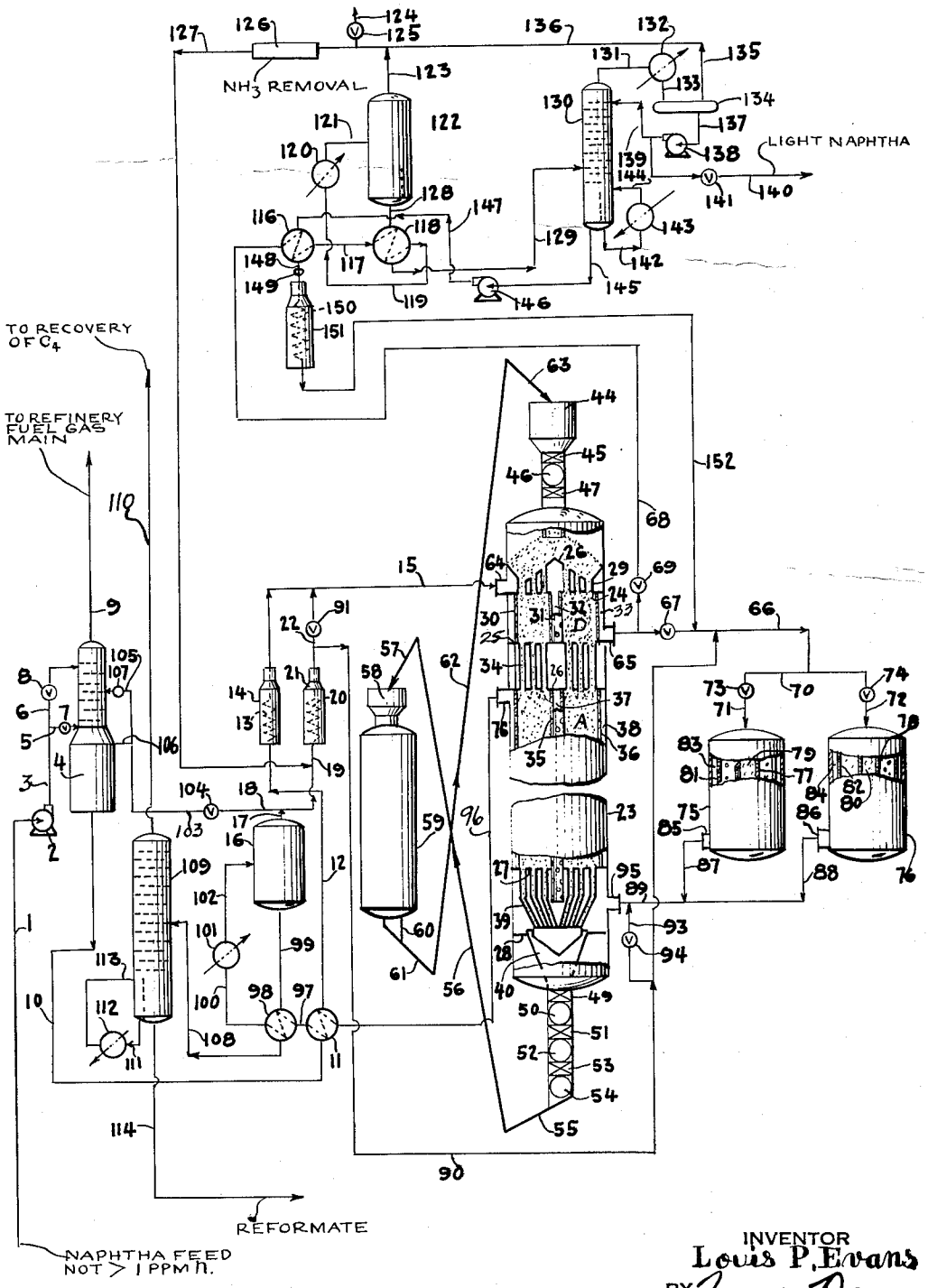
Oct. 10, 1961 L. P. EVANS 3,003,948

MULTICATALYST DEHYDROGENATION, SINGLE CATALYST DECONTAMINATION AND AROMATIZATION

Filed Dec. 19, 1958



INVENTOR
Louis P. Evans
BY Francis J. Hunter
AGENT

United States Patent Office 3,003,948 Patented Oct. 10, 1961

3,003,948

MULTICATALYST DEHYDROGENATION, SINGLE CATALYST DECONTAMINATION AND AROMATIZATION

Louis P. Evans, Woodbury, N.J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

Filed Dec. 19, 1958, Ser. No. 781,789
6 Claims. (Cl. 208—65)

The present invention relates to the decontamination of naphthas and the reforming of the decontaminated naphthas over a platinum-group metal reforming catalyst and, more particularly to the decontamination over a first catalyst, dehydrogenation over a platinum-group metal catalyst, and aromatization of the dehydrogenated naphtha over the aforesaid first catalyst. More specifically, the present invention relates to decontamination of a naphtha in the presence of a first particle-form solid catalyst having hydrogenating and desulfurizing capabilities as well as aromatizing capabilities and preferably, in addition, the capability of dehydrogenating naphthenes and aromatizing paraffins, dehydrogenating the decontaminated naphtha over a static bed of platinum-group metal reforming catalyst, and completing the reforming of the so-treated naphtha to produce the required octane over the aforesaid first catalyst. Preferably, the aforesaid first catalyst is employed in accordance with moving bed or fluidized technique while the platinum-group metal reforming catalyst is employed as a static bed.

