March 22, 1966 H. C. MYERS 3,242,066

METHOD OF PRODUCING HIGH OCTANE GASOLINE AND JET FUELS HAVING A LUMINOMETER NUMBER OF AT LEAST 150

Filed Nov. 1, 1961 4 Sheets-Sheet 1

FIG. 1L

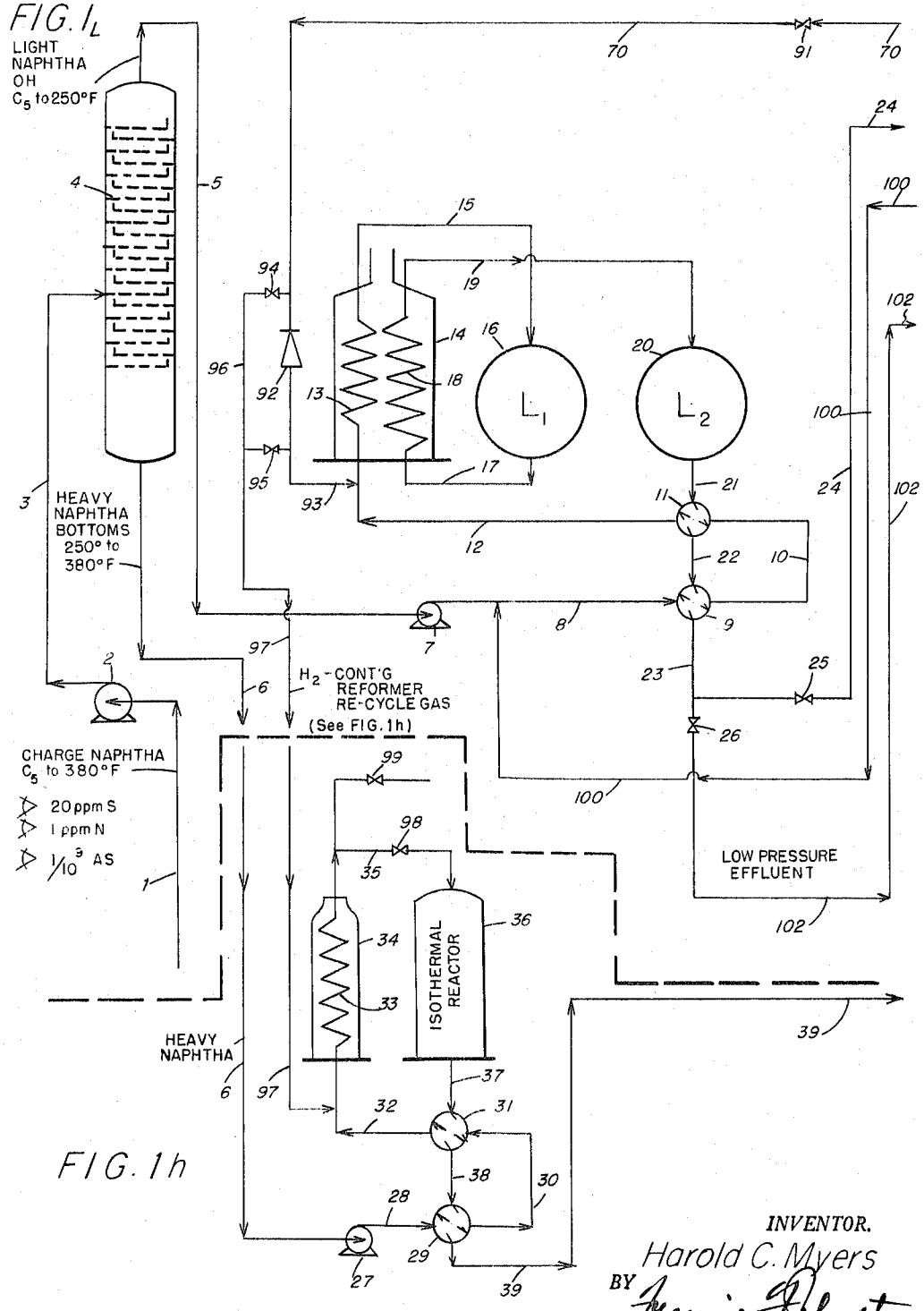


FIG. 1h

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Filed Nov. 1, 1961 4 Sheets-Sheet 2

FIG. 2e

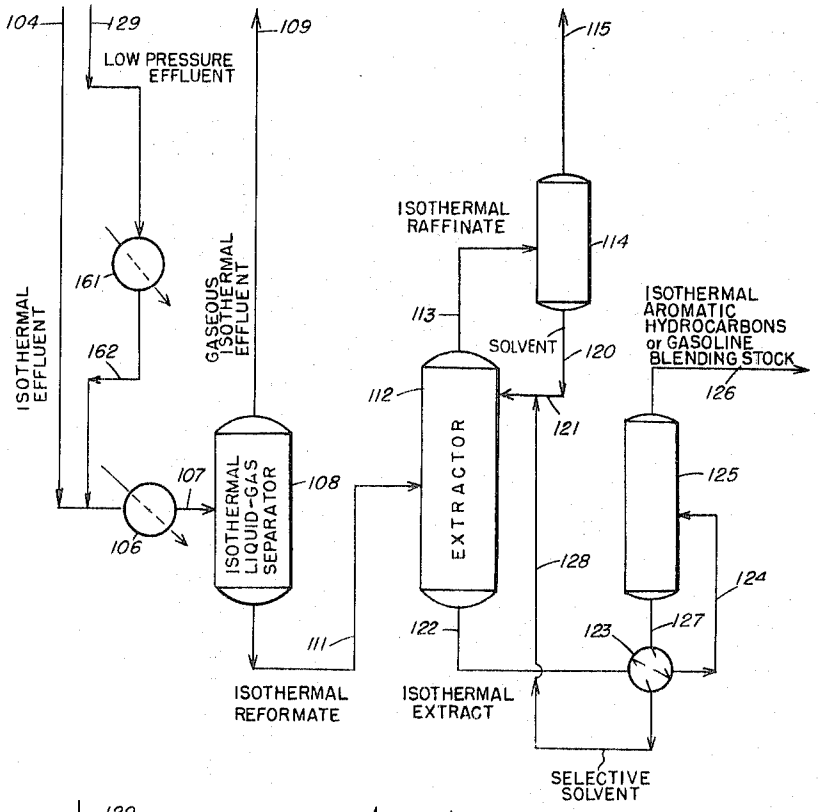
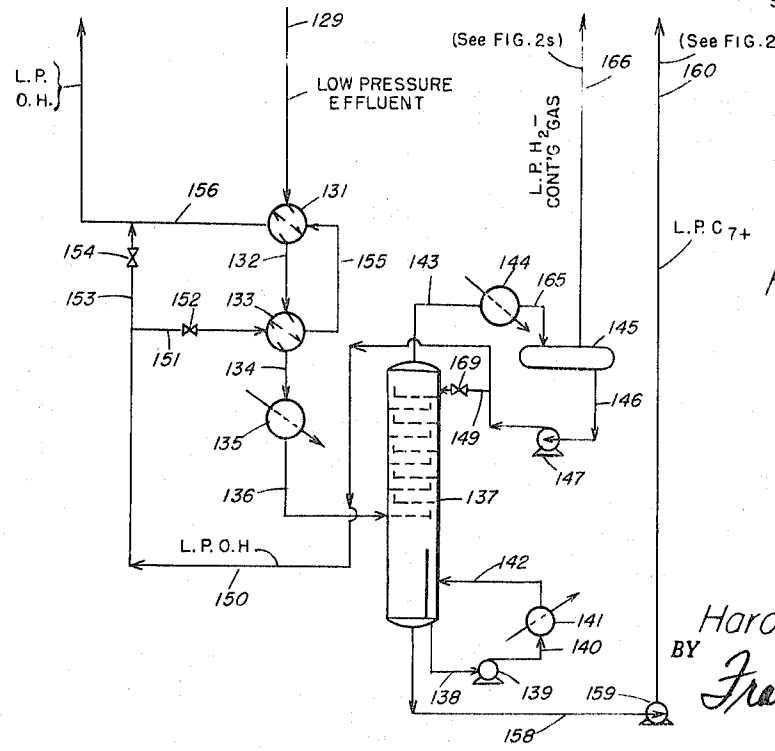


FIG. 2f



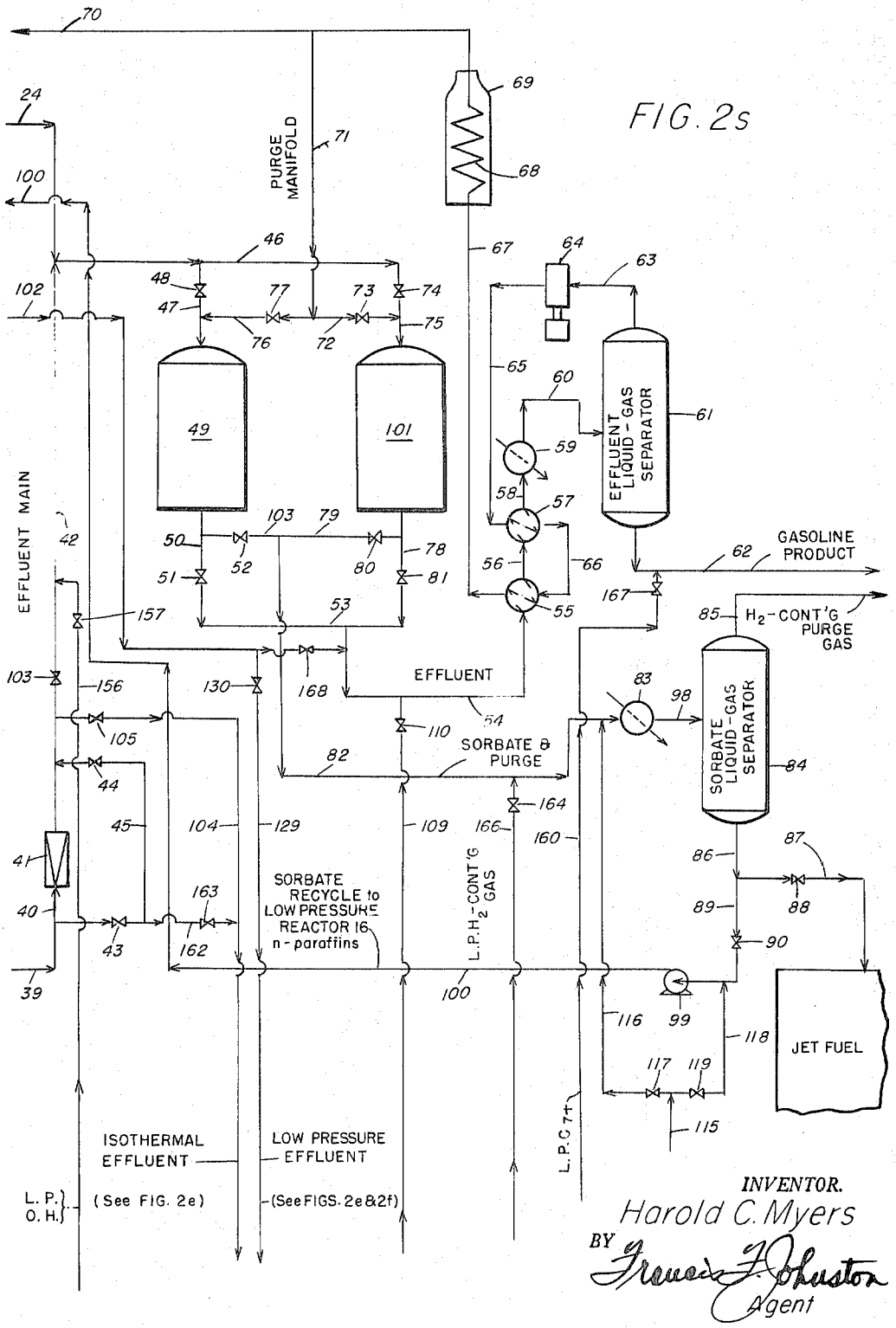
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Filed Nov. 1, 1961 4 Sheets-Sheet 3

