

Aug. 3, 1965

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3,198,728

METHOD OF IMPROVING FRONT END OCTANE RATING
AND INCREASING "LPG" PRODUCTION

Filed June 20, 1962

3 Sheets-Sheet 1

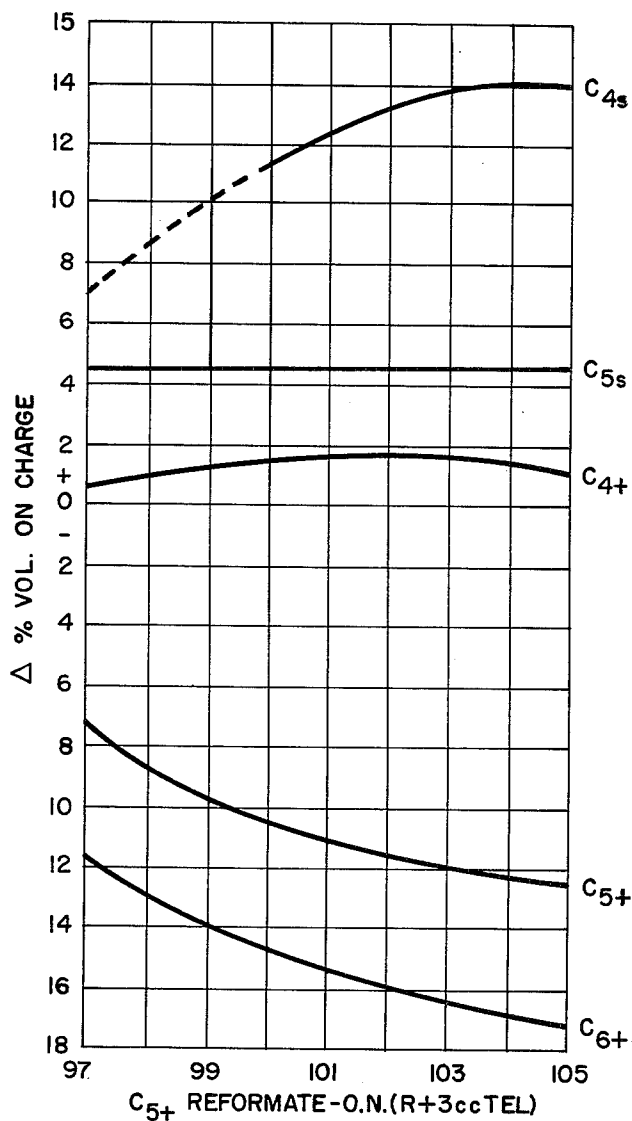


FIGURE 1A

FEED-180° TO 380°F MID-CONTINENT NAPHTHA
PRESSURE - 500 PSIG
VAPOR INLET TEMPERATURE AND LIQUID HOURLY BY
SPACE VELOCITY CORRELATED TO PRODUCE C₅+
REFORMATE OF INDICATED OCTANE RATING.

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3 Sheets-Sheet 2

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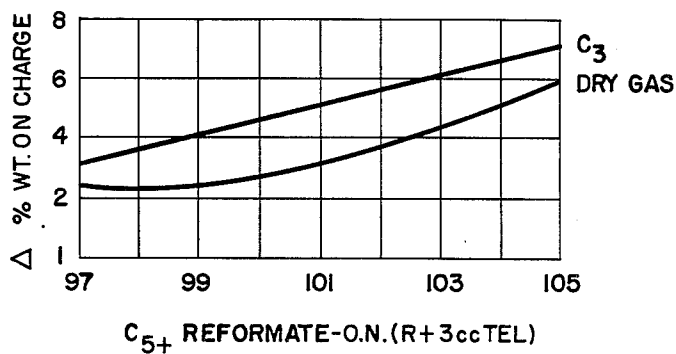


