Nov. 25, 1958 J. R. COLEY ET AL 2,861,944

CONVERSION OF METHYLCYCLOPENTANE TO BENZENE

Filed June 29, 1955 2 Sheets-Sheet 1

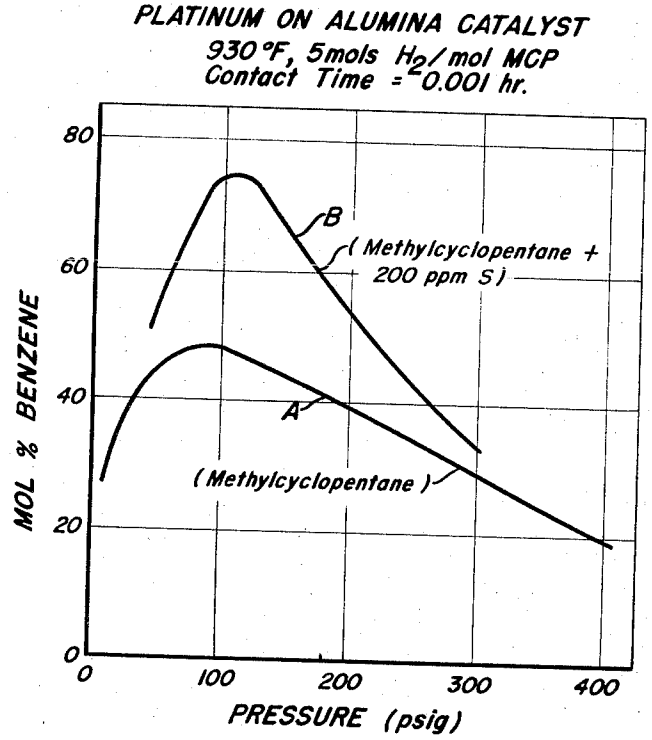


Fig. 1

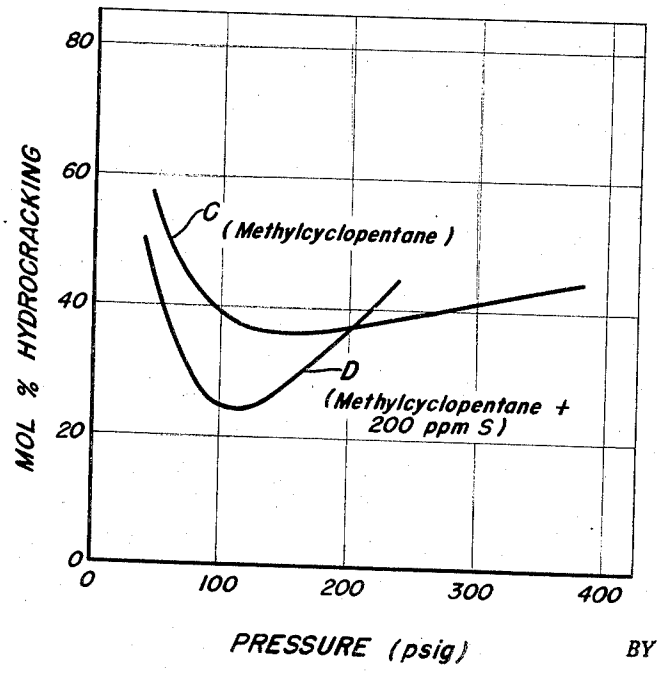


Fig. 2

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2 Sheets-Sheet 2

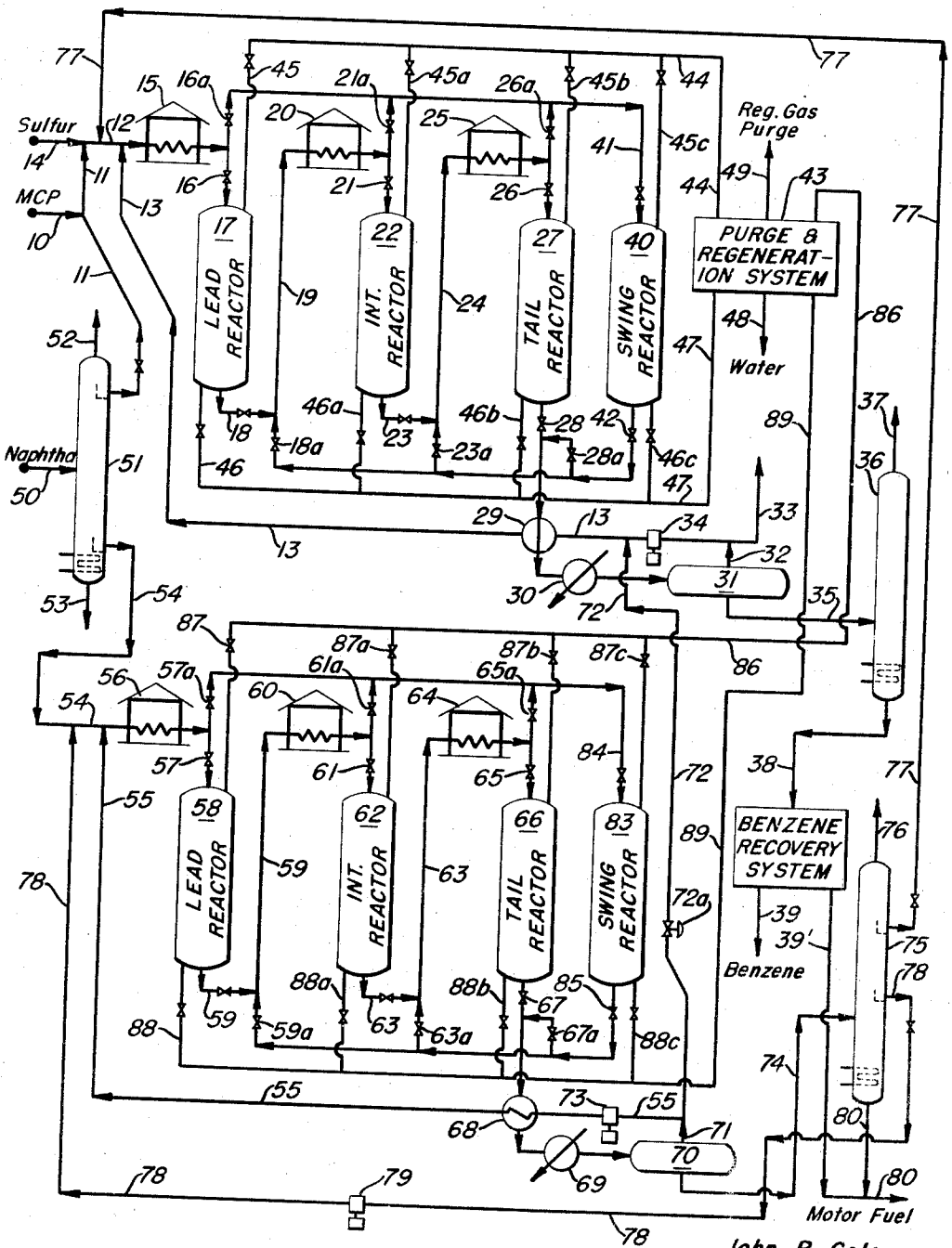


Fig. 3

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CONVERSION OF METHYLCYCLOPENTANE TO BENZENE

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Application June 29, 1955, Serial No. 518,764

12 Claims. (Cl. 208—92)

This invention relates specifically to conversion of methylcyclopentane to benzene with supported platinum catalyst at low pressure and it pertains more generally to low pressure hydroforming of light naphtha charging stocks containing substantial amounts of methylcyclopentane and to combinations of such low pressure operations with higher pressure hydroforming operations for maximizing yields of 95–100 octane number motor fuel and simultaneously producing benzene.

A specific object of the invention is to provide an improved process for converting methylcyclopentane, either in relatively pure state or in admixture with other hydrocarbons such as hexanes, to obtain increased yields of benzene accompanied by isomerization and cyclizing of any C_{6+} paraffinic hydrocarbons which may be present with a minimum amount of hydrocracking and coke formation. A further object is to accomplish this commercially by means of supported platinum catalyst in a regenerative low pressure hydroforming system in which catalyst activity, selectivity and stability remain high during on-stream operation and can be substantially restored by periodic regeneration and rejuvenation.