FIG. 2s



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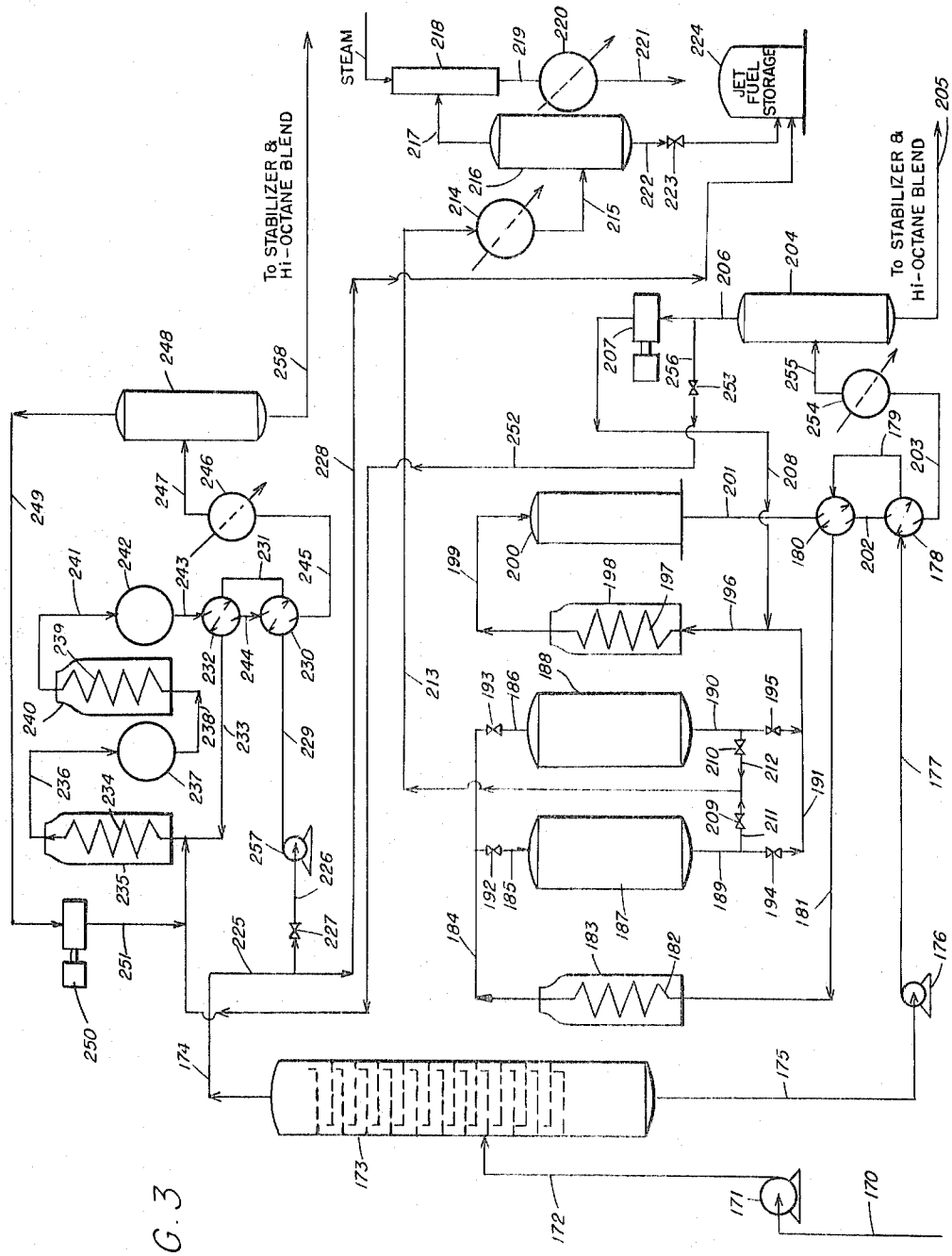


FIG. 3

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United States Patent Office

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3,242,066

METHOD OF PRODUCING HIGH OCTANE GASOLINE AND JET FUELS HAVING A LUMINOMETER NUMBER OF AT LEAST 150

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Filed Nov. 1, 1961, Ser. No. 149,251

3 Claims. (Cl. 208—93)

The present invention relates to a method of producing gasoline having an octane rating of at least 100 (Research +3 cc. TEL) and, alternatively, of producing gasoline having an octane rating of at least 100 and jet fuel having a luminometer number of at least 150 and more particularly, to a method of producing gasoline having an octane rating of at least 100 (Research +3 cc. TEL) and, alternatively, of producing gasoline having an octane rating of at least 100 and jet fuel having a luminometer number of at least 150 wherein a C_5 to 380° F. naphtha comprising paraffins and naphthenes and containing not more than innocuous concentrations of sulfur, nitrogen and arsenic (as hereinafter defined) is fractionated into a light naphtha having an end point of about 250° F. and a heavy naphtha having an initial boiling point not lower than the 90 percent point of the aforesaid light naphtha and an end boiling point of about 380° F. but not higher than about 420° F. The light naphtha is reformed in the presence of particle-form solid platinum-group metal reforming catalyst at reaction pressures in the range of 15 to 350 p.s.i.g. at a liquid hourly space velocity in the range 0.5 to 5 at reforming temperatures measured at the vapor inlet of the reaction zone(s) in the range of 800° to 1025° F. and in the presence of up to 10 mols of hydrogen per mol of light naphtha to produce a low pressure reaction zone effluent or a light naphtha reaction product comprising hydrogen and C_1 and heavier hydrocarbons. The low pressure reaction zone effluent is treated to separate the low octane rating components having five or more carbon atoms in the molecule from high octane rating components boiling in the gasoline range. The low octane rating components are used in whole or in part as jet fuel blending stock or recycled to the low pressure reforming zone(s) to extinction. The heavy naphtha is reformed under isothermal conditions (as defined hereinafter) of temperature in the range of about 900 to 1025° F. as measured at the vapor inlet of the isothermal reaction zone at a pressure of at least about 15 p.s.i.g., up to 1200 p.s.i.g. at a hydrogen-to-heavy naphtha mol ratio in the range of 1 to 20, preferably 4 to 10, and at a liquid hourly space velocity of at least about 15 up to about 150 to produce a high pressure isothermal effluent comprising hydrogen and C_1 and heavier hydrocarbons. The isothermal effluent is treated to separate C_5 and heavier high octane rating component from C_5 and heavier low octane rating components boiling in the gasoline range. The isothermal C_5 and heavier low octane rating components are a jet fuel blending stock. Alternatively, all or a part of the isothermal C_5 and heavier low octance rating components are recycled to the low pressure reforming zone(s) to extinction.

The literature of the art of upgrading gasoline hydrocarbons is replete with descriptions involving fractionation of naphtha into two or more fractions followed by reforming of the fractions separately under reforming conditions of different severity. Thus, for example, in 1938 U.S. Patent No. 2,141,185 issued in which a method

of reforming naphtha is described. The patented method comprises fractionating low octane naphtha into a lower boiling fraction and a higher boiling fraction. Each of these fractions is reformed three times separately, the high octane fraction of each reformate being separated by fractionation. In 1941 U.S. Patent No. 2,249,461 issued with a description of a method of manufacturing anti-knock gasoline which involved fractionating naphtha into seventy closely cut fractions, discarding the lowest boiling eleven fractions, segregating the balance into fractions having an octane rating above 68 and fractions having an octane rating below 68, and reforming the fractions having octane ratings below 68. Other U.S. patents describing methods of upgrading naphtha involving fractionating into two or more fractions are the following: 2,304,187; 2,324,165; 2,659,692; 2,740,751; 2,767,124; 2,773,809; 2,866,745; 2,905,619; 2,944,959. U.S. patents disclosing the production of two or more fuel products include U.S. Patent No. 2,401,649 issued in 1946 teaching a process for producing alkymer gasoline and aviation base gasoline of high aromatic and low paraffin content; U.S. Patent No. 2,729,596 issued in 1956 and describing the production of diesel and jet fuels; U.S. Patent No. 2,740,751 issued in 1956 and describing a method of producing motor fuel and aviation fuel; U.S. Patent No. 2,945,802 issued in 1960 and describing a method of producing jet fuel and aromatics by hydrocracking a hydrocarbon charge stock to convert at least a portion of the stock into jet fuel boiling range material, separating cracked naphtha and reforming the separated cracked naphtha.

Thus, while the art has been concerned with upgrading naphthas, the production of jet fuels and diesel fuels by processes involving fractionation either of the charge naphtha or the reformates produced, none has described a method in which the yield of gasoline having an octane rating of at least 100 and, alternatively, a method in which gasoline having an octane rating of at least 100 and jet fuel having a luminometer number of at least 150 are produced in greater yield of saleable high quality product than that of the conventional industrially practiced manipulations.

Before describing in general terms the method of the present invention, the use of certain terms will be clarified. Thus, a naphtha contains not more than innocuous concentrations of sulfur, nitrogen, and arsenic when the concentration of sulfur does not exceed 20 p.p.m. (parts per million), when the concentration of nitrogen does not exceed 1 p.p.m., and when the naphtha is essentially free of arsenic and in any event does not contain more than 2 p.p.b. (parts per 10^9) of arsenic. As used herein, "essentially free of arsenic" designates a concentration of arsenic in a reformer feed which, when said reformer feed is contacted with a bed of reforming catalyst comprising 0.35 percent of platinum by weight, is insufficient to deactivate said catalyst within the life of the catalyst, for example two years, as determined by other factors such as the temperature required to produce a reformate having an octane rating of at least 100 (Research+3 cc. TEL), the yield of reformate, and the mechanical strength of the catalyst. As used herein, the terms "isothermal conditions of temperature," "isothermal reactor," "isothermal reaction zone," "isothermicity" or in general any reference to temperature as being isothermal designates conditions within a zone such that the temperature of the reaction vapors leaving the zone, as measured at the vapor outlet thereof, is not more than 20

degrees Fahrenheit lower than the temperature of the reactant vapors entering the reaction zone as measured at the vapor inlet thereof.

