Dec. 23, 1958 H. A. HOLCOMB ET AL 2,865,837

REFORMING HYDROCARBONS FOR ENHANCED YIELDS

Filed Sept. 4, 1956

2 Sheets-Sheet 1

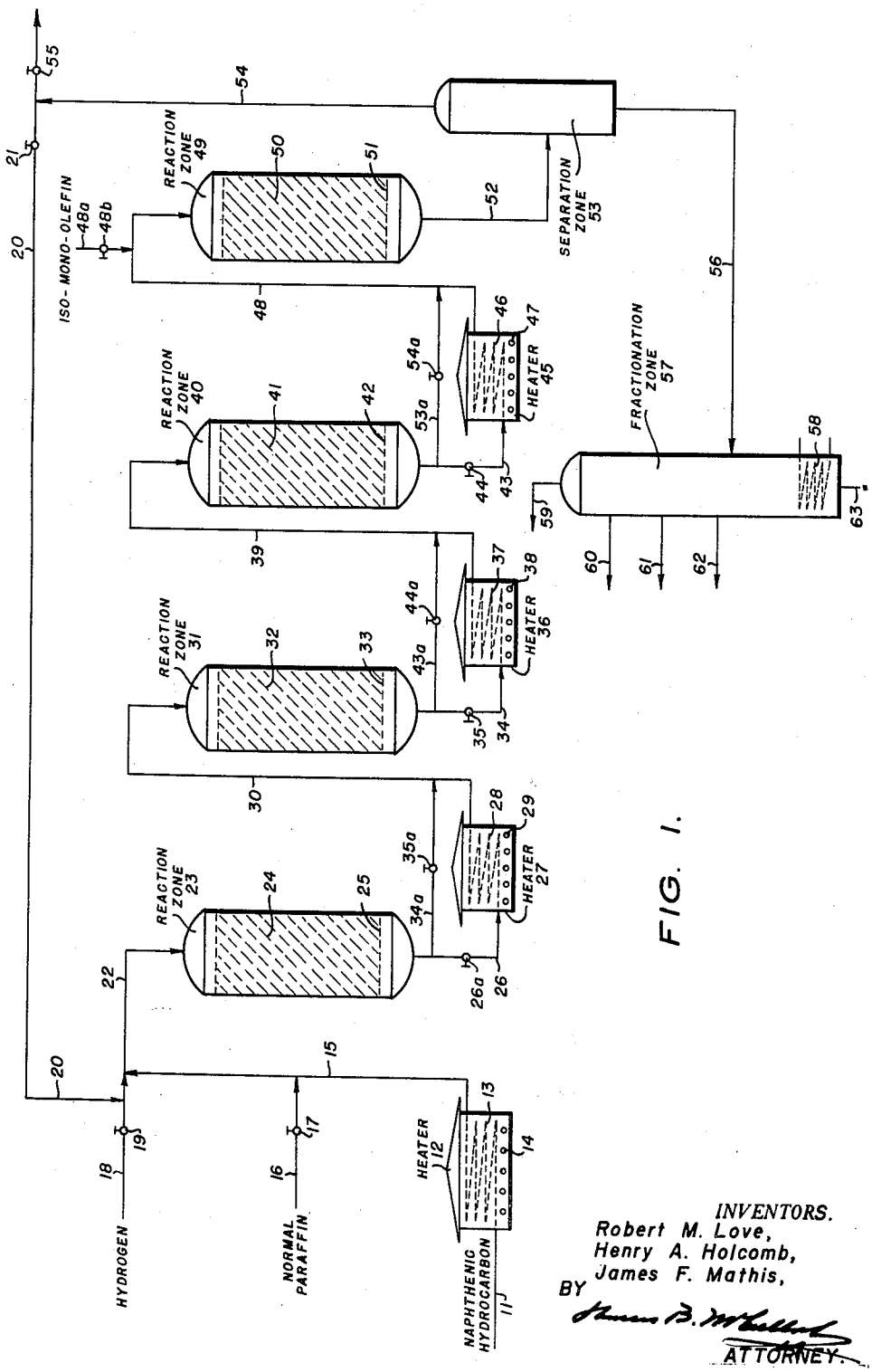

FIG. 1.