Known supported platinum catalyst naphtha hydroforming systems can readily convert most naphthenic naphthas boiling in the range of about 200 to 360° F. into motor fuels of 80 to 90 octane number. Non-regenerative supported platinum hydroforming systems cannot readily convert even this optimum boiling range charge into 95–100 octane number product without cumbersome and expensive solvent extraction and recycling operations. Regenerative supported platinum catalyst hydroforming systems now known can employ wider boiling range charges but they are not effective for converting methylcyclopentane to benzene or for producing benzene in addition to high quality motor fuel. An object of this invention is to provide an integrated method and means for maximizing yields of motor fuels having octane numbers of 95 to 100 with simultaneous production of benzene. A further object is to provide an improved integration of low pressure hydroforming with higher pressure hydroforming. A still further object is to produce benzene from the 140–180° F. fraction of naphtha with minimum losses to gas and coke formation and maximum isomerization and dehydroaromatization so that hydrocarbons separated from the benzene may be advantageously blended with higher boiling hydroformed naphtha for improving the yield of total 95+ octane number motor fuel. Other objects will be apparent as the detailed description of the invention proceeds.

The invention is based on the discovery that when methylcyclopentane is contacted with a supported platinum catalyst at an inlet temperature in the range of about 900 to 950° F., preferably about 930° F., in the presence of about 1 to 10, e. g. 5, mols of hydrogen per mol of charge and at a liquid hourly space velocity in the range of .5 to 8, preferably 2, benzene formation

increases rapidly with increasing pressure up to about 100 p. s. i. g. and then declines at higher pressures, hydrocracking of methylcyclopentane reaches a minimum at about 100 p. s. i. g., and the addition of about 50 to 1000, e. g. about 200, parts per million of sulfur has a combined effect of increasing benzene production up to as much as 50 percent while at the same time decreasing carbon formation on the catalyst and catalyst activity decline. The addition of 10 parts per million of chloride to methylcyclopentane under these conditions showed no beneficial effect on benzene formation. It thus appears that the defined amount of sulfur accelerates the isomerization of methylcyclopentane to cyclohexane and simultaneously inhibits coke formation and hydrocracking so that at the low pressure of about 100 p. s. i., i. e. in the range of about 50 to 150 p. s. i., a remarkably effective methylcyclopentane conversion to benzene may be effected and, simultaneously, any C_{6+} paraffin hydrocarbons present can be isomerized and/or dehydroaromatized.

The invention may be applied to methylcyclopentane per se or to a charge containing substantial amounts thereof when the objective is benzene production. The resulting benzene may then be separated and hydrogenated to form cyclohexane by the use of known catalysts and conditions along with hydrogen produced in the methylcyclopentane conversion step.

A preferred charge is a methylcyclopentane fraction of virgin naphtha alone or in combination with the low boiling fraction of a hydroformed product. By hydroforming a naphtha fraction boiling in the range of about 140 to 200° F. or preferably 140 to 180° F. and containing substantial amounts, i. e. 5 to 50 volume percent or more, of methylcyclopentane with a supported platinum catalyst at approximately 100 p. s. i. g. and at a temperature of about 900 to 975° F. in the presence of about 1 to 10 mols of hydrogen per mol of charge and also in the presence of 50 to 1000, e. g. about 200, parts per million of sulfur based on total hydrocarbon charge, remarkably high yields of benzene are obtained and at the same time the octane number of the other components of the light naphtha is remarkably enhanced. A particularly advantageous practice is to employ this low pressure sulfur-promoted light naphtha hydroforming operation in conjunction with a hydroforming operation now known to the art, such as Platforming, Cat-forming, Houdriforming or, preferably, Ultraforming. When employed with a regenerative hydroforming system such as Ultraforming, much of the same regeneration equipment may be employed for the low pressure system as is employed in the Ultraforming system. The fraction of ordinary Ultraformed product boiling below 200° F. may be charged with the methylcyclopentane fraction of virgin naphtha to the low pressure system for substantially increasing benzene production and over-all octane number improvement without suffering appreciable yield losses. Hydrogen from the Ultraforming portion of the system may supply that required in the low pressure sulfur-promoted hydroforming step. By separating benzene from the stabilized product of the low pressure step and combining the rest of the stabilized product with the high boiling portion of the intermediate or high pressure step, a motor fuel is obtained wherein the light, as well as the heavy, components are of exceptionally high octane number and remarkably high 100 octane number motor fuel yields are obtainable in addition to the production of valuable benzene. In some instances it may be desirable to recycle an intermediate fraction of the hydroformed product produced at higher pressure back to the higher pressure hydroforming step.

The invention will be more clearly understood from the following detailed description read in conjunction with

the accompanying drawings which form a part of the specification and in which:

Figure 1 is a graph illustrating the remarkable effect of pressure and the defined amount of added sulfur on the conversion of methylcyclopentane to benzene under preferred conditions.

Figure 2 is a graph showing the effect of pressure and the defined amount of sulfur on hydrocracking of methylcyclopentane under the same conditions, and

Figure 3 is a schematic flow diagram of a plant for effecting methylcyclopentane conversion in an integrated hydroforming system.

To demonstrate the effect of pressure and added sulfur in the hydroforming of methylclclopentane, a commercial methylcyclopentane was purified by hydrofining and stripping so that it contained less than 10 parts per million of sulfur and less than 1 part per million of chloride. The purified methylcyclopentane was hydroformed over a platinum-alumina catalyst containing .6 weight percent platinum at a temperature of about 930° F., a space velocity of about 2 volumes of methylcyclopentane per hour per volume of catalyst in the presence of 5,000 standard cubic feet of once-through hydrogen per barrel of methylcyclopentane charge and under pressures ranging from 50 to 400 p. s. i. g. Each test employed an on-stream period of 5 hours. Where sulfur was added it was employed in the form of tertiary butyl mercaptan. The reactor effluent in each case was analyzed for aromatics content, the catalyst was analyzed for coke deposit and the amount of converted charge which did not result in benzene were considered to be hydrocracked.

The results of this experimental program are graphically shown in Figures 1 and 2. Curve A shows that at about atmospheric pressure only about 20 to 25 percent of the methylcyclopentane was converted to benzene, that the conversion to benzene increased rapidly as pressure was increased to about 100 p. s. i. where approximately 45 percent of the charge was converted to benzene and that with further increases in pressure the conversion to benzene decreased quite rapidly. Curve B of Figure 1 shows that when about 200 parts per million of sulfur is added to the methylcyclopentane charge, the conversion of methylcyclopentane to benzene is markedly increased, being about 50 percent higher at about 100 p. s. i. than obtainable in the absence of added sulfur. The effectiveness of added sulfur in increasing benzene production is greatest in the region of about 100 p. s. i. and rapidly diminishes at higher and lower pressures.

Referring to Figure 2, Curve C shows that in the absence of added sulfur the hydrocracking of methylcyclopentane under the defined conditions reached a minimum in the region of about 100 p. s. i. Curve D shows that the presence of about 200 parts per million of added sulfur had a most remarkable effect of inhibiting hydrocracking at a pressure of about 100 p. s. i. g. although it apparently actually increased hydrocracking at pressures above about 200 p. s. i. g.

To avoid confusion, other factors have not been shown in the graphs but with respect to carbon formation on the catalyst, the addition of about 200 parts per million of sulfur in the optimum pressure range of about 50 to 150 p. s. i. g. effected about a two-fold to four-fold decrease in coke deposit. Although the total methylcyclopentane conversions at pressures above 200 p. s. i. were somewhat higher than total conversions obtained at about 100 p. s. i., this latter operating pressure resulted in larger yields of total benzene. Conversion products other than benzene may be blended with reformed gasoline to improve the yield and octane number thereof. The addition of 10 parts per million of chloride to methylcyclopentane (instead of the defined amount of sulfur) did not have appreciable effect on aromatic product and, in fact, at pressures about 100 p. s. i. and higher the addition of chloride to the charge appeared to be actually detrimental.

While the presence of added sulfur had very little effect on the dehydroaromatization of n-heptane, it was found that aromatics production from normal heptane under the described conditions likewise reached a maximum in the range of 50 to 150 or about 100 p. s. i. g. Thus a methylcyclopentane fraction of virgin naphtha could be hydroformed under the defined conditions for maximizing aromatics production while minimizing hydrocracking and coke formation.

While about 200 parts per million is the preferred amount of sulfur to be added to a methylcyclopentane charge which is to be hydroformed at a pressure of about 100 p. s. i. g., this amount may vary in a range of about 50 to 1000 or preferably 100 to 500 parts per million, larger amounts in these ranges being used when the charge contains large amounts of paraffins. Amounts of sulfur substantially in excess of 1000 parts per million have a deleterious effect on catalyst life and particularly on the activity and selectivity of the catalyst thereby resulting in decreased yields of desirable products and shorter on-stream operating periods. The sulfur is preferably added in the form of mercaptan sulfur, e. g. as tertiary butyl mercaptan, but it may be added in any other form, such as free sulfur, H_2S, alkyl sulfides or disulfides, cyclic sulfur compounds, or other organic sulfur compounds. If the methylcyclopentane fraction of a virgin naphtha stream inherently contains the desired amount of sulfur, no sulfur addition from an extraneous source will, of course, be necessary. The required amount of sulfur may be introduced with the hydrogen stream. The total sulfur introduced into a reactor should not exceed about 1000 parts per million based on total hydrocarbon charging stock introduced, which charging stock should contain at least about 5 percent and preferably about 50 percent or more of methylcyclopentane.

Referring now to the specific example described in connection with Figure 3, methylcyclopentane from line **10** is introduced through line **11** to line **12** where it is commingled with about 5 mols of hydrogen from line **13** per mol of charge and about 200 parts per million of sulfur in the form of tertiary butyl mercaptan introduced through line **14**. The total charge is passed by line **12** through heater **15** and transfer line **16** to lead reactor **17**. Effluent from this reactor passes by lines **18** and **19** through heater **20** and transfer line **21** to intermediate reactor **22**. Intermediate reactor effluent passes through lines **23** and **24** through heater **25** and transfer line **26** to tail reactor **27**. Final effluent leaves the tail reactor through line **28** and passes through exchanger **29** and cooler **30** to hydrogen separator **31** from which separated hydrogen is withdrawn through line **32**, net hydrogen being vented through line **33** and the required amount of recycle hydrogen being recycled by compressor **34** to line **13**.

The pressure in the reactors is maintained at about 100 p. s. i. g., i. e. in the range of about 50 to 150 p. s. i. g., the lead reactor being at somewhat higher and the tail reactor at somewhat lower pressure than the intermediate reactor to provide for pressure drop through the system. The inlet temperature to each of the reactors is about 930° F., e. g. in the range of about 900 to 950 but not higher than 975° F. Each of the reactors is preferably aluminized and provided with a refractory lining of low iron content. They may each contain about the same amount of catalyst although, if desired, the subsequent reactors may contain somewhat more catalyst than the lead reactor. The catalyst may be of any known type of supported platinum catalyst and the platinum is preferably supported on alumina; it may be prepared by compositing a platinum chloride with an alumina support as described, for example, in U. S. 2,659,701 and it preferably contains about .3 to .6 weight percent of platinum. The space velocity in each reactor is preferably in the range of about 1 to 10, the over-all space velocity preferably being in the range of about 1 to 4 volumes of liquid hydrocarbon charge per hour per volume of catalyst.

The product is withdrawn from separator **31** through line **35** to stabilizer and/or fractionation system diagrammatically represented as fractionating column **36** from which propane and lighter materials are withdrawn through line **37** and stabilized product is withdrawn to benzene recovery system **38** which may be of any known type such as silica gel absorption, extractive distillation or polyethylene glycol extraction (Udex), the benzene being withdrawn from the system through line **39** and products separated from benzene being withdrawn through line **39'** for blending with reformed motor fuel.

A swing reactor **40** (containing the same amount of the same type of catalyst as reactor **27**) is employed in this example with an inlet line **41** selectively connected to transfer lines **16***a*, **21***a* and **26***a* and with an outlet line **42** with selective connections **18***a*, **23***a* and **28***a*. Thus by proper valve manipulation, the swing reactor may take the place of any on-stream reactor so that the latter may be regenerated.

For effecting regeneration and/or rejuvenation a purge and regeneration system **43** may be employed with an upper manifold line **44** which may be selectively connected to individual reactors by lines **45**, **45***a*, **45***b* and **45***c*. The bottom of each reactor may be selectively connected by lines **46**, **46***a*, **46***b* or **46***c* to manifold line **47** connected to the other side of the purge and regeneration system. Thus, when catalyst in any reactor requires regeneration, it may be blocked out of on-stream position, purged with hydrogen, regenerated by burning carbonaceous deposits with oxygen diluted by flue gas, rejuvenated by contact with a gas having an oxygen partial pressure of at least .4 and preferably 1 or more atmospheres at a temperature of about 950 to 1050° F. for a period of about .5 to 5 hours or more, purged with flue gas and then purged with hydrogen. The regeneration and rejuvenation technique is described in greater detail in co-pending application Serial No. 416,072, filed March 15, 1954. Water is preferably removed from flue gas introduced and produced in the system during regeneration and such water is removed from the system through line **48**. Gases may be purged from the system through line **49**.

The methylcyclopentane hydroforming system thus far described is admirably suited for the conversion of methylcyclopentane or virgin naphtha fractions containing 5 to 50 percent or more of methylcyclopentane in order to obtain maximum benzene production with minimum hydrocracking. If desired, any unconverted methylcyclopentane may be separated from the product and recycled. Where cyclohexane is the desired product, the benzene thus produced may be hydrogenated in a separate system with net hydrogen from line **33** with catalysts and under conditions well known for that purpose.

Since production of maximum yields of 95–100 octane number motor fuels from petroleum naphthas is usually the desired objective of a refiner, the methylcyclopentane hydroforming system hereinabove described is preferably integrated with the type of naphtha hydroforming system now known to those skilled in the art, such as Platforming or, preferably, with an Ultraforming system. In such an integrated system a total naphtha charge (which may have been previously hydrofined) from line **50** is introduced into fractionator **51** from which components boiling below about 140° F. are taken overhead through line **52** and products higher boiling than about 400 to 425° F. are withdrawn as bottoms through line **53**. The methylcyclopentane fraction boiling in the range of about 140 to 200° F. or preferably 140 to 180° F. is removed as a side stream and introduced by line **11** to the low pressure hydroforming operation hereinabove described, said charge preferably being substantially free from water, i. e. containing less than about 40 parts per million and usually not more than about 10 parts per million of water. The naphtha fraction boiling in the range of about 180 to about 400° F. or, if desired, about 200 to 360° F. is withdrawn as a side stream through line **54**, admixed with about 5 mols of recycled hydrogen from line **55**, preheated in coil **56** and introduced by transfer line **57** to lead reactor **58**. Effluent from the lead reactor is passed by line **59** through reheater **60** and transfer line **61** to intermediate reactor **62**. Effluent from reactor **62** is passed by line **63** through reheater **64** and transfer line **65** to tail reactor **66**. Effluent from the tail reactor passes through line **67**, heat exchanger **68** and cooler **69** to hydrogen separator **70** from which separated hydrogen is removed by line **71**. The net hydrogen produced may be introduced by line **72** through a pressure reducing valve **72***a* to line **13** for use in the low pressure portion of the system. The amount of hydrogen required for recycle is returned by circulating compressor **73** and line **55** to preheater **56**.

The separated liquid is introduced from separator **70** through line **74** to product recovery system diagrammatically represented by fractionating column **75**, the propane and lighter gases being vented from the top thereof through line **76**. The light fraction of the reformed product boiling below about 180° to 200° F. is usually of much lower octane number than the heavier portions of the product and may be withdrawn as a side stream through line **77** and introduced to line **14** for hydroforming in the low pressure system wherein it may be further dehydroaromatized. If desired, an intermediate product fraction boiling in the range of about 180 to 250° F. may be recycled by line **78** and pump **79** to line **54**. The heavier, highest octane number components of the hydroformed product are withdrawn through line **80** and blended in line **39'** with the products from the low pressure hydroforming system to give the final gasoline product of 95+ octane number in maximum yields.

Reactors **58**, **62** and **66** may contain the same type of catalyst as described for use in reactors **17**, **22**, **27** and **40** and, like those reactors, are preferably aluminized. However, reactors **58**, **62** and **66** are operated at a pressure in the range of 200 to 500 p. s. i. g. or more, preferably in the range of 200 to 350 p. s. i. g., the lead reactor usually being somewhat above 300 p. s. i. g. and the remaining downstream reactors being at lower pressures because of pressure drop in the system. The inlet temperature to lead reactor **58** may be in the range of about 850 to 950° F., e. g. about 900° F., and the inlet temperature to the remaining reactors is preferably in the range of about 900 to 975, e. g. about 940° F. The space velocity in this system may be substantially the same as in the low pressure system.

As in the case of the low pressure system, a swing reactor **83** may be employed, this reactor containing about the same amount of the same type of catalyst as in tail reactor **66**. The inlet line **84** to the swing reactor may be selectively connected to transfer lines **57***a*, **61***a* and **65***a*. The outlet line **85** may discharge effluent from the swing reactor through lines **59***a*, **63***a* or **67***a*. Thus the swing reactor may take the place of any on-stream reactor to facilitate regeneration thereof and it may be operated in parallel with any of the on-stream reactors during periods when no regeneration is required.

The same regeneration system hereinabove described in connection with the low pressure system may be utilized for effecting catalyst regeneration and rejuvenation in the higher pressure system, upper regeneration manifold **86** being selectively connected to the reactors by lines **87**, **87***a*, **87***b* and **87***c* and the reactors being connected by lines **88**, **88***a*, **88***b* and **88***c* to lower regeneration manifold line **89**. It will thus be observed that the low pressure methylcyclopentane hydroforming unit is integrated with the higher pressure naphtha hydroforming unit by the use of a common fractionator **51**, a common regeneration system, by recycle operation which upgrades the octane number of low boiling hydroformed naphtha and by the utilization in the low pressure re-

forming of hydrogen produced in the high pressure reforming.

While a particular example of our invention has been described in considerable detail, it will be understood that other examples and alternative arrangements and conditions will be apparent from the above description to those skilled in the art. More than one intermediate reactor with its corresponding reheater may be employed in the low pressure system, the high pressure system, or both. Instead of employing the swing reactor system, other arrangements may be provided for blocking out on-stream reactors in order to provide for regeneration and rejuvenation.

We claim:

1. The method of converting methylcyclopentane in a naphtha charging stock, which method comprises fractionating said naphtha to obtain a light naphtha boiling within the range of 140 to 200° F. and containing at least about 5 percent of methylcyclopentane, hydroforming said light naphtha with a supported platinum catalyst at a pressure above about 50 but below 150 p. s. i. and at a temperature in the range of about 900 to 950° F. in the presence of about 1 to 10 mols of hydrogen per mol of charge and also in the presence of about 100 to 500 parts per million of sulfur based on hydrocarbon charge whereby the presence of the sulfur increases benzene production and decreases hydrocracking without substantial adverse effect on catalyst activity and selectivity.

2. The method of claim 1 wherein the light naphtha charge is chiefly methylcyclopentane.

3. The method of claim 1 wherein the light naphtha charge is a naphtha fraction boiling in the range of about 140 to 180° F.

4. The method of claim 1 wherein the light naphtha charge is a naphtha fraction boiling chiefly in the range of 140 to 180° F. in admixture with light hydroformed naphtha product boiling below 200° F.

5. The method of claim 1 which includes the step of adding sulfur to the light naphtha charge in an amount in the rang of about 50 to 400 parts per million.

6. The method of claim 1 wherein the hydroforming is effected in the presence of approximately 200 parts per million of sulfur based on methylclcyopentane charge.

7. The method of obtaining both benzene and large yields of 95+ octane number motor fuel from naphtha hydrocarbons, which method comprises fractionating naphtha hydrocarbons to obtain a methylcyclopentane fraction boiling chiefly in the range of about 140 to 180° F. and a heavier naphtha fraction boiling chiefly in the range of about 180 to 400° F., hydroforming the heavier naphtha fraction with a supported platinum catalyst at a hydroforming temperature and at a pressure in the range of about 200 to 750 p. s. i., hydroforming the methylcyclopentane fraction with supported platinum catalyst at hydroforming temperatures under a pressure above about 50 but below 150 p. s. i. and in the presence of about 100 to 500 parts per million of sulfur based on the hydrocarbon charge, separating benzene from stabilized products of the last named hydroforming step, and combining the rest of the stabilized products with products of the first named hydroforming step to obtain said 95+ octane number motor fuel.

8. The method of claim 7 wherein at least the methylcyclopentane hydroforming step is effected in a regenerative system and wherein hydrogen produced in the heavier naphtha hydroforming step is supplied to the methylcyclopentane hydroforming step.

9. The method of claim 7 wherein both hydroforming steps are effected in regenerative systems and which includes the steps of introducing regeneration gases to both hydroforming steps from a common regeneration system.

10. The method of claim 7 which includes the step of obtaining from heavier hydroformed naphtha product a fraction boiling below about 200° F. and introducing said last named fraction together with the methylcyclopentane fraction to the hydroforming operation which is effected at the pressure above 50 and below 150 p. s. i.

11. The method of minimizing hydrocracking and maximizing benzene production in the hydroforming over supported platinum catalyst of a naphtha fraction boiling in the range of about 140 to 200° F. and containing a substantial amount of methylcyclopentane, which method comprises hydroforming said fraction at a pressure of about 100 p. s. i. in the presence of about 200 parts per million of sulfur.

12. The method of claim 11 wherein the naphtha fraction boiling in the range of 140 to 200° F. consists chiefly of methylcyclopentane.

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