In general, the present invention provides for fractionating a naphtha into a light fraction or light naphtha and a bottoms or heavy fraction or heavy naphtha. The light naphtha is reformed at low pressure in the range of 15 to 350 p.s.i.g. while the heavy naphtha is reformed at pressures in the range of 15 to 1,200 p.s.i.g. at conditions of isothermicity. The low presure or light naphtha reformate and the isothermal or heavy naphtha reformate each is treated in a manner to produce a jet fuel of high luminosity and a highly aromatic blending stock or a highly aromatic blending stock and aromatic hydrocarbons of relatively high purity. Thus, as indicated in a highly schematic manner in the drawing, the flow sheet illustrates fractionation of naphtha, low pressure reforming of the light naphtha and isothermal reforming of the heavy naphtha and four preferred embodiments of the treatments of the light and heavy reformates. For example, Embodiment (A) provides for contacting both reformates with molecular sieve material to obtain a sieve effluent comprising cyclic hydrocarbons, i.e., naphthenes and aromatics, and isoparaffins. The sieve is unloaded or regenerated, i.e., the sorbate comprising normal paraffins is displaced, by contacting the loaded sieve material with suitable desorbant, preferably with hydrogen and especially with reformer gas comprising hydrogen and C_1 to C_2 hydrocarbons.

The molecular sieve material is an alkali metal alumino-silicate having pores the diameters of which are somewhat larger than the diameters of the molecules of normal paraffins but smaller than the diameters of isoparaffins, naphthenes and aromatic hydrocarbons and usually in the range of 4 to 5 Angstroms.

In Embodiment (B) the isothermal or heavy reformate only is contacted with the molecular sieve material and the sieve effluent blended with the total liquid, i.e., C_5 and heavier, low pressure or light reformate.

In Embodiment (C) the light reformate is contacted with molecular sieve material to provide light reformate sieve effluent and light reformate sieve sorbate. The heavy reformate is extracted with a selective solvent having greater solvency for non-paraffinic hydrocarbons than for paraffinic hydrocarbons to obtain a paraffinic raffinate and an aromatic extract. The aromatic hydrocarbons of the aromatic extract are separated from the selective solvent. The extracted aromatic hydrocarbons and the light reformtae sieve effluent provide one or more products. The sieve sorbate and the heavy raffinate paraffins provide a jet fuel. In Embodiment (D) the light reformate is fractionated to obtain a C_5 or a C_5–C_6 fraction as an overhead and a bottoms comprising C_7 and heavier hydrocarbons. The heavy reformate together with the light reformate overhead is contacted with molecular sieve material to provide a sieve effluent. The sieve effluent and the light reformate bottoms are products. The sieve sorbate is recycled to the low pressure reforming zone.

Alternatively, in Embodiments A, B and C supra all or a portion of the sieve sorbate can be recycled to the low pressure reforming zone. It is to be observed that in Embodiment A when the sieve sorbate of both reformates is recycled to the low pressure reforming or reaction zone the yield at 102 octane (Research+3 cc. TEL) is about five percent higher than the most efficient combination of low pressure reforming of the light naphtha and high pressure reforming of the heavy naphtha. That is to say, when C_5 to 380° F. Mid-Continent naphtha is processed in accordance with the combination of operations designated embodiment A, gasoline having an octane rating (R+3 cc. TEL) of 102.2 is produced in a yield of 83.2 percent by volume based on the charge. The most efficient combination of low pressure reforming of the light naphtha and high pressure reforming of the heavy naphtha provided a yield of only 78.4 percent by volume based on the charges. Thus, processing in accordance with the combination of operations designated Embodiment A provides a yield incease of about 5 percent (4.8%) by volume. Furthermore, the reforming of the heavy fraction under conditions of isothermicity at a liquid hourly space velocity of 30 is an added advantage. Under these condtions 93 percent of the naphthenes of the 250° to 380° F. heavy naphtha from Mid-Continent straight run naphtha was converted to aromatic hydrocarbons with no substantial cracking of naphthenes and paraffins when the vapor inlet temperature was 980° F. and the vapor outlet temperature was about 965° F. It will be observed that at a liquid hourly space velocity of 30 the catalyst requirements for a unit treating 20,000 barrels of naphtha per day for both the low pressure reforming of the light naphtha and the isothermal reforming of the heavy naphtha is but 42 percent of the quantity normally employed. Thus, there is a saving in capital investment of about $625,000 and an increased income of about $700,000 per year in a unit treating 20,000 barrels of naphtha per day to produce 10 RVP gasoline having an octaine rating of 102 (Research+3 cc. TEL). In the illustrative example, the stream of normal paraffins, i.e., the molecular sieve sorbate, comprises about 12.6 percent by volume of the C_5 to 380° F. charge naphtha. When charging 20,000 barrels of said charge naphtha per day about 2,520 barrels of jet fuel are obtained per day. The jet fuel thus produced has the properties essentially as set forth in Table A.

TABLE A

Yield, Percent Volume C_5 to 380° F. Naphtha		12.6
Luminometer Number		178.0
Heating Value, B.t.u./lb		19,000
Freezing Point, ° F		Below −76
Composition, Volume Percent:		
Paraffins:		
C_6	6.0	
C_7	21.7	
C_8	22.8	
C_9	25.3	
C_{10}	18.0	
C_{11}	5.6	99.4
Alkylbenzenes:		
C_8	0.2	
C_9	0.3	
C_{10}	0.1	0.6
		100.0

When processing C_5 to 380° F. straight run Mid-Continent naphtha the products are produced in the volumetric proportions set forth in Table B.

TABLE B

	Volume, percent
C_5–380° F. Naphtha 20 p.p.m. of sulfur. 1 p.p.m. of nitrogen. 2/10−9 of arsenic.	100
C_5 to 250° F. light naphtha	40.2
250° to 380° F. heavy naphtha	59.8
Molecular sieve effluent (recycling n-paraffins to extinction)	83.2
Molecular sieve effluent (n-paraffins to jet fuel)	74.6
n-Paraffin recycle	12.6

In illustrative Embodiment B only the heavy reformate, i.e., the isothermal reformate, is contacted with molecular sieve material and the heavy reformate sorbate, i.e., n-paraffins, recycled to the low pressure reforming zone. However, the yields of C_5+ (C_5 and heavier) product from the low pressure reforming of the light naphtha in the presence of the recycle of only the n-paraffins from the heavy reformate is substantially higher than that obtained when the light naphtha is reformed in the presence of the recycled n-paraffins sorbate from the total low pressure and high pressure reformate. Thus, when producing C_5+ product having an octane rating of 100.7 (Research+3 cc. TEL) recycle of only the sorbate of the

heavy reformate to the low pressure reforming zone provides a C_5+ product yield (by volume) of 84.4 percent as compared to a C_5+ product yield (by volume) of 80.5 percent when the n-paraffins, i.e., sorbates, from both reformates are reformed in admixture with the light naphtha. The yield advantage at 102 O.N. (R+3 cc. TEL) over low pressure reforming of the light fraction and high pressure reforming of the heavy fraction is about five percent. The volumetric proportions of the different streams are given in Table C.

TABLE C

	Volume, percent
C_5 to 380° F. naphtha charge (20 p.p.m. of sulfur, 1 p.p.m. of nitrogen, $2/10^{-9}$ of arsenic)	100.0
C_5 to 250° F. light naphtha	40.2
250° to 380° F. heavy naphtha	59.8
Light reformate C_5+ product	31.4
Heavy reformate sieve effluent	44.2
n-Paraffin recycle	8.4
Combined C_5+ reformate (102.7 O.N. R+3 cc.)	82.7

It is to be noted that, when the heavy naphtha is contacted with molecular sieve material before isothermally reforming the heavy naphtha, the yield of C_5+ product at an octane rating of 103.4 (Research+3 cc. TEL) is 76.1 percent by volume while the manipulation described briefly hereinbefore as Embodiment B yields C_5+ product in the proportion of 79.9 percent by volume. In addition, the contacting of the heavy naphtha before reforming requires a larger molecular sieve unit and concomitantly larger quantities of purge gas. Since the overall yield advantage for Embodiment B is practically the same as for Embodiment A, it is preferred to treat the C_5 to 380° F. naphtha in accordance with the combination of operations designated Embodiment B when the sorbate is to be recycled to extinction. The quantity of molecular sieve and the volume of hydrogen for regeneration are substantially lower for Embodiment B than for Embodiment A.

In Embodiment C when the light reformate is contacted with molecular sieve material to obtain light reformate sieve effluent and light reformate sorbate while the heavy reformate is extracted with a selective solvent for non-paraffinic hydrocarbons to provide a paraffinic raffinate and an aromatic extract, and the sieve effluent and the extracted aromatic hydrocarbon combined to provide a 105.5 octane (Research+3 cc. TEL) C_5+ product the overall yield is 67 percent by volume of the charge naphtha and the yield of 150 luminometer number jet fuel is 20.2 percent by volume on the C_5 to 380° F. charge naphtha. Only a 72 percent by volume yield of 105.5 octane C_5+ reformate and no jet fuel is obtained by combined low pressure reforming of the light naphtha and adiabatic high pressure reforming of the heavy naphtha.

In a modification of Embodiment C when the hydrocarbons of the heavy paraffinic raffinate are combined with the light reformate sorbate and recycled to extinction in the low pressure reforming zone a 7.6 percent increase in yield of C_5+ reformate product is obtained at an octane rating level of 104.3 (Research+3 cc. TEL) compared to the yield (by volume) of C_5+ reformate product when reforming the light naphtha at low pressure and the heavy naphtha adiabatically at high pressure.

In a further modification of Embodiment C when the light reformate and the heavy reformate are extracted with selective solvent for non-paraffinic hydrocarbons to produce a paraffinic raffinate and a non-paraffinic extract and the paraffins of the raffinate are recycled to extinction in the low pressure reforming zone there is a 7.7 percent advantage (by volume) at the octane rating level of 105.2 (Research+3 cc. TEL) over low pressure reforming of the light naphtha and adiabatic reforming of the heavy naphtha at high pressure. Volumetric proportions of the different streams in the three illustrative variations of Embodiment C based on the C_5 to 380° F. charge naphtha are tabulated in Table D.