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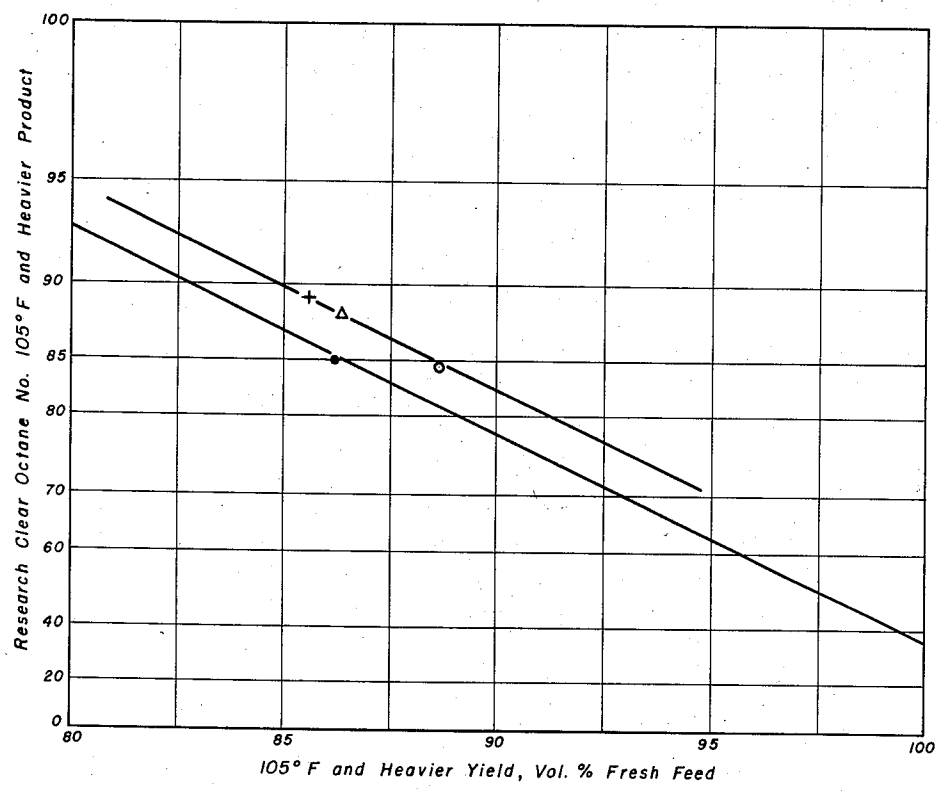
2 Sheets-Sheet 2

FIG. 2.



	Example
• 190°-260° F Virgin Naphtha	3
+ 20% Catalytic Pentylenes in Last Reactor	4
Δ 40% " " " " "	5

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REFORMING HYDROCARBONS FOR ENHANCED YIELDS

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Application September 4, 1956, Serial No. 607,639

11 Claims. (Cl. 208—65)

The present invention is directed to a method for converting hydrocarbons. More particularly, the invention is directed to a method of producing high yields of high octane number hydrocarbons. In its more specific aspects, the invention is directed to converting naphthenic hydrocarbons in admixture with other hydrocarbons in high yields of high octane number materials.

The present invention may be briefly described as a method for producing enhanced yields of high octane number hydrocarbons in which a naphthenic hydrocarbon fraction is charged in series to a plurality of reaction zones, each containing a bed of supported platinum catalyst and maintained at hydrocarbon conversion conditions. The specific feature of the present invention involves adding a normal paraffin in a sufficient amount to the naphthenic hydrocarbon feed at least to the lead reaction zone of said plurality of zones and adding an iso-olefin in a sufficient amount to the converted hydrocarbon charged to the tail reaction zone of the plurality of zones such that the normal paraffin is contacted with the catalyst for a time within the range from about 10 to about 20 seconds and such that the iso-olefin is contacted with the catalyst for a time within the range of about 2 to about 5 seconds whereby enhanced yields of high octane number hydrocarbons are obtained. While it is preferred to add the normal paraffin to the lead reaction zone, under some conditions, the normal paraffin may be added to the other of the plurality of zones depending on reaction conditions therein.

The naphthenic hydrocarbon fraction which may be employed as the feed may boil in the range from about 100° to about 400° F. and suitably may contain naphthenic hydrocarbons and paraffinic hydrocarbons and some aromatic hydrocarbons. It will be preferred, however, to maintain the amount of aromatic hydrocarbons at a minimum since these hydrocarbons do not undergo conversion in the reaction and since they already have high octane number values.