FIGURE 1 B

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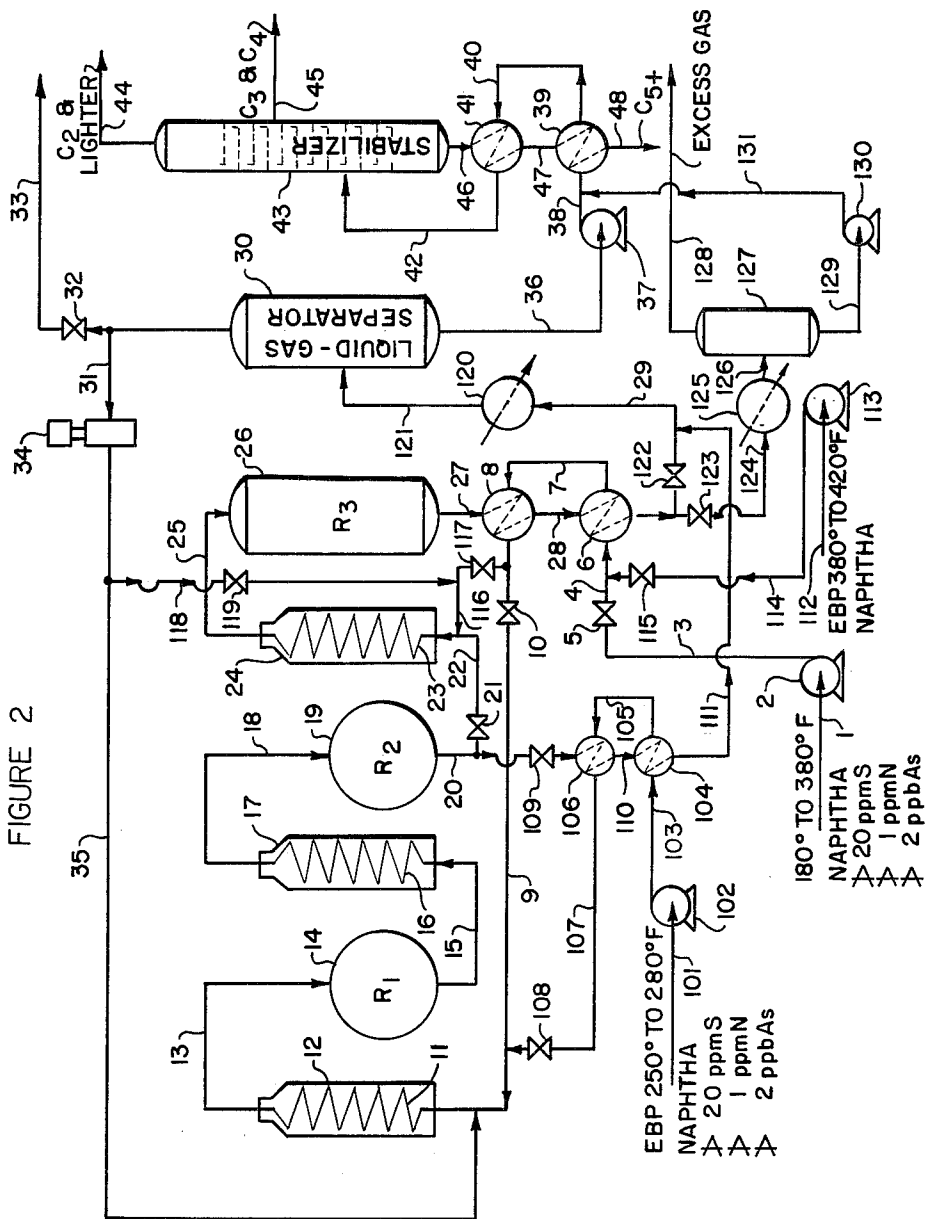
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3 Sheets-Sheet 3



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METHOD OF IMPROVING FRONT END OCTANE
RATING AND INCREASING "LPG" PRODUCTION

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Mobil Oil Company, Inc., a corporation of New York
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The present invention relates to reforming, and more particularly, to reforming naphtha in the presence of platinum-group metal reforming catalyst.

Recently it has been recognized that gasoline produced solely through reforming of naphtha in the presence of particle-form solid platinum group reforming catalyst generally are characterized by excessive road-octane depreciation because of the low octane rating of the reformat front end. That is to say, the C₅ to 220° F. TBP (True Boiling Point) fraction of the reformat has an octane rating lower than the octane rating of the C₅ to 380° F. gasoline. Thus, the C₅ to 220° F. TBP fraction of a C₅ to 380° F. platinum reformat had an octane rating (Research +3 cc. TEL) of 91 whereas the C₅ to 380° F. total reformat had an octane rating (Research +3 cc. TEL) of 100.

Various modifications of the generally practiced method of reforming naphtha to raise the octane rating thereof have been proposed to overcome this disadvantage of "platinum" reforming. For example, it has been proposed to fractionate the straight run naphtha into a light fraction (E.B.P. 220° to 250° F.) and a heavy fraction and to reform the light fraction at more severe reforming conditions than those at which the heavy fraction is reformed. The two reformates are then blended to provide a finished product having the required or target octane. It has also been suggested that the straight run naphtha be fractionated to provide a light fraction having an E.B.P. of 160° F. and comprising C₅ and heavier hydrocarbons, an intermediate fraction comprising hydrocarbons boiling in the range of about 160° to about 320° F., and a heavy fraction comprising hydrocarbons boiling in the range of about 320° to about 380° F. The whole of the intermediate fraction and a portion of the heavy fraction are reformed to obtain a C₅ and heavier reformat having an octane rating higher than the target octane rating. The C₅ and heavier reformates are mixed with the unreformed light fraction and the unreformed

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balance of the heavy fraction to provide a blend having the aforesaid target octane rating. It has also been suggested to fractionate straight run naphtha into a light fraction, C₅ to 250° F., and a heavy fraction, 250° to 380° F. The light fraction is reformed in the presence of platinum at a pressure of 400 p.s.i.g. or less while the heavy fraction is reformed at a pressure of 500 p.s.i.g. or more. The reformates are blended to provide a blend having the target octane rating. These and other manipulations of the basic method of reforming naphtha in the presence of platinum-group metal reforming catalyst have been proposed to overcome the disadvantage of the lower octane rating of the C₅ to 220° F. fraction of platinum reformat and to do so in a manner to provide an improved yield of C₅ and heavier reformat at the target octane rating. However, since all of the methods of raising the octane rating to at least 90 (Research +3 cc.) require concentration of the aromatic hydrocarbons by conversion of the paraffins to hydrocarbons having less than five carbon atoms the yields of salable product has suffered. The method of the present invention, in contrast, provides for raising the octane rating of the C₅ to 220° F. (TBP) fraction of reformat about four octane numbers relative to the octane rating of the C₅ to 220° F. (TBP) fraction of conventionally produced C₅ to 380° F. platinum reformat when the C₅ to 380° F. platinum reformat has an octane rating (Research +3 cc. TEL) of 99 while the volume of salable product, as "L.P.G.," is increased with little change in the volume of C₂ and lighter hydrocarbons. Thus, when producing C₅ and heavier reformat having octane ratings (Research +3 cc. TEL) in the range of 97 to 103 the yield of C₅+ reformat is about 7.2 to about 12.2 percent by volume less than the volume of C₅+ reformat produced in conventional reforming in the presence of platinum-group metal reforming catalyst. On the other hand, the volume of C₄'s is 11 to 14 percent greater than the volume of C₄'s produced in conventional reforming in the presence of platinum-group metal reforming catalyst while the quantity of C₃'s is about 3 to about 7 percent by weight less than the weight of the C₃'s produced when reforming by the method of the present invention. However, the total dry gas produced when reforming in accordance with the present method is only about 2 to about 5 percent by weight greater. The pertinent data as set forth in Table I.

Table I

Catalyst.....	Pt	NiWS	NiWS	Pt	NiWS	NiWS	Pt	NiWS	NiWS	Pt	NiWS	NiWS
Fill Ratio.....	0.2/0.2/1.0	0.53/0.53/1.62		.2/.2/1.0	.53/.53/1.62		.2/.2/1.0	.53/.53/1.62		.2/.2/1.0	.53/.53/1.62	
O.N (R+3 cc.) of—												
C ₅ + reformat.....	97	97	97	100	100	100	103	103	103	105	105	105
C ₄ + reformat, vol. percent of charge.....	91.2	92.0	+0.8	89.2	90.4	+1.2	85.0	86.9	+1.9	81.0	82.6	+1.6
C ₅ + reformat, vol. percent of charge.....	87.4	80.3	-7.1	83.7	73.7	-10.0	77.8	66.2	-11.6	73.0	60.8	-12.2
C ₆ + reformat, vol. percent of charge.....	82.3	70.9	-11.4	77.3	62.8	-14.5	70.4	54.2	-16.2	65.3	48.6	-16.7
Total C ₅ 's, vol. percent of charge.....	5.1	9.4	+4.3	6.4	10.9	+4.5	7.4	12.0	+4.6	7.7	12.2	+4.5
Total C ₄ 's, vol. percent of charge.....	3.8	11.7	+7.9	5.5	16.7	+11.2	7.2	20.7	+13.5	8.0	21.8	+13.8
C ₃ wt. percent of charge.....	3.0	6.2	+3.2	4.2	8.6	+4.4	5.5	11.4	+5.9	6.3	13.4	+7.1
Dry gas, wt. percent of charge.....	6.7	9.0	+2.3	9.2	12.4	+3.2	12.3	16.5	+4.2	14.8	19.9	+5.1

The differences are graphically presented in FIGURES 1A and 1B of the drawings.

Inspection of FIGURES 1A and 1B will establish that the production of C₃'s and C₄'s for L.P.G. (Liquid Petroleum Gas) is from about 10 percent to about 21 percent greater when reforming the 180° to 380° F. fraction of Mid-Continent naphtha by the present method than the production of C₃'s and C₄'s when reforming the 180° to 380° F. fraction of Mid-Continent naphtha by the conventional method.

As used hereinbefore and hereafter "conventional" platinum reforming is used to designate reforming of naphtha in the presence of particle-form solid platinum-group metal reforming catalyst, e.g., comprising 0.35 to about 1.0 percent by weight of platinum and about 0.35 to about 1.0 percent of chlorine on alumina support, at a pressure in the range of 500 to 1200 p.s.i.g., at a vapor inlet temperature in the range of 900° to 1,000° F., at an overall liquid hourly space velocity of about 0.5 to about 2.0 in the presence of hydrogen in the mol ratio of about 6 to about 10 mols of hydrogen per mol of naphtha feed and correlating the activity of the catalyst, the liquid hourly space velocity, and the vapor inlet temperature of the reactors to produce C₃+ reformat having the desired or target octane rating (Research +3 cc. TEL).

In general the present method of producing gasoline having a front end octane, i.e., the octane rating of the C₅ to 220° F. (TBP) fraction, about 3 to 5 octane numbers higher than the front end octane of conventionally reformed naphtha comprises contacting a 180° to 380° F. boiling range naphtha with platinum-group metal reforming catalyst at a pressure of at least 500 p.s.i.g., at a liquid hourly space velocity and reactor(s) vapor inlet temperature(s) dependent upon the dehydrogenating activity of the platinum-group metal reforming catalyst to convert at least a preponderant portion of the naphthenes to aromatics and in a subsequent treatment contacting previously reformed naphtha with catalyst at a pressure of at least about 500 p.s.i.g., at a liquid hourly space velocity and reactor vapor inlet temperature dependent upon the dealkylation and hydrocracking activity of the sulfide catalyst to produce C₃+ reformat having the target octane rating and the aforesaid increased yield of C₃'s and C₄'s. Suitable catalysts for the aforesaid subsequent treatment include catalyst comprising at least one sulfide of nickel and a sulfide of tungsten on a support comprising about 5 to about 15 percent by weight of alumina, about 85 to about 95 percent by weight of silica and the balance substantially water, e.g., comprising about 4 percent by weight of nickel, about 11 percent by weight of tungsten, and about 5 percent by weight of sulfur on a refractory oxide support comprising about 9.7 percent by weight of alumina, about 89.4 percent by weight of silica, about 0.2 percent by weight of chromia, and about 0.7 percent by weight of water. Other illustrative catalyst compositions suitable for the aforesaid subsequent treatment are set forth in the following tabulation:

	I	II	III	IV
SiO ₂ , percent by weight.....	89.4	86.4	82.5	41.7
Al ₂ O ₃ , percent by weight.....	9.7	12.8	16.7	8.9
Cr ₂ O ₃ , percent by weight.....	0.2	0.2	0.2	0.1
BaSO ₄ , percent by weight.....	—	—	—	48.7
H ₂ O, percent by weight.....	0.7	0.6	0.6	0.6
Total.....	100.0	100.0	100.0	100.0

Illustrative of the reaction conditions are the following:

Table II

DEHYDROGENATION STAGE

Catalyst:
0.35 percent by weight of platinum and
0.4 percent by weight of chlorine on Al₂O₃ support

Reaction Conditions	General	Preferred
Pressure, p.s.i.g.....	500 to 1,200	500 to 750
Vapor Inlet Temp. ° F.....	800 to 1,050	850 to 950
Liquid Hourly Space Velocity, V _n /hr./V _c	0.5 to 3.0	1.0 to 2.0
Hydrogen-to-naphtha mol ratio.....	4 to 15	6 to 12

V_n=volume of naphtha; V_c=volume of catalyst.

DEALKYLATION STAGE

Catalyst:
Nickel-Tungsten Sulfide on refractory oxide (Composition supra)

Reaction Conditions	General	Preferred
Pressure, p.s.i.g.....	500 to 1,500	500 to 750
Vapor Inlet Temp. ° F.....	800 to 1,100	850 to 1,000
Liquid Hourly Space Velocity, V _n /hr./V _c	0.5 to 3.0	1.0 to 2.0
Hydrogen-to-naphtha mol ratio.....	4 to 15	6 to 12

Thus, for example, the 180° to 380° F. (TBP) fraction of Mid-Continent naphtha, commonly designated dehexanized naphtha, was contacted with platinum group metal reforming catalyst comprising about 0.6 percent by weight of platinum and about 0.7 percent by weight of chlorine on alumina support at a pressure of 500 p.s.i.g., a hydrogen-to-naphtha mol ratio of 10 to 1, and an overall liquid hourly space velocity of about 1.5 at vapor inlet temperatures to convert about 94 to about 98 percent by volume of the naphthenes to aromatics. The effluent of the dehydrogenation stage was then contacted with the aforesaid nickel-tungsten-sulfur catalyst at a pressure of 500 p.s.i.g., a hydrogen-to-naphtha mol ratio of 10 to 1, and an overall liquid hourly space velocity of about 1.0 at vapor inlet temperature(s) to produce C₃+ reformat of the target octane rating.

It is to be observed that when dehexanized, i.e., 180° to 380° F., Mid-Continent naphtha is dehydrogenated only in a dehydrogenation stage having two dehydrogenation zones under the conditions set forth hereinafter in Table III about 94 percent by volume of the naphthenes in the feed are converted:

Table III

Catalyst:
0.35 percent by weight of platinum and
0.4 percent by weight of chlorine on alumina support.

Reaction Conditions	500 p.s.i.g.	500 p.s.i.g.
Pressure, p.s.i.g.....	500	500
Reaction Zone.....	R ₁	R ₂
Vapor Inlet Temp. ° F.....	980	980
Liquid Hourly Space Velocity, V _n /hr./V _c	15	3
Overall Liquid Hourly Space Velocity, V _n /hr./V _c	2.5	—

Hydrocarbon Class, percent vol.	Feed, 180°-380° F., M-C Naphtha	Raw Reformate	Change in Product Composition
C ₂ to C ₅ Paraffins.....	1.0	9.5	+8.5
C ₆ to C ₁₁ Paraffins.....	46.0	39.0	-7.0
C ₂ to C ₅ Olefins.....	—	0.1	+0.1
C ₆ + Olefins.....	—	1.3	+1.3
C ₆ to C ₁₂ Aromatics.....	7.5	47.4	+39.9
Naphthenes.....	42.5	2.7	-39.8
Others.....	3.0	0.0	-3.0
Total.....	100.0	100.0	—
Octane Rating:			
Research (Clear).....	48.0	—	—
Research (R+3 cc. TEL).....	72.3	97.1	+24.8

When the same dehexanized Mid-Continent naphtha, i.e., the 180° to 380° F. fraction of Mid-Continent naphtha is reformed under the following conditions (Table IV) conversion of the naphthenes is about 95 to 98 percent by volume.

Table IV

Feed:
180° to 380° F. fraction of Mid-Continent naphtha
Catalyst:
0.35 percent by weight of platinum and
0.4 percent by weight of chlorine on alumina support.

Run No.-----	20-158-4			20-158-6		
Reactor No.-----	R ₁	R ₂	R ₃	R ₁	R ₂	R ₃
Barrels of Catalyst Charge/10,000 b./d.-----	27.8	139		27.8	139	
Liquid Hourly Space Velocity, V _n /hr./V _c -----	15	3		15	3	
Overall Liquid Hourly Space Velocity, V _n /hr./V _c -----		2.5			2.5	
Total Bbls. of Catalyst Charged/10,000 b./d.-----		166.8			166.8	
Vapor Inlet Temperature-----	960	960	1,049	980	980	1,070
Octane Rating of C ₇ + Reformate (Research +3 cc. TEL)-----			100.2			103.5
Composition of Raw Reformate, Percent Volume:						
C ₃ and Lighter Paraffins-----			7.6			5.4
C ₃ and Lighter Olefins-----			1.4			2.2
C ₃ and Heavier Paraffins-----			31.5			23.6
C ₃ and Heavier Olefins-----			2.5			1.6
C ₃ and Heavier Aromatics-----			54.8			65.9
Naphthenes-----			2.2			0.8
Others-----			0.0			0.5
Total-----			100.0			100.0
Total C ₃ and Lighter-----			9.0			7.6
Total C ₃ + Naphthenes Converted, Per- cent by Volume-----			42.5-2.2 42.5=95			42.5-0.8 42.5=98

It is to be observed that dehydrogenating the charge naphtha in the presence of the minimum quantity of platinum-group metal reforming catalyst required to convert at least 90 percent of the naphthenes in the feed to aromatics is concomitant with a saving of about \$350,000 in the cost of the catalyst fill for a unit charging 10,000 barrels of naphtha daily. In addition the sale of L.P.G. and gasoline product nets a return substantially equal to that obtained when reforming naphtha of substantially the same composition to substantially the same octane rating employing platinum-group metal reforming catalyst as the sole reforming catalyst.

Accordingly, the present invention provides for contacting naphtha containing not more than innocuous concentrations of sulfur, nitrogen and arsenic in a dehydrogenation stage comprising at least two adiabatic reactors with particle-form solid platinum-group metal reforming catalyst at an overall liquid hourly space velocity in the dehydrogenation stage in the range of about 1.0 to about 3.0, reheating the total effluent of the dehydrogenation stage and contacting the reheated dehydrogenation stage total effluent with non-noble metal catalyst as defined hereinbefore at an overall liquid hourly space velocity of about 1.0 to about 3.0.

The naphtha feed has a composition in the ranges set forth in Table V. The platinum-group reforming catalyst preferably has a composition in the range set forth in Table V. The non-noble metal catalyst preferably has a composition set forth in Table V. The reforming conditions preferably are those set forth in Table V.

Table V

[Feed]

Boiling Range, ° F-----	180-380	250-400
Vol. Percent Paraffins-----	30 to 64	30 to 60
Vol. