposed in the Scott patent.

If the present invention is described in terms of a two stage conversion process rather than as an improvement

to reforming as described above, then the present invention comprises a process for producing gasoline employing in combination a reforming zone and an isomerization-hydrocracking zone comprising separating a heavy naphtha into a first fraction boiling below about 390° F. and a second fraction boiling between about 390° F. and 415° F., reforming the first fraction in the reforming zone under conditions which predominantly bring about dehydrogenation of naphthenes in the first fraction, adding the second fraction to the product from the reforming zone and subjecting the combined fractions to hydrocracking and isomerization in the presence of excess hydrogen to produce a gasoline of improved octane number.

The drawing is a schematic flow diagram of the present invention.

The present invention will be described in detail with reference to the drawing. A naphtha **1** such as a catalytically-cracked naphtha boiling between about 200 to 440° F. is desulfurized in **2** and then passed through line **3** into a fractionation zone **4** where the naphtha is separated into a fraction **5** boiling in the range above about 415° F., a 390° to 415° F. boiling range fraction **6**, a 200° to 390° F. boiling range fraction **7**, and a light end fraction boiling below about 200° F. The 200° to 390° F. cut is taken from the fractionator **4** and is reformed in reactor zones represented by zones **9**, **10** and **11**. The reforming of the 200° to 390° F. fraction is illustrative of the present invention but it should be noted that other naphtha fractions can be reformed as part of the present invention so long as the fraction has a final boiling point which is at about 390° F. or which is below 390° F. It should also be noted that the drawing shows three reforming zones as specifically exemplary of the present invention, but the process of the invention can be conducted in two or even one reactor with two contiguous zones or in more than two reactors.

Broadly, in the present invention the naphtha fraction boiling below about 390° F. is passed into a reforming zone provided with a reforming catalyst which can be any catalyst known in the art for reforming hydrocarbon fractions. For example, the catalyst can be any of the platinum-on-alumina or rhenium-platinum-on-alumina catalysts which generally contain between 0.1 to 2.0 percent platinum. Catalysts of this type are available commercially and are extensively described in the literature. The catalyst compositions can include various active forms of alumina, such as gamma, eta, and kappa, and the alumina may vary considerably in surface characteristics depending upon how the catalyst was made. The combination of platinum and the alumina produces a catalyst having a plurality of functions whereby such reactions as dehydrogenation, isomerization, cyclization and hydrocracking are promoted. In some cases a minor amount of a halogen, such as chlorine or fluorine, is incorporated in the catalyst to control the catalytic activity for promoting certain types of these reactions.

In some cases a conventional catalyst of altered characteristics can be used in the present invention. Usually reforming catalysts contain two components each of which substantially provide a characteristic function. For example, the cracking function of a platinum-on-alumina catalyst is substantially provided by the alumina component and the dehydrogenation function is substantially provided by the platinum component. Since, in the present invention, advantage is taken of the predominance of the dehydrogenation function in the earlier stages of reforming and the predominance of the hydrocracking function in the later stages, different, special altered catalysts can be used in the respective stages which catalysts will provide the more desired function in the respective stages. Thus for eample, a platinum-on-alumina catalyst with an increased amount of particularly active form of platinum can be used in the earlier stages to promote dehydrogenation and a catalyst with an increased amount or particularly active form of alumina can be used in the later stages to promote hydrocracking.

In the early stages of the reforming, conditions can be varied rather widely; thus temperatures of about 600° to about 1050° F. are suitable and the preferred range is from about 800° to about 950° F. Within these temperature limits weight space velocities of about 0.05 to about 10.0 pounds of naphtha, per hour, per pound of catalyst in the reaction zone may be employed advantageously; however, space velocities of about 0.25 to about 5.0 provide the best results. Hydrogen should be introduced into the reforming reactor at rates running from about 0.5 to about 20.0 moles of hydrogen per mole of hydrocarbon reactants. The reaction pressure in the reforming can be maintained between about 50 and about 1000 pounds per square inch gauge (p.s.i.g.). Best results are obtained by holding the reaction pressure within the range between about 100 and about 750 p.s.i.g.

Referring again to the drawing, the naphtha fraction of boiling range 200° to 390° F. is heated in **12** to about 900° F. and is passed **13** into a first reactor zone **9** into contact with a platinum on alumina catalyst. The zone **9** is maintained at an inlet temperature of about 900° F. and outlet temperature of about 825° F. The feed is passed to the zone at a pressure of about 450 p.s.i.g. and exits from zone **9** at a pressure of about 440 p.s.i.g. Hydrogen is recycled **14** to the feed zone **9** to maintain a hydrogen to oil mole ratio varying between about 3 and 10.

The naphtha fraction is passed from zone **9** via line **15**, is reheated **16** to 900° F. and is passed **17** to a second reactor zone **10** wherein the fraction is again contacted with platinum-on-alumina catalyst at temperatures between about 850 to 900° F. and pressures between 390 and 415 p.s.i.g.

As per the present invention, conditions in the early stages of the reforming as represented by reactor zones **9** and **10** of the drawing, are controlled to produce substantial dehydrogenation of naphthenes. The product of the early stages passes **18** from reactor zone **10** and is combined with the heavy naphtha fraction of boiling range 390° to 415° F. from line **6**. The higher boiling, heavier naphtha fraction of the present invention is specifically illustrated in the drawing as a fraction of boiling range 390° to 415° F.

In the drawing, hydrogen **19** is added to the combined naphtha fractions in line **20**. The combined feed is then heated **21** to about 950° F. and is passed **22** to later reactor zone **11** of inlet pressure of about 370 p.s.i.g. and outlet pressure of 340 p.s.i.g. The temperature in this zone is maintained at temperatures averaging 50–125° F. higher than the temperatures in the earlier zones. The later reactor zone is represented in the drawing by a single reactor zone **11** but again this zone can comprises a plurality of reactors or can comprise a latter stage of a single reactor in which a complete reforming operation is carried out per the present invention.

Chloride is added to the combined feed to the latter stages as illustrated in the drawing by line **23**. This chloride can be, for example, ethylene dichloride and is added for the purpose of inducing increased hydrocracking. The chloride is added in the range of 1 to 10 p.p.m. based on total naphtha feed to the reactors in the latter stage of the process.

The catalyst utilized in zone **11** can comprise any conventional reforming catalyst as described supra or an altered catalyst as also described supra. The operation in this zone produces a product **24** of increased octane. In comparison to conventional operation, which utilizes a feed with a boiling range below 390° F., the present process produces about a 5 volume percent increase in C_{5+} reformate of characteristics comparable to the product produced in the conventional operation. In comparison to a conventional operation which might use a 200° to 415° F. charge stock, the present invention produces a reformate with a lower end point and higher octane. This

improved reformate is produced without the heavy coking which would characterize a conventional reforming of a 200° to 415° F. charge stock.

The invention claimed is:

1. In a process for reforming naphtha in a multiple reactor reformer which process comprises: charging a naphtha feed boiling below about 390° F. sequentially into each reactor of said reformer to reform said feed; and recovering a product of increased octane number; the improvement which comprises: adding a heavy naphtha fraction boiling essentially throughout the range of 390° to 415° F. into a later reactor of said reformer combined with its feedstock in the presence of excess hydrogen to thereby increase said amount of product of increased octane number by subjecting the combined feedstocks to hydrocracking and isomerization.

2. A process for producing gasoline employing in combination a reforming zone and an isomerization-cracking zone comprising: separating a heavy naphtha into a first fraction boiling below about 390° F. and a second fraction boiling essentially throughout the range of 390° to 415° F.; reforming the first fraction in the reforming zone

under conditions which predominantly bring out dehydrogenation of naphthenes in the first fraction; adding the second fraction to the product from the reforming zone; and subjecting the combined fractions to hydrocracking and isomerization in the presence of excess hydrogen to produce a gasoline of improved octane number.

References Cited

UNITED STATES PATENTS

2,908,628	10/1959	Schneider et al.	208—65
2,990,363	6/1961	Evans	208—65
3,242,066	3/1966	Myers	208—93
3,392,107	7/1968	Pfefferle	208—65
3,540,996	11/1970	Maziuk et al.	208—65
3,394,073	7/1968	Strickland	208—65

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—64, 65, 93