The normal paraffin added to the lead reaction zone may suitably include normal paraffins having from 5 to 8 carbon atoms and may include normal pentane, normal hexane, normal heptane and normal octane.

The iso-olefin added to the tail reaction zone may suitably include either iso-mono-olefins or iso-diolefins such as isopentylenes, isohexylenes, isoheptylenes and isooctylenes, 2-methyl-butadiene-1,3, and the like, such as the diolefins corresponding to the iso-mono-olefins given by way of example. Normal pentane and isopentylenes comprise preferred normal paraffins and iso-mono-olefins to be introduced into the operation. Suitable diolefins may be obtained from the C_6 fraction of catalytic naphthas such as catalytically cracked naphthas.

The amounts of normal paraffin and the iso-mono-olefin employed may range from about 10 to about 60 percent by volume of the naphthenic hydrocarbon feed.

The catalyst employed in the present invention is a platinum catalyst and preferably is a supported platinum on alumina catalyst. The amount of platinum on the

catalyst is preferably about 0.6% by weight but amounts of platinum in the catalyst from about 0.1% to 2.0% by weight may be employed. In some cases as much as 4.0% by weight may be used although the lesser range is preferred. The support is preferably highly purified aluminum oxide. The aluminum oxide may suitably be a gamma alumina or an eta alumina derived from conventional sources of alumina hydrates or from specially derived alumina hydrates, such as those obtainable from aluminum alcoholates, phenolates, etc.

Temperatures employed in the practice of the present invention in the several reaction zones may range from about 800° to about 1000° F. The temperatures may progressively increase from the lead to the tail reaction zone within this range. The temperatures may increase incrementally from one reaction zone to another reaction zone from about 10° to about 100° F. However, the temperatures in the several zones may be approximately equal. Also, the temperatures in the lead zones may be greater than the temperature in the tail reaction zone.

Pressure employed in the practice of the present invention may range from about 200 to about 500 pounds per square inch gauge. A suitable and preferred pressure is about 300 pounds per square inch gauge.

The space velocity is preferably about 2.0 volumes of total feed hydrocarbon per volume of catalyst per hour entering the lead reaction zone. However, space velocities in the several zones may range from about 0.5 to about 5.0 v./v./hr., the space velocity in the tail zone increasing as hydrocarbon is added thereto.

The presence of hydrogen is required in the practice of the present invention and a preferred amount of hydrogen is about 4000 standard cubic feet of hydrogen per barrel of total feed. The amount of hydrogen may range from about 2000 to 6000 cubic feet per barrel of feed.

The reaction is preferably conducted in a plurality of reaction zones with the supported catalyst arranged in beds therein. However, it is to be understood that the operation may be conducted with a fluidized type operation wherein a fluidized powdered catalyst of the nature described is suspended in the vaporized hydrocarbon. Addition of iso-olefins to fluidized systems should alleviate the difficult heat supply problem inherent therein.

The reaction may be conducted under adiabatic or isothermal conditions.

Of importance in the practice of the present invention is the contact time. Specifically, the normal paraffin should contact the catalyst in the several reaction zones for a time within the range from about 10 to about 20 seconds. The iso-mono-olefin should contact the catalyst in the last or in several reaction zones for a time within the range from about 2 to about 5 seconds. By employing such contact times, the normal paraffin is isomerized selectively to isoparaffin and the iso-mono-olefin is hydrogenated selectively to the corresponding isoparaffin. Such reactions result in the enhancement of the quantity of isoparaffins in the product and result in a product which has an increased yield of isoparaffins as well as containing increased yields of aromatics produced from the reforming of the naphthenic hydrocarbons.

It is to be emphasized that the nephthenic hydrocarbon fraction which normally contains paraffins will have some of the paraffins isomerized to isoparaffins.

The present invention will be further illustrated by reference to the drawing in which:

Fig. 1 is in the form of a diagrammatic flow sheet of a preferred mode; and

Fig. 2 is a graph of data showing the relationship between the research clear octane number and the yield obtainable in the several examples.