TABLE D

	Embodiment C	Modification 1	Modification 2
C_5 to 380° F. straight run naphtha: 20 p.p.m. of sulfur, 1 p.p.m. of nitrogen, $2/10^{-9}$ of arsenic	100	100	100
C_5 to 250° F. light naphtha	40.2	40.2	40.2
250° to 380° F. heavy naphtha	59.8	59.8	59.8
Low pressure reformate sieve effluent	31.8	31.8	--
Solvent extracted isothermal reformate	35.2	35.2	--
n-Paraffin sorbate	2.8	2.8	--
n-Paraffin raffinate from isothermal reformate	17.4	2.8	--
n-Paraffin raffinate from combined light and heavy reformate	--	--	29.2
C_5+ reformate product	67.0	81.8	80.3
Jet fuel product	20.2	--	--
Total yield of liquid product	87.2	81.8	80.3

The embodiment D provides for excluding low octane rating C_5 and C_6 or C_5 paraffins from the C_5+ reformate product. At an octane level of 102 (Research+3 cc. TEL) a yield of 82.8 percent by volume is obtained. Combined low pressure reforming of the light naphtha and adiabatic high pressure reforming of the heavy naphtha produces only a 78.8 percent (by volume) yield of C_5+reformate, i.e., a yield advantage of 4 percent. The volumetric proportions of the different streams produced by use of Embodiment D are given in Table E.

TABLE E

	Volume percent	
C_5 to 380° F. naphtha: 20 p.p.m. of sulfur, 1 p.p.m. of nitrogen, $2/10^{-9}$ of arsenic	100.0	
C^5 to 250° F. light naphtha	40.2	
250° F. to 380° F. heavy naphtha	59.8	100.0
C_5 to C_6 fraction of light reformate to sieve	9.1	
n-Paraffin sorbate recycle to low pressure reforming zone	13.7	
Sieve effluent of heavy reformate plus C_5 to C_6 light reformate	48.0	
C_7+fraction of light reformate	34.8	82.8

A further Embodiment E of the present invention provides for fractionating C_6 to 380° F. naphtha to produce light naphtha BR C_6 to 250° F. and heavy naphtha BR 250° to 380° F. The heavy naphtha is contacted with molecular sieve material to provide a heavy effluent and a heavy sorbate. The heavy effluent is reformed isothermally to provide a C_5+ reformate of required octane rating (Research+3 cc. TEL). The heavy sorbate is combined with all or a portion of the light fraction to provide a jet fuel having a luminometer number of at least 150. The balance of the light fraction is reformed adiabatically at low pressure. A C_6 to 380° F. Mid-Continent straight run naphtha was fractionated to provide a light naphtha and a heavy naphtha in the proportions and having the compositions set forth in Table F.

TABLE F

	C_6 to 250° F.	250° to 380° F.
Volume percent of C_6 to 380° F. Naphtha containing— 20 p.p.m. of sulfur, 1 p.p.m. of nitrogen, $2/10^{-9}$ of arsenic	35.4	64.6
n-Paraffins	27.0	17.7
i-Paraffins	25.2	28.4
Naphthenes	45.2	42.8
Aromatics	2.6	10.6
Other	--	0.5
	100.0	100.0
Luminometer No. C_6 to 250° F.	136.0	--
Luminometer No. 250° to 380° F. sorbate	--	190.0

A jet fuel having a luminometer number of 150 can be produced by blending 56 percent (on the blend by volume) of the light naphtha and 44 percent (on the blend by volume) of the heavy naphtha sorbate. When the balance of the light naphtha and the heavy naphtha effluent are reformed (the light naphtha adiabatically at low pressure and the heavy naphtha effluent isothermally) the volumetric proportions of the different streams are as set forth in Table G.

TABLE G

		Volume percent
C_6 to 380° F. straight run naphtha:		
Sulfur, 200 p.p.m.		100.0
Nitrogen, 1 p.p.m.		
Arsenic, 1/10^{-9}		
C_6 to 250° F. light naphtha		35.4
Volume percent:		
n-Paraffins	27.0	
i-Paraffins	25.2	
Naphthenes	45.2	
Aromatics	2.6	
Other		
	100.0	
Luminometer No. 136, 250° to 380° F. heavy naphtha		64.6
Volume percent:		
n-Paraffins	17.7	
i-Paraffins	28.4	
Naphthenes	42.8	
Aromatics	10.6	
Other	0.5	
	100.0	
Molecular sieve effluent, volume percent		53.2
Molecular sieve sorbate, volume percent (Luminometer No. 190)		11.4
Jet Fuel (56% C_6 to 250° F., 44% molecular sieve sorbate), Luminometer No. 150		25.9
Gasoline Product (C_5 and heavier), Octane No. (R plus 3 cc. TEL) 104		57.3

Hence, the yield of 104 octane number gasoline is 573 barrels and the yield of 150 luminometer number jet fuel is 259 barrels from each 1000 barrels of C_6–380° F. Mid-Continent naphtha charged to the splitter.

By extraction of the C_6 to 250° F. light naphtha with silica gel before admixing with the sorbate from the heavy naphtha a jet fuel having a luminometer number in the range of 160 to 165 can be obtained with a slight sacrifice of gasoline production.

One important feature of the present method of producing high octane gasoline or high octane gasoline and jet fuel or aromatic hydrocarbons and jet fuel is the use of isothermal conditions for the reforming of the heavy naphtha. At minimum liquid hourly space velocity in the isothermal reactor only about 0.03 to 0.035 barrel of reforming catalyst per barrel of heavy naphtha or 30 to 35 barrels of catalyst per 1000 barrels of heavy naphtha charged per day are required. At maximum liquid hourly space velocity (150) the values are 0.00665 per barrel and 6.65 per 1000 barrels of heavy naphtha charged per day.

Illustrative of some modifications of the basic concept of the present invention are, to wit: (1) fractionate C_5 to 420° F., preferably C_5 to 380° F. mixture of hydrocarbons comprising paraffins and naphthenes to obtain light naphtha comprising paraffins and naphthenes having an end boiling point (E.B.P.) of about 250° F. and containing C_5 or C_6 and heavier hydrocarbons and a heavy naphtha comprising hydrocarbons boiling in the range of about 250° F. to about 420° F., preferably about 250° F. to about 380° F., (2) adiabatically reform at least the naphthenes of the aforesaid light naphtha at a pressure in the range of about 15 to about 350 p.s.i.g., preferably about 100 to about 300 p.s.i.g., (3) isothermally reform the heavy naphtha, and (4) treat the reformates so produced to obtain (1) only gasoline having an octane rating of at least 100 (Research+3 cc. TEL), (2) aromatic hydrocarbons and jet fuel having a luminometer number of at least 150, or (3) gasoline having an octane rating of at least 100 (Research+3 cc. TEL), and jet fuel having a luminometer number of at least 150.

TABLE H

Properties and compositions of full boiling range Mid-Continent naphtha and of light and heavy naphtha therefrom

	Full Boiling Range	Light Naphtha	Heavy Naphtha
Percent Full Boiling Range Naphtha	100	40.2	59.8
Gravity, ° API	56.4	65.8	50.8
ASTM Distillation—IBP, ° F	118		
10%	177	166	294
20%	199	172	297
50%	258	191	314
90%	337	217	358
EBP—Octane Rating:			
Research, Clear	46.5	65.7	29.2
Research + 3 cc. TEL	72.0	84.9	53.2
Motor, Clear	46.7	63.1	33.8
Motor, + 3 cc. TEL	73.0	83.8	57.5
Hydrocarbon Distribution:			
Paraffins	52.1	58.8	46.1
Naphthenes	40.2	39.1	42.8
Aromatics	7.4	2.1	10.6
Other	0.3	0.0	0.5
Total	100.0	100.0	100.0

In this embodiment the effluents of both the low pressure reforming zone and the isothermal reforming zone are treated at temperatures in the range of about 600° to about 800° F., i.e., at a temperature above the dew point and below cracking temperature of the C_5 and heavier hydrocarbons by contact with molecular sieve material. In the following description of the flow of liquids and gases as illustrated by the drawing only a brief description of the separation of low octane from high octane components of the C_5 and heavier reformate is provided. For a more exhaustive trreatment of this subject and the recovery of the sorbate, i.e., for regeneration or unloading of the sieve material by the "thermal swing," "pressure swing," "liquid displacement," or vacuum techniques reference is made to the brochure published by Linde and Co. entitled, "Octane Improvement;" U.S. Patents Nos. 2,858,901; 2,859,170; 2,859,173; 2,859,256; 2,859,257; and 2,901,519; "Oil and Gas Journal," 57, No. 13, pp. 52 and 53 (March 23, 1959); "World Petroleum," April 1959; "Petroleum Refiner," 38, No. 4, pp. 125–134 (April 1959); and "Chemical Engineering," 66, 104, 1959, No. 16, August 10, 1959.

Thus, C_5 to 380° F. naphtha comprising paraffins and naphthenes and containing not more than innocuous concentrations of sulfur, nitrogen, and arsenic is drawn from a source not shown through pipe **1** by pump **2**. The charge naphtha is discharged into pipe **3** and heated by means not shown to a temperature at which the components thereof boiling up to about 250° F. are volatile. The heated naphtha flows to fractionator, e.g., a splitter, **4**. In fractionator **4** an overhead comprising C_5 and heavier hydrocarbons having an E.B.P. of about 250° F. is taken through pipe **5**. The light naphtha so obtained comprises paraffins and naphthenes. A bottoms, i.e., heavy naphtha having an initial boiling point (I.B.P.) of about 250° F. and not lower than the 90 percent point of the light naphtha and an E.B.P. substantially that of the charge naphtha and preferably not higher than 380° F. is withdrawn from fractionator **4** through pipe **6**.

The flow of light naphtha from fractionator **4** to effluent main **42** will be described first. Thereafter, the flow of heavy naphtha from fractionator **4** to effluent main **42** will be described.

The light naphtha flows from fractionator **4** through pipe **5** to the suction side of pump **7**. Pump **7** discharges the light naphtha into pipe **8** at a pressure in exess of the pressure in low pressure reactor **16**. The light naphtha flows through pipe **8** to indirect heat exchanger **9** where the light naphtha is in heat transfer relation with the low pressure effluent flowing from indirect heat exchanger **11** through conduit **22**. From indirect heat ex-

changer 9 the light naphtha flows through pipe 10 to indirect heat exchanger 11. In heat exchanger 11 the light naphtha is in heat transfer relation with the low pressure effluent flowing from reactor 20 through conduit 21. From indirect heat exchanger 11 the light naphtha flows through conduit 12 to coil 13 in heater or furnace 14. At a point in conduit 12 intermediate to heat exchanger 11 and coil 13 hydrogen containing reformer recycle gas is admixed with the light naphtha to form a light naphtha charge mixture. After start-up and when the pressure at isothermal reactor 36 is higher than the pressure at reactor 16 the hydrogen-containing gas is reformer gas, recovered, when employing molecular sieves as a means of separating n-paraffins from other constituents of reformates, at liquid-gas separator 61 (FIGURE 2_s) flowing therefrom through conduit 63 to compressor 64 and thence through conduits 65, 66, 67, coil 68, and conduit 70 under control of valve 91 to reducing valve 92 and conduit 93.

When the isothermal reactor 36 and reactor 16 are at substantially the same pressure the reformer recycle gas bypasses reducing valve 92 and with valves 94 and 95 open flows through conduit 96 in part to conduit 93 and conduit 12 and in part to conduits 97 and 32. When the isothermal reactor is at a pressure substantially higher than that of reactor 16 a portion of the reformer recycle gas bypasses reducing valve 92 and with valve 94 open and valve 95 closed flows in part through conduits 96 and 97 to conduit 32 and in part through reducing valve 92 through conduits 93 and 12. In conduit 12 the hydrogen-containing reformer recycle gas is admixed with the light naphtha to provide a light naphtha charge mixture having a hydrogen-to-light naphtha mol ratio of 0.25 to 10. Alternatively, compressor 64 can compress the hyrogen-containing reformer recycle gas to a pressure in excess of that at reactor 16 but below the pressure at isothermal reactor 36. The hydrogen-containing gas in excess of that used in reactor 16 is then recompressed by a compressor not shown to a pressure in excess of that at isothermal reactor 36.

The light naphtha charge mixture flows through conduit 12 to coil 13 in heater 14. In coil 13 the light naphtha charge mixture is heated to a reforming temperature to provide a temperature at the vapor inlet of low pressure reactor 16 in the range of 800° to about 1000° F., preferably about 900° to about 980° F.

The heated light naphtha charge mixture flows from coil 13 through conduit 15 to low pressure reactor (L_1). In low pressure reactor 16 the light naphtha charge mixture is contacted with particle-form solid platinum-group metal reforming catalyst, preferably platinum-group metal reforming catalyst comprising about 0.35 to about 0.6 percent by weight of platinum on refractory oxide, preferably alumina, support. The liquid hourly space velocity (v./hr./v.) and the reforming temperature are interdependent and dependent upon the target or required octane rating of the C_5 and heavier cyclic hydrocarbons and branched-chain paraffins of the low pressure effluent. The light naphtha charge mixture flows through reactors 16 and 20 at a liquid hourly space velocity of the light naphtha in the range of 0.5 to 2. The first low pressure effluent flows from reactor 16 through conduit 17 to coil 18 in furnace 14. In coil 18 the first low pressure effluent is reheated to a reforming temperature to provide a temperature at the vapor inlet of reactor 20, the same as, lower or higher than, the temperature at the vapor inlet of reactor 16. The reheated first low pressure effluent flows from coil 18 through conduit 19 to low pressure reactor 20. The liquid space velocity employed in low pressure reactor 20 is dependent upon the activity of the catalyst (preferably of the same composition as that in reactor 16), and the extent to which the paraffins in the first low pressure effluent are to be isomerized and dehydrocyclized. At any given inlet temperature and with a catalyst having substantially the same activity the liquid hourly space velocity will be lower the higher the required conversion of the paraffins. The overall liquid hourly space velocity for reactors 16 and 20 is in the range of about 0.5 to about 2.0.

The effluent of reactor 20, designated final low pressure effluent, flows from low pressure reactor 20 through conduit 21 to indirect heat exchanger 11, through conduit 22, indirect heat exchanger 9 and through conduits 23 and 24 (valve 25 open, valve 26 closed) to effluent main 42 (FIGURE 2_s).

The flow of the heavy naphtha from fractionator 4 to the effluent main 42 will be described now. The bottoms of fractionator 4 having an initial boiling point of about 250° F. and not lower than the 90 percent point of the light naphtha and an end boiling point preferably of about 380° F. and by choice as high as 420° F. flows from fractionator 4 through pipe 6 to the suction side of pump 27 (FIGURE 1_h). Pump 27 discharges the heavy naphtha into pipe 28 at a pressure in excess of that in isothermal reactor 36. The pressure in reactor 36 is in the range 15 to 1200 p.s.i.g. and preferably in the range 500 to 1200 p.s.i.g.

The heavy naphtha flows through pipe 28 to indirect heat exchanger 29 where the heavy naphtha is in heat transfer relation with the isothermal effluent flowing from indirect heat exchanger 31 through conduit 38. From heat exchanger 29 the heavy naphtha flows through pipe 30 to indirect heat exchanger 31. In indirect heat exchanger 31 the heavy naphtha is in heat transfer relation with the isothermal effluent flowing from isothermal reactor 36 through conduit 37. From exchanger 31 the heavy naphtha flows through conduit 32 to coil 33 in heater 34. At a point in conduit 32 intermediate to exchanger 31 and to coil 33 reformer recycle gas flowing from compressor 64 (FIGURE 2_s) through conduits 65, 66, 67, coil 68 (FIGURE 2_s) and conduit 70 under control of valve 91 (FIGURE 1_L), conduit 96, conduit 97 and conduit 32 (FIGURE 1_L) is admixed with the heavy naphtha to provide a heavy naphtha charge mixture having a hydrogen-to-heavy naphtha mol ratio in the range of 1 to 10, preferably 4 to 6. The heavy naphtha charge mixture flows through conduit 32 to coil 33. In coil 33 the heavy naphtha charge mixture is heated to a temperature to provide at the vapor inlet of isothermal reactor 36 a reforming temperature in the range of about 940° to about 1020° F. and preferably about 960° to about 980° F. The heated heavy naphtha charge mixture flows from heater 34 through conduit 35 (valve 98 open; valve 99 closed) to isothermal reactor 36.

In isothermal reactor 36 the temperature and liquid hourly space velocity are correlated to convert substantially all of the naphthenes to aromatic hydrocarbons with a minimum of hydrocracking. Vapor inlet temperatures in the range of 940° to 1020° F. with liquid hourly space velocities in the range of 30 to 150, preferably 30 to about 100 are usually employed. The heavy naphtha charge mixture is in contact with particle-form platinum-group metal reforming catalyst, preferably platinum-group metal reforming catalyst comprising about 0.35 to about 0.6 percent by weight of platinum on a refractory oxide support, preferably alumina.

The heavy naphtha charge mixture flows downwardly in isothermal reactor 36 to produce an isothermal effluent. The isothermal effluent flows from reactor 36 through conduit 37 to heat exchanger 31 through conduit 38 to heat exchanger 29 and through conduit 39 to isothermal effluent main 40.

When the pressure in isothermal effluent main 40 is greater than the pressure at which the low pressure effluent enters effluent main 42 by substantially more than the pressure drop from conduit 39 to effluent main 42, the pressure of the isothermal effluent is reduced by means of pressure reducing valve 41 (FIG. 2_s). When the pressure of the isothermal effluent is not greater by

more than the pressure drop between conduit 39 and effluent main 42, the isothermal effluent flows from conduit 39 to conduit 40 (FIGURE 2_S), conduit 45 (valves 43 and 44 open) to conduit 42. Under the alternative pressure conditions the flow is from conduit 39 to conduit 40, and pressure reducing valve 41 to conduit 42.

In the embodiment of the present invention presently being described the low pressure effluent and the isothermal effluent are mixed and contacted with molecular sieve material. Accordingly, for purpose of description, the isothermal effluent and the low pressure effluent cooled by the heat exchange described hereinbefore to not higher than 800° F. and not lower than the dew point of the mixture at the pressure in effluent main 42, usually not lower than about 600° F. flow through effluent main 42 to sieve manifold 46 (FIGURE 2_S)

A plurality of sieves are required to make the separation continuous and to integrate the sieve separation with the reforming operation. Accordingly, while one or more sieves are being loaded other sieves are being unloaded or regenerated. For the purpose of this description it will be assumed that sieve 49 is unloaded and sieve 101 is loaded and being unloaded contemporaneously employing the hydrogen-containing reformer gas as a purge.

Thus, the mixed low pressure effluent and isothermal effluent, designated mixed effluent, flows through effluent main 42 to sieve manifold 46. With valves 74, 77 and 52 closed and valves 48 and 51 open the mixed effluents flow from sieve manifold 46 through branch 47 into sieve 49. The mixed effluents flow downwardly through the sieve material having pores 4 to 5 Angstroms in diameter leaving as a sorbate in the sieve material the straight chain paraffins and producing a sieve effluent comprising isoparaffins, aromatics, and any unconverted naphthenes. The sieve effluent having a temperature in the range of 600° to 800° F. flows from sieve 49 through conduit 50 (valve 51 open; valves 52 and 80 closed) to sieve effluent manifold 53. From manifold 53 the sieve effluent flows through conduit 54 to indirect heat exchanger 55. In heat exchanger 55 the sieve effluent is in heat transfer relation with the purge gas (described hereinafter) flowing from indirect heat exchanger 57 through conduit 66. From heat exchanger 55 the sieve effluent flows through conduit 56 to indirect heat exchanger 57. In indirect heat exchanger 57 the sieve effluent is in heat transfer relation with the purge gas flowing from compressor 64 through conduit 65. From heat exchanger 57 the sieve effluent comprising hydrogen, isoparaffins, and cyclic hydrocarbons of the mixed effluent flows through conduit 58 to cooler 59. In cooler 59 the sieve effluent is cooled to a temperature at which C_4 and heavier isoparaffins and aromatics are condensed at the existing pressure. The cooled sieve effluent flows from cooler 59 through conduit 60 to effluent liquid-gas separator 61.

In separator 61 the uncondensed sieve effluent, designated reformer gas, comprising hydrogen and C_1 to C_3 hydrocarbons not sorbed by the sieve separates from the C_4 and heavier isoparaffins and aromatics, designated gasoline product. The gasoline product flows from sieve separator 61 through pipe 62 to means for recovering aromatic hydrocarbons, to gasoline blending, etc. not shown. The reformer gas flows from sieve separator 61 through conduit 63 to compressor 64. Compressor 64 recompresses the reformer gas to a pressure required for purging sieve 101 or preferably to a pressure in excess of that at reactor 16 (FIGURE 1_L).

As stated before, it has been assumed for the purpose of this illustration that sieve 101 is being unloaded or purged or regenerated while sieve 49 is being loaded. In other words, the sorbate comprising n-paraffins is removed in any suitable manner known to the art. The method selected for illustration is that of displacing the paraffinic sorbate with hydrogen-containing reformer gas separated from the sieve effluent in effluent separator 61. Accordingly, a portion of the reformer gas flowing from compressor 64 through conduits 65, 66, 67 and coil 68 in which the reformer gas is heated to substantially the temperature of the sieve material in sieve 101 and usually in the range of about 600° to about 800° F. flows from coil 68 through conduit 70 to purge manifold 71. From purge manifold 71 the purge gas flows through purge branch 72 under control of valve 73 which is regulated to pass the portion of the reformer gas not required in the low pressure reactors and the isothermal reactor to maintain the required hydrogen-to-naphtha mol ratios set forth herein. The hydrogen-containing purge gas flows from purge branch 72 to reactor effluent branch 75, downwardly through the sieve material in sieve 101 to sieve effluent branch 78 removing the n-paraffin sorbate during its passage. With valve 81 closed and valve 80 open the purge gas and sorbate flow through sieve purge branch 79 to purge manifold 82. The purge gas and sorbate flow through purge manifold 82 to cooler 83 where the purge gas-sorbate mixture is cooled to a temperature at which C_4 and heavier n-paraffins are condensed at the existing pressure. From cooler 83 the condensed and uncondensed purge gas-sorbate mixture flows through conduit 98 to sorbate liquid-gas separator 84.

In sorbate liquid-gas separator 84 the uncondensed purge gas-sorbate mixture comprising C_1 to C_3 paraffins and hydrogen, designated hydrogen-containing purge gas, separates from sorbate comprising C_4 and heavier paraffins. The purge gas flows from sorbate separator 84 through conduit 85 to other hydroprocesses or fuel main.

The n-paraffin sorbate comprising C_4 and heavier n-paraffins in whole or in part flows from separator 84 through pipes 86 and 87 under control of valve 88 to jet fuel storage. Alternatively, the n-paraffin sorbate flows in whole or in part from separator 84 through pipes 86 and 89 under control of valve 90 to the suction side of pump 99. Pump 99 discharges the sorbate into pipe 100 through which the sorbate flows to pipe 8 (FIGURE 1_L) to mix with the light naphtha charge mixture.

EMBODIMENT B

In the modification of the basic concept of the present invention designated Embodiment B only the isothermal effluent is contacted with the molecular sieve material. Accordingly, the light naphtha is reformed as previously described to produce a low pressure final effluent flowing from low pressure reactor 20 through conduit 21 to heat exchanger 11, conduit 22, heat exchanger 9, and conduit 23 (valve 26 open; valve 25 closed) to conduit 102. The low pressure final effluent flows through conduit 102 to conduit 54 (FIGURE 2_S) where it mixed with the sieve effluent of the isothermal effluent.

The heavy naphtha is reformed isothermally as previously described to obtain an isothermal effluent flowing from isothermal reactor 36 (FIGURE 1_h) through conduit 37 to heat exchanger 31, conduit 38, heat exchanger 29 and conduit 39 to conduit 40 (FIGURE 2_S), effluent main 42, sieve manifold 46, and sieve branch 75 (valve 74 open; valve 48 closed) to sieve 101. The isothermal effluent flows downwardly through sieve 101 which sorbs the n-paraffins in the isothermal effluent to produce a sieve effluent comprising isoparaffins and aromatics. The sieve effluent flows from sieve 101 through sieve effluent branch 78 (valve 81 open; valve 80 closed) to effluent manifold 53 and thence to conduit 54 where the isothermal sieve effluent mixes with the low pressure final effluent as stated before.

The mixture of isothermal sieve effluent and low pressure final effluent flows through conduit 54 to heat exchanger 55, conduit 56, heat exchanger 57 and conduit 58 to cooler 59. In cooler 59 the mixture of isothermal sieve effluent and low pressure final effluent comprising hydrogen and C_1 and heavier isoparaffins, aromatics and n-paraffins from the low pressure final effluent is cooled to a temperature at which the C_4 and heavier hydrocarbons are condensed. The cooled mixture of isothermal sieve effluent and low pressure final effluent flows from

cooler 59 through conduit 60 to effluent gas-liquid separator 61.

In effluent separator 61 the uncondensed mixture, designated reformer gas and comprising hydrogen and C_1 to C_3 hydrocarbons flows from separator 61 through conduit 63 to compressor 64.

The condensate, designated gasoline product, flows from effluent separator 61 through pipe 62 to stabilization, gasoline blending, storage, distribution, etc.

The reformer gas flowing from separator 61 to compressor 64 is recompressed and discharged into conduit 65 through which the recompressed reformer gas flows to exchanger 57, conduit 66, exchanger 55 and conduit 67 to coil 68 in heater 9 as previously described herein. The reheated reformer gas flows from heater 69 through conduit 70 under control of valve 91 (FIGURE 1_L) to the low pressure reformer 16 and the isothermal reformer 36 as previously described herein. The balance of the reformer gas is used to purge the loaded sieve. Since in Embodiment B as described hereinbefore sieve 101 has been loaded, the unloading or purging of sieve 49 will be described.

A portion, i.e., the balance, of the reformer gas not used in reactors 16, 20, and 36, flows from conduit 70 to purge manifold 71 and thence through purge branch 76 (valve 77 open; valves 73 and 48 closed) to sieve 49. The purge gas flows downwardly through sieve 49 displacing the n-paraffin sorbate to effluent branch 50 and purge branch 103 (valves 51 and 80 closed; valve 52 open). The purge gas and n-paraffin sorbate flow from purge branch 103 to purge manifold 82 and thence to cooler 83. In cooler 83 the temperature of the purge gas-sorbate mixture is reduced to that at which at the existing pressure C_4 and heavier hydrocarbons are condensed. The cooled mixture flows from cooler 83 through conduit 93 to sorbate gas-liquid separator 84. In sorbate liquid-gas separator 84 the uncondensed mixture comprising hydrogen and C_1 to C_3 hydrocarbons separates from the condensed sorbate and flows through conduit 85 to other hydroprocesses or fuel. The condensed sorbate comprising C_4 and heavier n-paraffins flows from separator 84 through pipe 86 in whole or in part through pipe 87 under control of valve 88 to storage as jet fuel or in whole or in part through pipe 89 under control of valve 90 to the suction side of pump 99 for recycle through pipe 100 to pipe 8 and the low pressure reactors 16 and 20.

EMBODIMENT C

In Embodiment C the low pressure final effluent is contacted with the molecular sieve material while the isothermal effluent is extracted with a selective solvent having greater solvency for nonparaffinic hydrocarbons than for paraffinic hydrocarbons. There are numerous selective solvents useful for this purpose known to those skilled in the art. These selective solvents include liquid sulfur dioxide, the polyalkylene glycols, and others. For illustrative purposes diethylene glycol has been chosen as the selective solvent. Since the manipulation of these selective solvents is well known to those skilled in the art only a brief description is provided.

The light naphtha is reformed as previously described to obtain a low pressure final effluent flowing from low pressure reactor 20 (FIGURE 1_L) through conduit 21, exchanger 11, conduit 22, exchanger 9 and conduit 23 to conduit 24 (valve 25 open; valve 26 closed). The low pressure final effluent flows through conduit 24 to effluent main 42 and thence to sieve manifold 46. Sieve 49 being on-stream the low pressure final effluent flows from sieve manifold 46 through branch 47 to sieve 49. The low pressure final effluent flows downwardly through sieve 49 depositing n-paraffins to provide a sieve effluent comprising iso-paraffins, aromatics, and hydrogen. The sieve effluent flows from sieve 49 through sieve effluent branch 50 (valve 51 open; valve 52 closed) to sieve effluent manifold 53, conduit 54, exchanger 55, conduit 56, exchanger 57 and conduit 58 to cooler 59. In cooler 59 the sieve effluent is cooled to a temperature at which C_4 and heavier hydrocarbons are condensed at the existing pressure. From cooler 59 the cooled sieve effluent flows through conduit 60 to effluent separator 61. In separator 61 the uncondensed sieve effluent, designated reformer gas, separates and flows through conduit 63 to compressor 64 and thence in major part to reactors 16 and 36 and in minor part to regenerate or unload sieve 101. The condensed sieve effluent flows from separator 61 through pipe 62 as gasoline product.

The heavy naphtha is reformed in isothermal reactor 36 to produce isothermal effluent which flows from reactor 36 through conduit 37, exchanger 31, conduit 38, exchanger 29, and conduit 39 to conduit 40. When the pressure of the isothermal effluent is greater than the pressure drop plus the pressure at extractor 112 (FIGURE 2_e) the isothermal effluent flows through conduit 40, pressure reducing valve 41, effluent main 42 (valve 103 closed; valve 105 open) and conduit 104 to cooler 106 (FIGURE 2_e). In cooler 106 the isothermal effluent is cooled to a temperature at which C_5 and heavier hydrocarbons are condensed at the existing pressure. The cooled isothermal effluent flows from cooler 106 through conduit 107 to isothermal liquid-gas separator 108.

In isothermal liquid-gas separator 108 the uncondensed isothermal effluent comprising hydrogen and C_1 to C_5 hydrocarbons separates from the condensed isothermal effluent comprising C_5 and heavier paraffins, naphthenes (if any), and aromatics. The uncondensed or gaseous isothermal effluent flows from separator 108 through conduit 109 (valve 110 open) to conduit 54 (FIGURE 2_s) and thence with the sieve effluent to effluent separator 61 (FIGURE 2_s).

The condensed isothermal effluent, designated isothermal reformate, flows from separator 108 through conduit 111 to extractor 112. During the passage from separator 108 to extractor 112 the isothermal reformate is heated in any suitable manner to extraction temperature which, for diethylene glycol, is in the range of about 200° F. to 350° F. In extractor 112 the isothermal reformate is contacted with selective solvent having a greater solvency for non-paraffinic hydrocarbons than for paraffinic hydrocarbons. For the purpose of this illustration the selective solvent diethylene glycol will be used. Thus, the selective solvent, diethylene glycol, flows from fractionator 125 through pipe 127 to indirect heat exchanger 123. In heat exchanger 123 the selective solvent is in heat transfer relation with the isothermal extract flowing from extractor 112 through pipe 122. From indirect heat exchanger 123 the selective solvent flows through pipe 128 to pipe 121 being heated to extraction temperature if necessary by any suitable means during passage to pipe 121 or thereafter. Selective solvent separated from the isothermal raffinate flows from fractionator 114 through pipe 120 to pipe 121. The selective solvent at extraction temperature flows from pipe 121 into extractor 112. The selective solvent flows countercurrently downward through extractor 112 in intimate contact with the upwardly flowing isothermal reformate extracting the aromatic hydrocarbons of the isothermal reformate therefrom to produce isothermal extract comprising selective solvent and aromatic hydrocarbons and isothermal raffinate comprising unextracted paraffinic hydrocarbons. The isothermal raffinate leaves extractor 112 through pipe 113 and flows therethrough to fractionator 114. In fractionator 114 the paraffinic hydrocarbons separate from entrained selective solvent and flow therefrom through pipe 115 in whole or part to pipe 116 (FIGURE 2_s) under control of valve 117 to conduit 82 and admixture with sieve sorbate or in whole or part to pipe 118 under control of valve 119 to pipe 89 and the suction side of pump 99 for recycle to the low pressure reforming reactor 16 (FIGURE 1_L). The isothermal extract flows from extractor 112 through

pipe 122 to indirect heat exchanger 123, and pipe 124 to fractionator 125. In fractionator 125 the non-paraffinic hydrocarbons of the isothermal extract separate from the selective solvent and flow through pipe 126 to recovery of substantially pure aromatic hydrocarbons boiling in the range of 176° to 380° F., to admixture with the gasoline product flowing through pipe 62 (FIGURE 2$_s$), or to storage or distribution per se as gasoline product. The selective solvent separated in fractionator 125 returns to the extractor via pipe 127, exchanger 123, and pipes 128 and 121 as previously described.

In a modification of Embodiment C the low pressure effluent and the isothermal effluent are condensed and the C_5 and heavier fraction of each effluent extracted with a selective solvent for non-paraffinic hydrocarbons.

In this instance the low pressure effluent flows from reactor 20 through conduit 21, exchanger 11, conduit 22, exchanger 9, conduit 23 (valve 25 closed; valve 26 open), conduit 102, (FIGS. 1$_L$ and 2$_s$), conduit 129, (FIGS. 2$_s$ and 2$_e$); (valve 130 open; valve 168 closed) cooler 161, and conduit 162 to cooler 106.

The heavy naphtha is reformed isothermally as previously described. The isothermal effluent flows from isothermal reactor 36 through conduit 37, exchanger 31, conduit 38, exchanger 29, and conduit 39 to conduit 40, (FIG. 2$_s$). When the isothermal effluent is at a pressure not substantially greater than that in conduit 104 the isothermal effluent flows from conduit 40 through conduits 45 and 162 to conduit 104 (valves 43 and 163 open; valve 44 closed). When the pressure of the isothermal effluent is substantially greater than that in conduit 104, the isothermal effluent flows from conduit 40 through pressure reducing valve 41, conduit 42 (valve 103 closed; valve 105 open) to conduit 104. The isothermal effluent flows through conduit 104 to cooler 106. In cooler 106 the isothermal effluent and the low pressure effluent are cooled to a temperature at which C_5 and heavier hydrocarbons are condensed. The cooled mixed effluents flow from cooler 106 through conduit 107 to separator 108.

In separator 108 the uncondensed mixed effluents comprising hydrogen and C_1 to C_4 hydrocarbons separate from the condensed mixed effluents comprising paraffinic and non-paraffinic C_5 and heavier hydrocarbons. The uncondensed mixed effluents flow from separator 108 through conduit 109 to conduit 54 (FIG. 2$_s$; valve 110 open) and thence through conduit 54 to exchanger 55, conduit 56, exchanger 57, conduit 58, cooler 59 and conduit 60 to separator 61. In separator 61 the hydrogen and C_1 to C_3 hydrocarbons separate and flow from separator 61 through conduit 63 to compressor 64 and is thereby recycled to the reactors 16 and 36. The C_4 and heavier hydrocarbons flow from separator 61 through conduit 62 to recovery. The condensed mixed effluents, designated extractor feed, flow from separator 108 (FIG. 2$_e$) through pipe 111 to extractor 112. In extractor 112 the extractor feed is contacted with a selective solvent for non-paraffinic hydrocarbons to provide a paraffinic raffinate which flows from extractor 112 through pipe 113 to fractionator 114 and non-paraffinic extract which flows from extractor 112 through pipe 122, exchanger 123, and pipe 124 to fractionator 125.

In fractionator 114 the paraffinic hydrocarbons separate from selective solvent and flow through pipe 115 in whole or in part to pipe 118 (FIG. 2$_s$; valve 117 closed; valve 119 open) and thence to pipe 89 and the suction side of pump 99 for recycle to the low pressure reactor 16 (FIG. 1$_L$).

The non-paraffinic extract is fractionated in fractionator 125 to provide an overhead comprising aromatic hydrocarbons boiling in the range of 176° to 380° F. The aforesaid overhead flows from fractionator 125 through pipe 126 to means for the recovery of specific aromatic hydrocarbons, to means for blending to provide gasoline or to distribution as gasoline.

EMBODIMENT D

As stated hereinbefore Embodiment D of the present invention provides for excluding n-paraffins having six or less carbon atoms from the high octane C_5+product. Accordingly, illustrative of the embodiment is the fractionation of naphtha to obtain a C_5 to 250° F. E.B.P. light naphtha and a 250° to 380° F. heavy naphtha. The light naphtha is reformed at low pressure as previously described to produce low pressure effluent comprising hydrogen and C_1 and heavier hydrocarbons. The low pressure effluent flows from reactor 20 through conduit 21 to exchanger 11, conduit 22, exchanger 9, conduit 23 (valve 26 open; valve 25 closed) and conduit 102 to conduit 129 (FIGURE 2$_s$; valve 130 open; valve 168 closed). The low pressure effluent flows through conduit 129 (FIGURE 2$_f$) to indirect heat exchanger 131, conduit 132, indirect heat exchanger 133, conduit 134, cooler 135, and conduit 136 to fractionator 137 having a reboiler, e.g., pipe 138, pump 139, pipe 140, heat exchanger 141, and pipe 142. The flow of low pressure effluent and accumulator liquid from accumulator 145 are controlled in conjunction with cooler 135 and the reboiler to ensure that the accumulator liquid comprises substantially C_5 and C_6 paraffins and the bottoms C_7 and heavier hydrocarbons. Accordingly, the low pressure effluent flows into fractionator 137. A temperature is maintained in fractionator 137 at which C_5 and C_6 hydrocarbons are volatile while C_7 and heavier hydrocarbons are liquid. The C_5 and C_6 hydrocarbons together with hydrogen and C_1 to C_4 hydrocarbons are taken overhead through conduit 143 to cooler 144. In cooler 144 the overhead is cooled to a temperature at which C_5 and heavier hydrocarbons are condensed. The cooled overhead flows from cooler 144 through conduit 165 to accumulator 145. In accumulator 145 the hydrogen and C_1 to C_4 hydrocarbons of the low pressure effluent, designated L.P. H_2-containing gas, flow therefrom through conduit 166 under control of valve 164 (FIGURE 2$_s$) to conduit 82 and thence to cooler 83 and conduit 98 to sorbate separator 84. The condensed C_5 and heavier hydrocarbons, i.e., the accumulator liquid, flow from accumulator 145 through pipe 146 to the suction side of pump 147. Pump 147 discharges the accumulator liquid into pipe 150. A portion of the accumulator liquid, sufficient for reflux, is diverted from pipe 150 through pipe 149 under control of valve 169 to fractionator 137. The balance and usually the major part of the accumulator liquid flowing in pipe 150 flows in whole or in part under control of valves 152 and 154 to pipe 153, and pipe 156 or pipe 151, heat exchanger 133, pipe 155, heat exchanger 131 and pipe 156. The accumulator liquid i.e., C_5 and C_6 hydrocarbons, flows through pipe 156 under control of valve 157 (FIGURE 2$_s$) to effluent main 42.

The 250° to 380° F. heavy naphtha is reformed isothermally as previously described in isothermal reactor 36 (FIGURE 1$_h$) to provide isothermal effluent flowing from reactor 36 through conduit 37 to heat exchanger 31, conduit 38, heat exchanger 29 and conduit 39 to conduit 40 (FIGURE 2$_s$). Since the accumulator liquid usually is under a pressure of less than 15 p.s.i.g., the isothermal effluent usually flows through conduit 40 and pressure reducing valve 41 to effluent main 42. The isothermal effluent and the aforesaid accumulator liquid mix in effluent main 42 to provide a mixture having a temperature within the range of about 600° to about 800° F. The mixture then is contacted with molecular sieve material in sieves 49 or 101 to produce sieve effluent which flows from sieve manifold 53 through conduit 54, exchanger 55, conduit 56, exchanger 57, conduit 58, cooler 59 and conduit 60 to effluent separator 61. In separator 61 the hydrogen and C_1 to C_4 hydrocarbons separate and flow therefrom through conduit 63 to compressor 64 for use as purge gas and reformer

recycle gas. The condensed sieve effluent flows from separator **61** through pipe **62** as gasoline product.

The C_7 and heavier hydrocarbons of the low pressure effluent flow from fractionator **137** (FIGURE 2_f) through pipe **158** to the suction side of pump **159**. Pump **159** discharges the C_7 and heavier low pressure effluent into pipe **160**. The C_7 and heavier low pressure effluent flows through pipe **160** under control of valve **167** (FIGURE 2_s) to pipe **62** to mix with the sieve effluent flowing from separator **61** as stated hereinbefore.

Those skilled in the art will understand that the description provided hereinbefore discloses fractionation of naphtha into light naphtha having an end boiling point of about 250° F. and a heavy naphtha having an initial boiling point not lower than the 90 percent point of the light naphtha and not substantially higher than the end boiling point of the light naphtha. At least a portion of the light naphtha is reformed at a pressure in the range of about 15 to about 300 p.s.i.g. and at least a portion of the so-produced low pressure effluent is treated to separate low octane components of the low pressure effluent from the high octane components thereof.

The heavy naphtha is isothermally reformed at liquid hourly space velocities of at least 30 to produce isothermal effluent. The isothermal effluent is treated to separate the high octane components of the isothermal effluent from the low octane components thereof. The separated low octane components in whole or in part are blended to provide jet fuel having a luminometer number of at least 150 or in whole or in part recycled to the low pressure reforming zone(s).

Since reforming under essentially isothermal conditions results in less naphthene cracking than conventional adiabatic reforming, the yeld of C_6 and heavier reformate is higher. A very economically attractive method for producing high quality jet fuels and contemporaneously producing higher volatility, high octane number gasoline is that described as Embodiment E.

EMBODIMENT E

In that embodiment of the present invention in which the normal paraffins of the 250° to 380° F. fraction of the naphtha are separated therefrom and mixed with a portion of the light naphtha, i.e., boiling range C_6 to 250° F., the flow of liquids and gases is as illustrated in FIGURE 3. Thus, a C_6 to 380° F. fraction comprising normal paraffins and naphthenes is drawn from a source not shown through pipe **170** by pump **171**. Pump **171** discharges the C_6 to 380° F. fraction of naphtha into pipe **172**. The naphtha flows from pump **171** through pipe **172** to fractionator **173**. Intermediate to pump **171** and fractionator **173** the C_6 to 380° F. naphtha is heated in any suitable manner to a temperature at which hydrocarbons having a boiling point at atmospheric pressure not higher than 250° F. are volatile. The heated C_6 to 380° F. naphtha is fractionated in fractionator **173** to provide a C_6 to 250° F. overhead having a luminometer number of about **136** and a bottoms fraction having an initial boiling point not lower than the 90 percent point of the overhead and preferably about 250° F. and an end boiling point substantially the same as that of the highest boiling constituent of the charge to the fractionator and preferably about 380° F. The bottoms fraction flows from fractionator **173** through pipe **175** to the suction side of pump **176**. The bottoms fraction or heavy naphtha, i.e., boiling range about 250° to about 380° F. preferably, is discharged into pipe **177** at a pressure sufficiently in excess of the pressure in isothermal reactor **200** to overcome the pressure drop between pump **176** and isothermal reactor **200**. The heavy naphtha flows through pipe **177** to indirect heat exchanger **178** where the heavy naphtha is in indirect heat transfer relation with the effluent of the isothermal reactor flowing from indirect heat exchanger **180** to conduit **202**. From indirect heat exchanger **178** the heavy naphtha flows through pipe **179** to heat exchanger **180**. In heat exchanger **180** the heavy naphtha is in indirect heat transfer relation with the effluent of isothermal reactor **200** flowing therefrom through conduit **201**. The heavy naphtha flows from heat exchanger **180** through pipe **181** to coil **182** in heater **183** were it is heated to a temperature above the dewpoint thereof at the existing pressure.

The molecular sieves **187** and **188** can be loaded and unloaded in any suitable manner known to those skilled in the art. For the purpose of illustration loading at a temperature above the dewpoint of the highest boiling constituent of the heavy naphtha at the existing pressure and unloading by reducing the pressure has been schematically indicated. Accordingly, the heavy naphtha is heated in heater **183** to a temperature in excess of the dewpoint of the heaviest constituent of the heavy naphtha at the pressure existing in pipe **181**. Usually the heavy naphtha will be heated to a temperature in the range of about 400° to about 600° F. The heated heavy naphtha flows from hater **183** to sieve manifold **184** having branches **185** and **186**. It will be assumed that sieve **187** is unloaded or regenerated and that sieve **188** is loaded or under regeneration. Accordingly, with valve **193** closed and valve **192** open the heated heavy naphtha flows downwardly through sieve **187** in contact with the molecular sieve material having pores of about 4 to 5 Angstroms in diameter. The sieve effluent flows from sieve **187** through pipe **189** (valve **209** closed; valve **194** open) to sieve manifold **191** and thence through pipe **196** to coil **197** in heater **198**. At a point in conduit **196** intermediate to sieve manifold **191** and heater **198** hydrogen-containing gas, after startup, reformer gas flowing from separator **204** to compressor **207** and thence through conduit **208** to conduit **196** is admixed with the sieve effluent. In conduit **196** the hydrogen-containing gas is mixed with the sieve effluent to provide an isothermal charge mixture comprising hydrogen and cyclic hydrocarbons in the mol ratio of about 7 to about 10 mols of hydrogen per mol of cyclic hydrocarbons in the heavy naphtha. The isothermal charge mixture is heated in furnace **198** to a reforming temperature in the range of about 960° to about 1000° F. The isothermal charge mixture flows from heater **198** through conduit **199** to isothermal reactor **200**. The isothermal charge mixture enters reactor **200** at a reforming temperature within the range of 960° to 1000° F. The isothermal charge mixture flows downwardly through isothermal reactor **200** at a liquid hourly space velocity of at least about 15 and as high as 150. The effluent of the isothermal reactor **200**, designated isothermal effluent, flows fro misothermal reactor **200** through conduit **201** to indirect heat exchanger **180**, conduit **202**, indirect heat exchanger **178** and conduit **203** to cooler **254**. In cooler **254** the isothermal effluent is cooled to a temperature at which C_4 and heavier hydrocarbons are condensed at the existing pressure. The uncondensed isothermal effluent comprising hydrogen and C_1 to C_3 hydrocarbons separates from the condensed isothermal effluent comprising C_4 and heavier hydrocarbons in liquid-gas separator **204**.

The hydrogen and C_1 to C_3 hydrocarbons of the isothermal effluent, designated isothermal hydrogen, flows from separator **204** through conduit **206** to compressor **207**. Compressor **207** recompresses the isothermal hydrogen to a pressure in excess of that in conduit **196**. The recompressed isothermal hydrogen flows from compressor **207** through conduit **208** to conduit **196** to mix with the sieve effluent as described hereinbefore. Any isothermal hydrogen in excess of that required to maintain the aforesaid hydrogen to sieve effluent mol ratio is diverted from conduit **206** through conduit **256** under control of valve **253** and conduits **252** and **233** for use in the low pressure reforming unit.

The condensed C_4 and heavier hydrocarbons of the isothermal reformate, designated isothermal condensate,

flow from liquid gas separator 204 through pipe 205 to a stabilizer and high octane blending.

As stated hereinbefore, an overhead comprising C_6 to 250° F. E.B.P. hydrocarbons of the C_6 to 380° F. naphtha flows from fractionator 173 through pipe 174 to pipe 225. A portion of the light naphtha, i.e., C_6 to 250° F. fraction of the feed naphtha flows through pipe 228 to jet fuel storage tank 224. The balance of the light naphtha under control of valve 227 flows through pipe 226 to the suction side of pump 257. Pump 257 discharges the light naphtha into pipe 229 at a pressure in excess of the pressure in low pressure reactor 237. The light naphtha flows through pipe 229 to indirect heat exchanger 230 where the light naphtha is in indirect heat transfer relation with the effluent of low pressure reactor 242 flowing from indirect heat exchanger 232 through conduit 244. From indirect heat exchanger 230 the light naphtha flows through pipe 231 to indirect heat exchanger 232 where the light naphtha is in indirect heat transfer relation with the effluent of low pressure reactor 242 flowing therefrom through conduit 243.

From indirect heat exchanger 232 the light naphtha flows through conduit 233 to coil 234 in heater 235. At a point in conduit 233 intermediate to indirect heat exchanger 232 and heater 235 hydrogen-containing gas, such as reformer gas flowing from high pressure separator 204 through conduits 256 and 252 and low pressure reformer gas flowing from compressor 250 through conduit 251 is mixed with the light naphtha in a proportion to provide a light naphtha charge mixture having a hydrogen to light naphtha mol ratio of about 4 to about 10. The light naphtha charge mixture flows from conduit 233 through coil 234 in heater 235 to conduit 236 and low pressure reactor 237.

The light naphtha charge mixture is heated in furnace 235 to a temperature to provide a vapor temperature at the vapor inlet of low pressure reactor 237 in the range of about 920° to about 980° F.

The light naphtha charge mixture flows downwardly through reactor 237 in contact with particle-form platinum-group metal reforming catalyst. The effluent of low pressure reactor 237 flows through conduit 238 to coil 239 in heater 240 and thence through conduit 241 to low pressure reactor 242. In heater 240 the effluent of low pressure reactor 237, designated first low pressure effluent, is heated to a temperature such that the temperature of the reheated first low pressure effluent entering reactor 242 is the same as, lower than, or higher than, the temperature of the vapors at the inlet to the low pressure reactor 237 and in the range of about 900° to about 1025° F.

The reheated first low pressure effluent flows downwardly through reactor 242 with particle-form platinum group metal reforming catalyst. The effluent of low pressure reactor 242 flows therefrom through conduit 243 to indirect heat exchanger 232, conduit 244, through heat exchanger 230, and conduit 245 to cooler 246.

In cooler 246 the effluent of low pressure reactor 242, designated final low pressure effluent, is cooled to a temperature at which at the existing pressure C_4 and heavier hydrocarbons are condensed. The cooled final low pressure effluent flows from cooler 246 through conduit 247 to liquid gas separator 248. In liquid gas separator 248 the uncondensed portion of the final low pressure effluent, designated low pressure reformer gas, and comprising hydrogen and C_1 to C_3 hydrocarbons separates from the condensed final low pressure effluent. The low pressure reformer gas flows from liquid gas separator 248 through conduit 249 to compressor 250 where the low pressure reformer gas is recompressed to a pressure at least equal to that in conduit 233.

The condensed final low pressure effluent comprising C_4 and heavier hydrocarbons flows from liquid gas separator 248 through pipe 258 to a stabilizer and thence to high octane blending.

As was stated hereinbefore in the description of the treatment of the heavy naphtha it was assumed that sieve 188 was loaded with normal paraffins sorbed from a previous charge of heavy naphtha. The paraffinic sorbate is displaced from the molecular sieve material in 188 in any suitable manner. For the purpose of illustration, displacement of the sorbate is shown as by reducing the pressure. Thus, with valves 193 and 209 closed and valve 210 open the sieve 188 is connected to steam eductor 218. Accordingly, steam is introduced into eductor 218 and flows therefrom through conduit 219 to barometric condenser 220 and condensate pipe 221 thereby reducing the pressure in sieve 188 to a pressure less than atmospheric at which the sorbed normal paraffins of the heavy naphtha are volatilized at the temperature of the sieve. Accordingly, the volatilized normal paraffinic sorbate flows from sieve 188 through pipe 190 (valve 195 closed; valve 210 open) to sieve sorbate manifold branch 212 and sieve sorbate manifold 213. The normal paraffinic sorbate flows through sorbate manifold 213 to cooler 214 where the temperature of the sorbate is reduced to that at which hydrocarbons boiling in the range of 250° to 380° F. at atmospheric pressure are condensed. The condensed sorbate flows from cooler 214 through conduit 215 to liquid gas separator 216. In liquid gas separator 216 constituents of the sorbate boiling below 250° F. flow therefrom through pipe 217 to eductor 218. The condensed 250° to 380° F. hydrocarbons flow from separator 216 through pipe 222 under control of valve 223 to storage tank for jet fuel 224.

Reforming conditions in the low pressure reforming zone(s) and in the isothermal reforming zone are as set forth in Table J.

TABLE J

LOW PRESSURE SECTION

Catalyst	Broad	Preferred
Platinum-group metal, percent by weight.	0.35 to 2.0	0.35 to 0.6.
Halogen, percent by weight	Up to 1.0	Chlorine up to 0.7.
Support, balance	Refractory Oxide.	Alumina.
Pressure, p.s.i.g	15 to 350	100–300.
Temperature, ° F	900 to 1,025	920 to 980.
Liquid Hourly Space Velocity (v./hr./v.).	0.25 to 3	1–2.
Hydrogen-to-light naphtha mol ratio.	Up to 20	4 to 10.

ISOTHERMAL SECTION

Platinum-group metal, percent by weight.	0.35 to 2.0	Platinum, 0.35 to 0.6.
Halogen, percent by weight	Up to 1.0	Up to 0.7.
Support, balance	Refractory Oxide.	Alumina.
Pressure, p.s.i.g	15 to 1,200	500 to 1,200.
Temperature, ° F	930–1,025	960 to 980.
Liquid Hourly Space Velocity (v./hr./v.):		
Isothermal	At least 15	30 to 150.
Adiabatic	0.25–3	1–2.
Hydrogen-to-heavy naphtha mol ratio.	Up to 20	7 to 10.

I claim:

1. A method for producing a jet fuel having a luminometer number of at least about 150 from a hydrocarbon fraction boiling in the range from about C_5 hydrocarbons up to about 450° F. which comprises separating said hydrocarbon fraction at about its 250° F. boiling point into a lower boiling fraction and a higher boiling fraction, separately reforming said lower boiling fraction in the presence of particle-form solid platinum-group metal reforming catalyst at a liquid hourly space velocity below about 5, separately reforming said higher boiling fraction in the presence of particle-form solid platinum-group metal reforming catalyst at a liquid hourly space velocity substantially above about 5, recovering a re-

formate product boiling above about C_5 hydrocarbons from each of said separate reforming steps, separating the thus recovered reformate products into paraffinic and non-paraffinic hydrocarbons, and combining the separated paraffinic hydrocarbons obtained from said reformate products to produce a jet fuel having a luminometer number of at least about 150.

2. The method of claim **1** wherein the reformate products are contacted with molecular sieve material having 4 to 5 Angstrom pores.

3. The method of claim **1** wherein the hydrocarbon fraction boils in the range of C_6 hydrocarbons to about 380° F., wherein the higher boiling fraction is contacted with molecular sieve material having 4 to 5 Angstrom pores, wherein a sieve effluent comprising naphthenes substantially devoid of n-paraffins and a sieve sorbate having a luminometer number in excess of 150 are produced, and wherein said sieve sorbate is mixed with the lower boiling fraction in proportions to produce jet fuel having a luminometer number of at least 150.

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