It has been known for some time that in the reforming of naphtha over a platinum-group metal catalyst in a multi-bed system at pressures of 500 p.s.i.g. or more that most of the carbon is deposited in those reactors in which reactions other than the dehydrogenation of naphthenes take place. Thus, in a three reactor system wherein dehydrogenation of naphthenes take place primarily in the first reactor, the coke is deposited primarily in the third reactor. That is to say, the coke deposited upon the catalyst in the third reactor amounts to about 25 per cent based on the weight of catalyst, whereas the amount of coke deposited on the same amount of catalyst in the first reactor, where the principal reaction is dehydrogenation of naphthenes, is less than five percent. From this it follows that, when the reactions other than dehydrogenation of the naphthenes are carried out in accordance with moving bed or fluidized technique the on-stream time can be increased an industrially important amount.

Furthermore, it is known that when reforming naphtha at pressures less than 500 p.s.i.g., e.g., at 15 to 250 p.s.i.g. the deposition of coke is greater than when reforming to the same octane rating under pressures of the order of 500 p.s.i.g. or more. But even at pressures less than 500 p.s.i.g. there is more coke deposited in those beds of catalyst in which the principal reactions are others than dehydrogenation of naphthenes. Accordingly, it is an object of the present invention to provide a method of reforming naphtha at pressures less than 500 p.s.i.g., preferably at pressures of about 15 to about 250 p.s.i.g., in which dehydrogenation occurs principally in the presence of one or more static beds of platinum-group metal particle-form reforming catalyst while the reactions of dehydrocyclization or aromatization and hydrocracking occur principally in the presence of a moving bed or fluidized bed of base metal oxide reforming catalyst. Other objects and advantages of the present invention will become apparent to those skilled in the art from the following description of the present invention taken in conjunction with the illustrative but non-limiting flowsheet of the drawing which illustrates one embodiment of the

present invention. When the effluent from the pretreating section of the first reactor contains not more than 1 p.p.m. (part per million) of nitrogen calculated on the naphtha there is no need to remove the ammonia. However, when the effluent from the pretreating section of the first reactor contains more than 1 p.p.m. of nitrogen sufficient ammonia must be removed therefrom to reduce the nitrogen content of the feed to the second and third reactors to not more than 1 p.p.m. of nitrogen calculated on the naphtha.

The present invention will be described hereinafter first for a pretreating section effluent which does not contain more than 1 p.p.m. of nitrogen calculated on the naphtha and then for a pretreating section effluent which does contain more than 1 p.p.m. of nitrogen calculated on the naphtha.

Thus, a naphtha containing an amount of nitrogen which can be reduced to not more than 1 p.p.m. in the presence of the catalyst employed and under the reaction conditions in the pretreating section of reactor **23**, for example a naphtha charge stock containing not more than about 10 p.p.m. of nitrogen when using a mixture of oxides of cobalt and molybdenum is contacted with a moving bed of catalyst having hydrogenating and hydrodesulfurizing capabilities together with the capabilities of dehydrocyclizing and hydrocracking paraffins. Illustrative of this type of catalyst is a catalyst comprising oxides of one or more metals selected from the group consisting of chromium, molybdenum, tungsten, cobalt, nickel, silicon, zirconium, titanium, magnesium and cerium at least one of which reversibly combines with sulfur. The presently preferred catalysts which can be used for this purpose are (A) a mixture of oxides of chromium, aluminum and molybdenum, and (B) a mixture of oxides of cobalt and molybdenum. The use in the first stage of a catalyst at least one component of which reversibly combines with the sulfur liberated from the naphtha feed has the advantage that the generated sulfur does not contaminate the hydrogen-containing gas and hence reuse of the hydrogen-containing gas does not require a separate gas recycle purifying circuit. Consequently, the hydrogen-containing recycle gas can be circulated through not only the reactor of the first stage but also through the reactor(s) of the second stage.

The hydrodesulfurization and reforming of the hydrodesulfurized naphtha is carried out at pressures of about 15 to about 250 p.s.i.g., preferably about 100 to about 200 p.s.i.g.

In the flow sheet of the invention an embodiment of the invention has been selected for the purpose of illustration in which feed naphtha is contacted in the presence of hydrogen with a moving bed of particle-form solid reforming catalytic material. (A fluidized bed of catalyst can be used in place of the moving bed of catalyst in the illustrative flow sheet.)

The temperature to which the feed naphtha is heated in coil **13** in heater **14** is dependent upon (1) the required reaction temperature in section D (desulfurization section) of reactor **23**, (2) the temperature to which the hydrogen-containing gas is heated in coil **20** in heater **21**, and (3) the mol ratio of hydrogen-containing gas to feed naphtha. When hydrodesulfurization is the principal reaction in section D of reactor **23** the reaction temperature therein is between about 600° and about 850° F. It is desirable to heat the feed naphtha to the lowest temperature at which the required temperature for decontamination can be maintained in section D at the designed catalyst-to-oil ratios while heating the hydrogen-containing gas to the maximum practical temperature. Thus, the feed naphtha is heated to a temperature within the range of about 550° to about 800° F. and the molar ratio of

the hydrogen-containing gas to feed naphtha is about 0.1 to about 3.0. Under these conditions the hydrogen-containing gas is heated to a temperature within the range of about 1000° to about 1200° F.

However, section D can also be operated under conditions such that a portion of the naphthenes in the feed naphtha is dehydrogenated and the feed naphtha is decontaminated in section D of reactor **23**. For this purpose the temperature in section D is within the range of about 800° to about 1000° F. The temperature of the feed naphtha entering section D is within the range of about 770° to about 970° F. The mol ratio of the hydrogen-containing gas to feed naphtha is about 0.5 to about 5.0; and the hydrogen-containing gas is heated to a temperature within the range of about 1000° to about 1200° F.

Accordingly, feed naphtha drawn from a source not shown through pipe **1** by pump **2** is discharged into pipe **3**. The feed naphtha flows through pipe **3** and branches **5** and **6** under control of valves **7** and **8** respectively to absorber **4**. The quantities of feed naphtha flowing through branches **5** and **6** is controlled as hereinafter described. In absorber **4** the feed naphtha is contacted with a stripping gas to remove water, oxygen, and deposit precursors. For this purpose, a hydrogen-containing gas is employed. Since the feed naphtha will absorb gasoline hydrocarbons from a gas it is preferred to contact the feed naphtha with hydrogen-containing gas flowing from liquid-gas separator **16** through conduit **18** and under control of valves **104** and **107**. Accordingly, hydrogen-containing gas flows from liquid-gas separator **16** through conduits **18**, **105**, and **106** into absorber **4**. The amounts of feed naphtha flowing through pipes **5** and **6** and the amount of gas flowing from separator **16** through conduits **105** and **106** is balanced to remove substantially all of the water, oxygen and deposit precursors from the feed naphtha and to remove substantially all of the gasoline, i.e., C_4 and heavier hydrocarbons from the gas.

The stripped gas flows from absorber **4** through conduit **9** to the refinery fuel gas main or to hydrogenation processes. The enriched feed naphtha flows from absorber **4** through pipe **10** to heat exchanger **11**.

In heat exchanger **11** the enriched feed naphtha is in indirect heat exchange relation with the effluent from the third or aromatizing section A of reactor **23** flowing through conduit **96**. From heat exchanger **11** the enriched feed naphtha flows through pipe **12** to coil **13** in heater **14**. In coil **13** in heater **14** the enriched naphtha is heated to a decontaminating or naphthene dehydrogenating reaction temperature within the range of about 550° to about 970° F. dependent upon the required temperature in section D of reactor **23**, the temperature to which the hydrogen-containing gas is heated in coil **20** in heater **21**, and the recycle gas to naphtha mol ratio.

The heated enriched feed naphtha flows from coil **13** in heater **14** through conduit **15** to vapor inlet **64** of section D of reactor **23**. Hydrogen-containing gas heated to a temperature within the range of about 900° to about 1200° F. in coil **20** in heater **21** flows through conduit **22** under control of valve **91** to a point in conduit **15** intermediate heater **14** and reactor inlet **64**. In conduit **15** the heated hydrogen-containing gas is mixed with the aforesaid heated enriched feed naphtha in the ratio of about 500 to about 1500 s.c.f. of hydrogen per barrel of feed naphtha or in the ratio of about 0.6 to about 1.8 mols of hydrogen per mol of feed naphtha. The charge mixture so formed flows through conduit **15** to inlet **64** of the decontaminating section D of reactor **23**.

Reactor **23** is divided into two reaction zones, i.e., first reaction zone D and third reaction zone A and two sealing zones. Decontaminating zone D is formed by plates **24** and **25**. A sealing zone is formed immediately beneath decontaminating zone D between plates **25** and **26**. Aromatizing zone A is formed immediately below the aforesaid disengaging zone between plates **26** and **27**. The second sealing zone is formed immediately below zone A between plates **27** and **28**.

The flow of catalyst through reactor **23** will be described first and thereafter the flow of vapors through reactor **23** will be described.

A catalyst comprising up to about 18 percent chromium oxide and the balance at least 72 percent alumina impregnated with about 3 to about 15 percent molybdenum is employed in reactor **23**.

When reactor **23** is operated under a pressure in excess of about 100 p.s.i.g. the catalyst transfer means illustrated in the drawing is employed. For operations at pressures between about 15 and about 100 p.s.i.g. a feed leg such as described in U.S. Patent No. 2,829,087, issued April 1, 1958, can be employed.

Accordingly, since it will be assumed that reactor **23** is operated at a pressure of about 180 p.s.i.g., a catalyst transfer means such as illustrated is employed. Hot active catalyst in feed hopper **44** flows under control of valve **45** into pressuring chamber **46** (valve **47** closed). Pressuring chamber **46** is purged (valves **45** and **47** closed) with any inert gas such as flue gas, nitrogen or the like by means of an inlet and a vent not shown. After purging, the pressure in chamber **46** is raised to that of decontaminating section D or preferably 5 to 10 pounds higher with hydrogen-containing gas, preferably recycle gas, from gas-liquid separator **16**. When the pressure in chamber **46** has been raised to at least the pressure in decontaminating zone D, the pressuring gas is shut-off and valve **47** opened. The catalyst flows from pressuring chamber **46** into reactor **23** onto distributing plate **26**. Valve **47** is closed and pressuring chamber purged with an inert gas. After purging pressuring chamber **46** valve **45** is opened, chamber **46** filled with catalyst and the cycle repeated.

Plate **26** is provided with a plurality of orifices each of which is subtended by a catalyst conduit **29**. The catalyst flows from plate **26** downwardly through conduits **29** into decontaminating section D. In decontaminating section D the catalyst column is annular in shape and confined between foraminous partition **30** and tubular foraminous partition **31**. This provides a central inlet conduit **32** and a peripheral collecting zone **33**.

The zone immediately below decontaminating zone D is adapted to permit catalyst to flow from decontaminating zone D into aromatization zone A with no substantial loss of vapors from zone D into zone A where zone A is at a pressure up to 5 p.s.i. less than the pressure in zone D. The sealing means comprises a plurality of conduits represented by conduits **34**. Alternatively, conduits **34** do not extend to plate **26** and recycle gas is introduced into the space between plate **25** and plate **26** to provide a substantially total seal.

The hot catalyst flows through conduits **34** into aromatization zone A. In zone A the catalyst flows as an annular column confined between foraminous partition **35** and tubular foraminous partition **36**. Foraminous partition **35** being tubular provides means **37** for introducing reactants into the catalyst bed. An annular collecting zone **38** is formed between foraminous partition **36** and the liner or inside of the shell of reactor **23**.

The catalyst flows downwardly as a substantially continuous annular column of particle-form solid catalytic material through zone A to the catalyst draw-off zone immediately below aromatization zone A. The catalyst is drawn off by any suitable means such as conduits **39** as more fully described in U.S. Patent No. 2,412,135. The catalyst flows downwardly through conduits **39** into collector **40** and thence under control of regulator **49** into surge chamber **50** (valve **51** closed). Depressuring chamber **52** is purged with an inert gas such as flue gas and then pressured with hydrogen-containing gas such as recycle gas by means not shown. After pressuring chamber **52** to about the pressure of aromatization zone A valve

51 is opened (valve 53 closed) and the catalyst in surge chamber 50 flows into depressuring chamber 52. Valve 51 is closed and chamber 52 depressured to atmospheric pressure (by means not shown). Chamber 52 is then purged with an inert gas. Valve 53 opens and the catalyst flows from chamber 52 into surge chamber 54. From surge chamber 54 the catalyst flows down chute 55 to means feeding a catalyst transfer means 56 such as a bucket elevator, a pneumatic lift or the like whereby the catalyst is elevated to chute 57. The catalyst flows down chute 57 to kiln hopper 58 and thence into kiln 59.

Kiln 59 is of any suitable type wherein the coke can be burned off the catalyst in a stream of combustion-supporting gas such as air. Kilns of this type are well-known to those skilled in the art and have been described in several publications including U.S. Patent Nos. 2,726,994 and 2,724,683. From kiln 59 the regenerated catalyst flows through conduit 60 to chute 61. The regenerated catalyst flows down chute 61 to means feeding a catalyst transfer device 62 such as a bucket elevator, a pneumatic lift or the like. Elevator 62 discharges the regenerated catalyst into chute 63 down which the regenerated catalyst flows to reactor feed hopper 44.

Returning now to conduit 15; the charge mixture of enriched feed naphtha and hydrogen in the proportions set forth hereinbefore and at a temperature within the range of about 600° to about 1000° F. dependent upon the considerations set forth hereinbefore flows through conduit 15 to decontaminating zone vapor inlet 64. The charge mixture flows from vapor inlet 64 to conduit 32 formed by the tubular foraminous partition 31. From conduit 32 the vapors of the charge mixture flow radially through the foraminous partition 31 into the annular substantially continuous substantially compact column of first or decontaminating catalyst and through the foraminous partition 30 into annular collecting zone 33. From collecting zone 33 the vapors now designated zone D effluent flow through zone D outlet 65 to conduit 66 having valve 67 and branch 68 with valve 69.

When the zone D effluent, as was set forth hereinbefore, contains not more than 1 p.p.m. of nitrogen it is usually unnecessary to separate the non-condensible components of the zone D effluent from the naphtha or condensible components of the zone D effluent. Accordingly, the zone D effluent flows through conduit 66 (valve 69 closed; valve 67 open) to reactor manifold 70.

Since the reaction temperature and space velocity in zone D were those under which little or no dehydrogenation of naphthenes occurred in zone D, in accordance with the principles of the present invention reaction conditions in reactors 75 and 76 are such as to dehydrogenate at least 85 percent of the naphthenes present in the effluent from zone D. (The effluent from zone D hereinafter is designated pretreated feed naphtha.)

While reactors 75 and 76 are illustrated as radial flow adiabatic reactors those skilled in the art will understand that adiabatic reactors designed for vertical flow as well as isothermal reactors can be used.

In the illustrated radial flow reactors the bed of catalyst is confined in the form of an annulus by peripheral foraminous partitions 81 and 82 and central tubular foraminous partitions 77 and 78 in reactors 75 and 76 respectively. An annular collecting zone is provided in each reactor between the peripheral foraminous partition 81 or 82 and the liner or shell of the reactors 75 or 76 respectively. The annular collecting zone in reactor 75 is designated 83 and that in reactor 76 is numbered 84.

The catalyst in reactors 75 and 76 is a platinum-type catalyst, e.g., comprising about 0.35 to about 2 percent by weight of a metal of the platinum group on a refractory oxide carrier such as alumina, silica-alumina, silica or the like with or without about 0.1 to about 0.8 percent of a halogen, i.e., chlorine, fluorine, bromine.

The reaction conditions for fresh or fresh regenerated catalyst are as follows:

	Broad	Preferred
Temperature, ° F.	[1] 800 to 1,000	880 to 980
Hydrogen-to-naphtha mol ratio	1 to 10	4 to 8
Liquid hourly space velocity, v./hr./v.	3 to 15	6 to 12

[1] Limited by the maximum practical reaction temperature to which the catalyst can be exposed without irreversible deactivation and usually about 20° F. less than the aforesaid maximum practical reaction temperature.

In the drawing two static bed reactors piped for parallel flow of the pretreated naphtha feed are shown. While one reactor can be used, it is preferred to use two for ease of construction, operation and maintenance.

The pretreated naphtha feed, the unused hydrogen and the products of decontamination other than sulfur (it is preferred to use in the reactor 23 a catalyst such as a molybdenum oxide-chromium oxide-alumina catalyst which forms a metal sulfide with the sulfur produced by hydrogenation of the sulfur-containing components of the naphtha feed) and containing not more than about 1 p.p.m. of nitrogen based on the naphtha feed, flow through conduit 66 to manifold 70. At some point on conduit 66 intermediate valve 67 and manifold 70 hydrogen-containing gas, preferably hydrogen-containing recycle gas flowing from heater 21 through conduit 22 to conduit 90 and thence to conduit 66, is mixed with the effluent of zone D containing not more than 1 p.p.m. of nitrogen based upon the naphtha feed in an amount to provide, with the hydrogen in the zone D effluent, a hydrogen-to-naphtha mol ratio of about 1 to 10. The reforming charge mixture thus provided flows through conduit 66 to manifold 70 and manifold branches 71 and 72 under control of valves 73 and 74 respectively to reactors 75 and 76.

The reforming charge mixture flows into central conduits 79 and 80, radially through the tubular foraminous partions 77 and 78 into the catalyst beds in reactors 75 and 76. The reaction products flow from the catalyst beds through the foraminous partitions 81 and 82 into the annular collection zones 83 and 84 of reactors 75 and 76 respectively. The reaction products flow from collecting zone 83 (reactor 75) through reactor outlet 85 into conduit 87 and thence to conduit 89. The reaction products flow from collecting zone 84 (reactor 76) to reactor outlet 86 to conduit 88 and thence to conduit 89.

The components of the reaction products in conduit 89 boiling in the gasoline range comprise at least about 85 percent of the naphthenes of the naphtha feed as aromatic hydrocarbons together with substantially all of the paraffins of the naphtha feed as paraffins.

The effluents of the static bed reactors, now designated dehydrocyclization feed, have a temperature of about 800° to 950° F. When necessary additional hydrogen-containing gas, preferably recycle gas flowing from heater 21 through conduits 22, 90 and 93 under control of valve 94 is mixed with the dehydrocyclization feed in conduit 89 in amount required to provide a dehydrocyclization charge mixture temperature of about 900°–1050° F. The dehydrocyclization charge mixture flows through conduit 89 to reactor inlet 95 of aromatization zone A of reactor 23.

From aromatization zone A inlet 95 the dehydrocyclization charge mixture flows upwardly through central conduit 37 and radially therefrom through foraminous partition 35 and the catalyst bed and foraminous partition 36 to annular collecting zone 38. From annular collecting zone 38 the reaction products of the aromatization and hydrocracking of the dehydrocyclization feed flow through aromatization zone A vapor outlet 76 to conduit 96. The aromatization zone effluent, now designated final effluent, flows through conduit 96 to heat exchanger 11 where the final effluent is in indirect heat exchange relation with the naphtha feed flowing from absorber 4 through pipe 10 as described hereinbefore.

From heat exchanger **11** the final effluent flows through conduit **97** to heat exchanger **98** where the final effluent is in indirect heat exchange relation with the condensate flowing from liquid-gas separator **16** through pipe **99**. From heat exchanger **98** the final effluent flows through conduit **100** to cooler **101** where the final effluent is cooled to a temperature at which under the existing pressure C_4 and heavier hydrocarbons are condensed. The cooled final effluent flows from cooler **101** through conduit **102** to liquid-gas separator **16**. In liquid-gas separator **16** the uncondensed components of the final effluent are separated from the C_4 and heavier hydrocarbons.

The uncondensed final effluent, now designated recycle gas and comprising hydrogen, traces of ammonia and C_1 to C_4 hydrocarbons flows through conduit **17** to conduit **18**. A portion about equal to the gas make in reactors **23**, **75** and **76** is diverted through conduit **103** to conduits **105** and **106** as previously described herein. The balance of the recycle gas flows through conduits **18** and **19** to coil **20** in heater **21** as described hereinbefore.

The condensed portion of the final effluent, now designated condensate, comprising C_4 and heavier hydrocarbons and traces of hydrogen and ammonia, flows from separator **16** through pipe **99** to heat exchanger **98** as previously described herein. From heat exchanger **98** the condensate flows through pipe **108** to fractionator **109**.

In fractionator **109** C_4 and lighter hydrocarbons and other components of the condensate volatile at temperatures not higher than the boiling point of C_4 hydrocarbons are taken overhead through pipe **110** to means for the recovery of C_4 hydrocarbons. A portion of the bottoms in fractionator **109**, comprising hydrocarbons heavier than C_4, flows through a re-boiler comprising pipe **111**, heat exchanger **112** and pipe **113**. Any means for heating the bottoms of fractionator **109** to a temperature at which C_4 hydrocarbons are volatile can be used in place of the re-boiler illustrated. The net product portion of the bottoms of fractionator **109** flows through pipe **114** for finishing, e.g., addition of tetraethyl lead, anti-icing additive, etc. as high octane gasoline.

When the naphtha feed contains more than 1 p.p.m. of nitrogen and a nitrogen-sensitive catalyst is employed in any of the reactors **75** and **76**, provision must be made to remove sufficient of the ammonia produced in zone D of reactor **23** from the effluent of zone D to ensure that the charge mixture entering reactors **75** and **76** does not contain more than 1 p.p.m. of nitrogen based on the naphtha feed.

The molybdenum oxide-chromium oxide-aluminum oxide catalyst preferred for decontamination of the feed naphtha and aromatization of the dehydrocyclization feed is substantially insensitive to nitrogen. Accordingly, the charge naphtha is heated, mixed with hydrogen-containing gas and introduced into decontamination zone D of reactor **23** as previously described herein. However, since the charge naphtha contains more than 1 p.p.m. of nitrogen, the effluent of zone D contains more than 1 p.p.m. of nitrogen and perforce the excess nitrogen must be removed from the zone D effluent before contacting the pretreated charge naphtha with the nitrogen-sensitive platinum-type catalyst.

Accordingly, with valve **67** closed and valve **69** open the zone D effluent flows through conduit **68** to heat exchanger **116** where the zone D effluent is in indirect heat exchange relation with the bottoms of splitter **130** flowing from pump **146** through pipe **147**. From heat exchanger **116** the zone D effluent flows through conduit **117** to heat exchanger **118** where the zone D effluent is in indirect heat exchange relation with the zone D condensate flowing from liquid-gas separator **122** through pipe **128**. From heat exchanger **118** the zone D effluent flows through conduit **119** to cooler **120** where the zone D effluent is cooled to a temperature at which C_4 and heavier hydrocarbons are condensed at the existing pressure. From cooler **120** the zone D effluent flows through conduit **121** to liquid-gas separator **122**. In liquid-gas separator **122** the uncondensed zone D effluent is separated from the condensed zone D effluent. The uncondensed zone D effluent, designated impure recycle gas, flows from separator **122** through conduit **123** to conduit **136**.

The impure recycle gas flows through conduit **136** to means **126** for removing ammonia, e.g., dilute sulfuric acid. From means for removing ammonia **126** the purified recycle gas flows through conduit **127** to conduit **19**.

The condensed portion of the zone D effluent, now designated zone D condensate, flows from separator **122** through pipe **128** to heat exchanger **118** and thence through pipe **129** to fractionator **130**. In fractionator **130** a temperature is maintained at which C_1 to C_4 hydrocarbons, ammonia and other components of the zone D condensate are volatile. The ammonia and light hydrocarbons are taken as an overhead through conduit **131** to cooler **132** where the overhead is cooled to a temperature at which C_4 and heavier hydrocarbons are condensed. The overhead flows from cooler **132** through conduit **133** to accumulator **134**. In accumulator **134** the C_3 and lighter hydrocarbons, hydrogen, and ammonia separate from the C_4 and heavier hydrocarbons of the overhead and flow through conduit **135** to conduit **136** where the accumulator overhead mixes with the impure recycle gas. In the event that there is a net make of gas in zone D the net gas make can be vented through conduit **124** under control of valve **125** to absorber **4**. The condensed overhead flows from accumulator **134** through pipe **137** to the suction side of pump **138**. Pump **138** discharges the condensed overhead into pipe **139**. A portion of the condensed overhead flows through pipe **139** to fractionator **130** for use as reflux. The balance flows through pipe **140** under control of valve **141** for recovery as light naphtha.

A portion of the bottoms of fractionator **130** flows through the re-boiler system comprising pipe **142**, heat exchanger **143** and pipe **144** or any other suitable means for heating the fractionator bottoms to the temperature necessary to maintain in fractionator **130** a temperature at which C_4 and lighter hydrocarbons are volatile.

The balance of the bottoms of fractionator **130** flows through pipe **145** to the suction side of pump **146**. Pump **146** discharges the balance of the bottoms into pipe **147** through which the fractionator bottoms, now designated pretreated naphtha flows to heat exchanger **116**. In heat exchanger **116** the pretreated naphtha is in indirect heat exchange relation with the zone D effluent as described hereinbefore. From heat exchanger **116** the pretreated naphtha flows through pipe **148** under control of valve **149** to coil **150** in heater **151**. In coil **150** the pretreated naphtha is heated to a reaction temperature within the range of about 800° to about 1000° F. dependent upon the amount of recycle gas and the temperature of the recycle gas flowing through conduit **90** to be mixed with the pretreated naphtha in conduit **66**. From coil **150** the pretreated naphtha flows through pipe **152** to conduit **66**. The pretreated naphtha and the hydrogen-containing gas, preferably recycle gas flowing through conduit **90**, mixed therewith in the ratio of about 1 to 10 mols of hydrogen per mol of naphtha to form a charge mixture flows through conduit **66** to manifold **70** and thence to reactors **75** and **76** as hereinbefore described.

Those skilled in the art will understand, from the description of the illustrative examples of the present invention given hereinbefore that the present invention provides a method of pretreating and reforming naphtha wherein the naphtha is contacted with a first particle-form solid reforming catalyst having hydrodecontaminating capabilities in the presence of hydrogen in a first reaction zone, the effluent of said first zone containing not more than 1 p.p.m. of nitrogen based upon said naphtha when contacted with the platinum-group metal reforming catalyst, is contacted in at least one second reaction zone with a second reforming catalyst comprising a

platinum-group particle-form solid reforming catalyst to convert a preponderant portion, preferably at least 85 percent of the naphthenes present in said naphtha to aromatics, and the effluent of said second reaction zone is contacted in a third reaction zone with the aforesaid first reforming zone. That the reaction conditions in the first reaction zone are decontaminating or decontaminating and dehydrogenating conditions. That the reaction conditions in the second reaction zone are dehydrogenating conditions. That the reaction conditions in the third zone are those necessary for dehydrocyclization, or dehydrocyclization and hydrocracking, of paraffins. That the effluent of the third reaction zone is separated into a liquid portion having the required octane and a gaseous portion comprising hydrogen and light hydrocarbons which is recycled to said first, second and third reaction zones. It is preferred that the reforming catalyst having hydrodecontaminating capabilities used in the first and third reaction zones react with the sulfur in the feed naphtha in the presence of hydrogen to form a sulfide of one of the components of the catalyst stable under the conditions of temperature and hydrogen partial pressure existing in the hydrodecontaminating zone, and that the sulfide thus formed be oxidizable to a gaseous sulfur compound under the conditions under which the aforesaid catalyst is regenerated. Those skilled in the art will understand that it is preferred to pass the first reforming catalyst through the first and third reaction zones as a substantially compact annular column of catalyst, and that the amount of first reforming catalyst and the temperature thereof is proportioned to the amount of charge mixture, i.e., charge naphtha plus hydrogen-containing gas, and the temperature thereof to maintain the required hydrodecontaminating, or hydrodecontaminating and naphthene dehydrogenating, temperature in the first reaction zone and the required dehydrocyclizing, or dehydrocyclizing and hydrocracking, temperature in the third reaction zone. The first reforming catalyst enters the first reaction zone at a temperature of about 600° to about 1000° F., preferably about 750° to about 850° F. The first catalyst enters the third reaction zone at a temperature within the range of about 850° to about 1200° F., preferably about 900° to about 1000° F.

I claim:

1. A method of pretreating and reforming naphtha which comprises flowing hot, active, nitrogen-insensitive, sulfur-insensitive particle-form first reforming catalyst successively through a first reaction zone and a third reaction zone, said particle-form first reforming catalyst having hydrodecontaminating capabilities, at least one component of said first reforming catalyst forming a sulfide stable under the conditions of temperature and hydrogen partial pressure in said first reaction zone and oxidizable to a gaseous sulfur compound during regeneration, in said first reaction zone contacting said flowing first reforming catalyst with feed naphtha containing more than 1 p.p.m. of nitrogen at a temperature of at least 800° F. to obtain a first reaction zone effluent comprising ammonia, hydrogen sulfide, hydrogen, and C_1 and heavier hydrocarbons, in a second reaction zone contacting at least the C_5 and heavier hydrocarbons of said first reaction zone effluent with particle-form nitrogen-sensitive platinum-group metal in the presence of hydrogen and not more than 1 p.p.m. of nitrogen based upon the naphtha feed to said first reaction zone under reforming conditions of temperature, pressure, and liquid hourly space velocity to dehydrogenate at least 85 percent of the naphthenes in the naphtha feed to said first reaction zone to aromatics to obtain a second reaction zone effluent comprising hydrogen, and C_5 and heavier aromatics and paraffins, in the aforesaid third reaction zone, without separation of any substantial portion of said reaction zone effluent, contacting substantially all of said second reaction zone effluent with said particle-form first reforming catalyst discharged from said first reaction zone at substantially paraffin dehydrocyclizing temperature under paraffin dehydrocyclizing conditions of temperature, pressure, and catalyst-to-oil ratio to dehydrocyclicize paraffins in said second reaction zone effluent and to substantially complete dehydrogenation of naphthenes in said second reaction zone effluent to obtain a third reaction zone effluent, cooling said third reaction zone effluent to a temperature at which C_4 and heavier hydrocarbons condense, separating uncondensed third reaction zone effluent comprising hydrogen and C_1 to C_3 hydrocarbons from condensed C_4 and heavier hydrocarbons, and recycling said uncondensed third reaction zone effluent to at least said first reaction zone.

2. The method of pretreating and reforming naphtha as set forth and described in claim 1 wherein the temperature in said first reaction zone is a naphthene dehydrogenating temperature.

3. The method as set forth and described in claim 1 wherein the first reforming catalyst comprises oxides of chromium, molybdenum, and aluminum.

4. The method of pretreating and reforming naphtha as set forth and described in claim 1 wherein the naphtha feed to the first reaction zone contains more than 10 p.p.m. of nitrogen, wherein the first reaction zone effluent is separated into (1) ammonia-containing recycle gas. (2) C_4 and heavier hydrocarbons, wherein said ammonia-containing recycle gas is treated to remove ammonia, wherein said treated recycle gas is recycled to said first reaction zone, wherein said C_4 and heavier hydrocarbons are separated into light naphtha and second reaction zone feed, and wherein said second reaction zone feed is mixed with at least a portion of the heated uncondensed third reaction zone effluent.

5. The method of pretreating and reforming naphtha as set forth and described in claim 1 wherein the hot, active, nitrogen-insensitive, sulfur-insensitive particle-form first reforming catalyst flows as a substantially compact annular column downwardly through said first and third reaction zones, wherein the amount and temperature of said first reforming catalyst and the amount and temperature of charge mixture comprising feed naphtha and hydrogen are proportioned in said first reaction zone to maintain at least hydrodecontaminating temperature in said first reaction zone, and wherein the amount and temperature of said first reforming catalyst and the amount and temperature of the second reforming zone effluent are proportioned in said third reaction zone to maintain at least paraffin dehydrocyclicizing temperature in said third reaction zone.

6. The method of pretreating and reforming naphtha as set forth and described in claim 1 wherein the first reforming catalyst comprises oxides of chromium, molybdenum, and aluminum, wherein the first reaction zone effluent contains not more than 1 p.p.m. of nitrogen based on the feed naphtha introduced into the first reaction zone, and wherein substantially the whole of the first reaction zone effluent flows directly to the second reaction zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,573,149	Kassel	Oct. 30, 1951
2,629,683	Haensel	Feb. 24, 1953
2,664,386	Haensel	Dec. 29, 1953
2,758,062	Arundale et al.	Aug. 7, 1956
2,758,064	Haensel	Aug. 7, 1956