Referring specifically to the drawing, numeral 11 des-

ignates a charge line by way of which a naphthenic hydrocarbon fraction boiling in the range indicated is introduced into the system from a source not shown. The naphthenic hydrocarbon fraction is introduced into a heater or furnace **12** provided with heating coils **13** and supplied with heat through gas burners **14** which raise the temperature of the naphthenic hydrocarbon to the desired range. The heated and vaporized hydrocarbon then passes from the furnace **12** by way of line **15**; normal paraffin, such as normal pentane, is injected thereto by way of line **16** controlled by line **17** and hydrogen is added thereto by way of line **18** controlled by valve **19** or recycled hydrogen is introduced into line **18** by recycle line **20** controlled by valve **21** from a source to be described hereinafter. In any event, the mixture of naphthenic hydrocarbon, normal paraffin and hydrogen, the latter preferably being heated either separately or with the naphthenic hydrocarbon, is introduced by way of line **22** into a lead reaction zone **23** which contains a bed **24** of platinum catalyst, of the nature specified before, arranged on a grid plate **25**. The hydrocarbon feed mixture is converted in reaction zone **23** and the converted or partially converted hydrocarbons issue therefrom by way of line **26** controlled by valve **26***a* which discharges the partially converted product including the normal paraffin into a heater or furnace **27** provided with a heating coil **28** and heated by means of gas burners **29**. The reheated and partially converted product is then routed by way of line **30** into a second reaction zone **31** provided with a bed of platinum catalyst **32** arranged on a grid plate **33**. It may be desirable to bypass all or part of the partially converted products from reaction zone **23** around the heater **27** and to this end bypass line **34***a* controlled by valve **35***a* is provided.

The partially converted products discharge through the bed **32** of reaction zone **31** and are further converted with the converted products discharging therefrom through line **34** controlled by valve **35** into a heater or furnace **36** provided with heating coils **37** and gas burners **38**. The reheated products then discharge from furnace **36** by way of line **39** into reaction zone **40** which is provided with a bed of platinum catalyst **41** supported on grid plate **42**. Bypass line **43***a* controlled by valve **44***a* is also provided to allow the converted products from zone **31** to bypass the furnace **36** in part or completely as may be desired.

The products are further converted in reaction zone **40** and are discharged therefrom by way of line **43** controlled by valve **44** into a heater or furnace **45** provided with a heating coil **46** and heated with gas burners **47**. The converted products are discharged from furnace **45** into line **48** and then introduced thereby into a tail reaction zone **49** in admixture with an isoolefin introduced by line **48***a* controlled by valve **48***b*. Zone **49** is provided with a bed **50** of supported platinum catalyst on grid plate **51**. It is understood that the iso-olefin may be added to line **43** and heated in furnace **45** or may be separately heated. The converted products issue from zone **49** by way of line **52** and are discharged thereby into a separation zone **53**. It may be desirable to bypass the furnace **45** and to this end bypass line **53***a* is provided controlled by valve **54***a* allowing the furnace **45** to be completely or partially bypassed by the converted products.

The converted products are discharged by line **52** into separation zone **53** by way of which a separation is made between the normally gaseous constituents and the normally liquid constituents, the gases being discharged by line **54**, compressed, as required, and recycled by way of line **20** to line **18**. If the amount of fixed gases which include hydrogen exceed the amount required in the several reaction zones, then the hydrogen-containing gases may be discharged by opening valve **55** in line **21**.

The liquid product is withdrawn from separation zone **53** by line **56** and discharged thereby into a fractional distillation zone **57** which may be a single fractional distillation tower or a plurality of fractional distillation towers. For purposes of briefness, zone **57** is shown as a single fractional distillation tower which it will be understood to include internal vapor-liquid contacting means, such as bell cap trays, and the like, auxiliary equipment, such as refluxing, cooling and condensing equipment, and the like.

In the drawing, zone **57** is provided with a heating means illustrated by a steam coil **58** and is provided with lines **59**, **60**, **61**, and **62** for withdrawal of desirable products therefrom. A bottoms fraction may be withdrawn by line **63**. The fractions withdrawn by lines **59**, **60**, **61** and **62** may include converted isoparaffins, and aromatics or mixtures thereof. The bottoms fraction in line **63** and the side stream fraction of line **62** may include unconverted hydrocarbons and may be recycled to line **11** as desired.

By operating in accordance with the present invention, a suitable reaction or contact time is provided for the normal paraffins and a suitable reaction time is provided for the iso-mono-olefins, such that enhanced yields of the aromatic and isoparaffinic hydrocarbons are obtained.

The invention will be further illustrated by the following examples:

EXAMPLE 1

A virgin crude petroleum naphtha boiling in the range from about 190° to about 260° F. was contacted in a four reactor adiabatic system in series with a platinum on alumina catalyst containing 0.6 weight percent of platinum, the naphtha being flowed into the lead reactor and in series through the other reactors. The space velocity was 2 v./v./hr. and 4,000 standard cubic feet of recycle hydrogen per barrel of feed was employed at a pressure of 300 pounds per square inch gauge. The following yields and octane number relationships were found by analysis of the product:

Table I

105° F. and Heavier Product Yield, Vol. Percent on Fresh Feed	Research Clean Octane Number of 105° F. and Heavier Product
Feed	60
90	78
88	82.5
86	86
84	88.7
82	91.2
80	93.3
75	97.3
70	100.3

It was found that at 85 Research clear octane number the contact time was about 16.8 seconds. The inlet temperatures to the several reactors varied from about 900° to about 975° F.

EXAMPLE 2

A blend of 20 volumes of a pentylene-rich stream obtained from a catalytic cracking operation and 80 volumes of a 260° to 300° F. virgin crude naphtha was reformed under the same conditions as Example 1 with reaction inlet temperatures of 945, 956, 954 and 955 in the four reactors, respectively.

The catalyst temperatures in the four reactors were 908, 934, 941, and 952, respectively. The yield of iso and normal pentanes based on the components of the pentylene feed was 66.4 mol percent. The ratio of isopentane to normal pentane in the product was 1.83 compared to 1.94 which would have been obtained if only hydrogenation of the pentylenes been effected. The contact time was about 16.8 seconds.

It may be concluded from these results that the hydrogenation of pentylenes for the conversion of isopentylene to isopentane may be effectively carried out only by operating at lower contact times than those utilized in this example.

EXAMPLE 3

The same crude virgin naphtha of Example 1 was reformed under the same conditions of Example 1 with reactor inlet temperatures of 924°, 935°, 934° and 934°, respectively, in the four reactors in series. The average catalyst bed temperatures corresponding to these inlet temperatures were 830°, 867°, 879°, and 896° F., respectively. The yield octane relationship obtained in the product from this run was as follows:

105° F. and heavier product yield, vol. percent on feed	86.2
105° F. and heavier product, Research clear octane number	85

It will be seen that these values are approximately the same as those obtained in Example 1. In this example, the contact time was a total of about 16.8 seconds, whereas the contact time in the last reactor was about 4.10 seconds.

EXAMPLE 4

Immediately following Example 3 with the same reactor inlet temperatures on the same virgin crude naphtha, catalytic pentylenes, the analysis of which follows, were charged to the inlet of the fourth or last reactor at a rate of 20 volume percent of the total virgin crude naphtha feed to the lead reactor. The hydrogen recycle gas rate was increased so that a rate of 4,000 standard cubic feed of hydrogen per barrel of total feed to the reactor system was maintained. The reactor inlet temperatures were 926°, 937°, 933° and 931° F. prevailing for the several reactors in series at corresponding average catalyst bed temperatures of 835°, 872°, 881° and 939° F. The increase in the average temperature in the last reactor was occasioned by the exothermic nature of the hydrogenation reactions involving the pentylenes, it being understood that the reactions in reforming are normally endothermic in nature and require reheating between reactors.

Table II.—Catalytic pentylenes analysis

Compound:	Wt. percent
i-Pentane	30.2
n-Pentane	2.8
Pentene-1	10.3
Trans-pentene-2	11.4
Cis-pentene-2	9.5
2 M-butene-1	12.0
2 M-butene-2	20.6
105° F. and heavier	3.2

The 105° F. plus product yield based on the virgin crude naphtha charged in this example was 85.6 volume percent with a research clear octane number of 89.3. This represents a yield advantage of about 1.9 volume percent at the 89.3 octane level over that shown in Example 1 for operations with the same virgin crude naphtha alone. The higher octane number level in this example over Example 3 at the same inlet reactor temperatures was obtainable by the higher average reactor temperature in the fourth or tail reactor. In Example 4 herein the overall contact time was 14.1 seconds whereas the contact time in the last reactor was 3.3 seconds.

In addition to the increase in the 105° F. plus product from the virgin naphtha the yield of iso plus normal pentane from the pentylenes added to the last reactor was 81.1 mol percent of that which would have been obtained by hydrogenation alone. The mol ratio of isopentane to normal pentane in the product from pentylenes was 1.94 compared to 1.83 for the pentylenes introduced into the last reactor zone. This showed that isopentane would not isomerize to normal pentane after it has been formed by hydrogenation.

EXAMPLE 5

The conditions of Example 4 were maintained and an additional 20 volume percent, making a total of 40 volume percent of a catalytic pentylenes based on the total virgin naphtha feed, were added to the last reaction zone feed. Reactor inlet temperatures of 924°, 934°, 936° and 866° provided average reactor or catalyst temperatures of 834°, 871°, 887° and 940° F. in this example. Again the recycle gas rate was increased to maintain a rate of 4,000 standard cubic feet of hydrogen per barrel of total feed to the reactor system. Under these conditions, the yield of 105° F. and heavier materials based on the virgin crude naphtha was 86.4 volume percent for a research clear octane number of 88.1. This represents a yield advantage of about 1.9 volume percent at the 88.1 octane level over that shown for Example 1 for operations with the virgin crude naphtha alone. In this run the total contact time was 12.4 seconds and the contact time in the fourth reactor was only about 2.8 seconds. The yield of iso plus normal pentanes was 92.4 mol percent of that which would have been made by hydrogenation alone with no loss. The mol ratio of iso to normal pentane in the pentylenes product was 1.93 compared to 1.83 for the pentylenes feed. The yield of isopentane was 94.1 mol percent of that available from the pentylene feed. The similar yield for normal pentane was 89.3 mol percent. This example conclusively shows that the yield-product distribution relationships were better from the standpoint of pentylenes alone at 40 volume percent level in the last reactor than at the 20 volume percent level.

EXAMPLE 6

Example No. 4 was repeated except that 20 volume percent of the crude virgin naphtha of a normal pentane-rich fraction were added to the fourth reactor instead of the catalytic pentylenes. With reactor inlet temperatures of 923°, 934°, 934° and 933° the average reactor temperatures were 831°, 870°, 882°, and 903° F. The composition of the pentane feed is given in Table III:

Table III

Component:	Vol. percent
Isopentane	20.2
Normal pentane	76.6
Pentylenes	1.8
105° F. and heavier	1.4

In this operation the contact time in the fourth reactor was about 3.4 seconds.

Under the conditions of this example the yields of 105° F. and heavier material produced from the virgin crude naphtha was 88.7 volume percent and the octane number was 84.3 research. This represents a yield advantage of 1.7 volume percent of 105° F. and heavier fraction at 84.3 research octane number over that obtained with the virgin crude naphtha alone with the same octane number. The yield of iso plus normal pentanes was 100 mol percent of that from the feed pentanes. The mol ratio of iso to normal pentane was 0.39 compared to 0.26 for the feed. The isopentane yield based on feed isopentane was 139.2 mol percent indicating that some isomerization of normal pentane to isopentane occurred.

The data in these several examples are presented in Fig. 2 graphically and show conclusively an improved yield for the presence of catalytic pentylenes in the last reaction zone.

From these examples it is clear that it was desirable to add the normal paraffins to the lead reaction zone of a plurality of reaction zones to enhance the isomerization thereof by providing the extended contact time whereas it is desirable to add the iso-mono-olefin to the tail reaction zone such that the iso-mono-olefin is only hydrogenated but is not further converted.

The present invention is of great value and utility in that enhanced yields of high octane number material are

possible by operating the reforming zone employing a platinum catalyst in which the paraffin is subjected to a relatively long reaction time and the iso-mono-olefin is subjected to a relatively short reaction time.

It is contemplated that the present invention may be operated by providing an elongated reaction zone containing a bed of supported platinum catalyst maintained at hydrocarbon conversion conditions such as described herein with the paraffinic hydrocarbon being charged to the feed to said reaction zone and with the iso-mono-olefin being charged into the reaction zone at a selected intermediate point therein to provide the relatively long contact time for the normal paraffin and the relatively short contact time for the isoparaffin.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A method for producing enhanced yields of high octane hydrocarbons in which a naphthenic hydrocarbon fraction is charged in series to a plurality of reaction zones each containing a bed of supported platinum catalyst and maintained at hydrocarbon conversion conditions which comprises adding a normal paraffin in a sufficient amount within the range from about 10 to about 60% by volume of the naphthenic hydrocarbon to the naphthenic hydrocarbon feed to the lead reaction zone of said plurality of zones and adding an isoolefin in a sufficient amount within the range from about 10 to about 60% by volume of the naphthenic hydrocarbon to the converted hydrocarbon charged to the tail reaction zone of said plurality of zones such that the normal paraffin is contacted with the catalyst for a time within the range from about 10 to about 20 seconds and such that the isoolefin is contacted with the catalyst for a time within the range from about 2 to about 5 seconds whereby enhanced yields of high octane hydrocarbons are obtained.

2. A method in accordance with claim 1 in which the normal paraffin is normal pentane and the iso-olefin is an isopentylene.

3. A method in accordance with claim 1 in which the plurality of reaction zones comprise four reaction zones maintained at conversion conditions including a progressively increasing temperature from the lead to the tail reaction zone within the range from about 800° F. to about 1000° F.

4. A method in accordance with claim 1 in which the iso-olefin is an iso-mono-olefin.

5. A method in accordance with claim 1 in which the iso-olefin is an iso-diolefin.

6. A method for producing enhanced yields of high octane hydrocarbons in which a naphthenic hydrocarbon fraction boiling in the range from about 100° to about 400° F. is contacted in the presence of a free hydrogen-containing gas in series with a platinum catalyst in a plurality of reaction zones each containing a bed of supported catalyst containing from about 0.1% to about 4.0% by weight of platinum on purified alumina and maintained at hydrocarbon conversion conditions which comprises adding a normal paraffin containing 5 to 8 carbon atoms in a sufficient amount within the range from about 10 to about 60% by volume of the naphthenic hydrocarbon to the naphthenic hydrocarbon feed to the lead reaction zone of said plurality of zones and adding an iso-mono-olefin containing 5 to 8 carbon atoms in a sufficient amount within the range from about 10 to about 60% by volume of the naphthenic hydrocarbon to the converted hydrocarbon charged to the tail reaction zone of said plurality of zones such that the normal paraffin is contacted with the catalyst for a time within the range from about 10 to about 20 seconds and such that the iso-mono-olefin is contacted with the catalyst for a time within the range from about 2 to about 5 seconds whereby enhanced yields of high octane hydrocarbons are obtained.

7. A method in accordance with claim 6 in which the normal paraffin is normal pentane and the iso-mono-olefin is an isopentylene.

8. A method in accordance with claim 6 in which the plurality of reaction zones comprise four reaction zones maintained at conversion conditions including a progressively increasing temperature from the lead to the tail reaction zone within the range from about 800° F. to about 1000° F.

9. A method in accordance with claim 6 in which the conversion conditions in said plurality of reaction zones includes a temperature increasing incrementally from one reaction zone to another by about 10° F. to about 100° F.

10. A method in accordance with claim 6 in which the conversion conditions include a pressure within the range from about 200 to about 500 pounds per square inch gauge and a space velocity in the range from about 0.5 to about 5.0 volumes of hydrocarbon fraction per volume of catalyst per hour.

11. A method for producing enhanced yields of high octane hydrocarbons in which a naphthenic hydrocarbon fraction is charged to a reaction zone containing a bed of supported platinum catalyst and maintained at hydrocarbon conversion conditions which comprises adding a normal paraffin in a sufficient amount within the range from about 10 to about 60% by volume of the naphthenic hydrocarbon to the naphthenic hydrocarbon feed and adding an iso-olefin to said reaction zone in a sufficient amount within the range from about 10 to about 60% by volume of the naphthenic hydrocarbon at a selected point such that the normal paraffin is contacted with the catalyst for a time within the range from about 10 to about 20 seconds and such that the iso-olefin is contacted with the catalyst for a time within the range from about 2 to about 5 seconds whereby enhanced yields of high octane hydrocarbons are obtained.

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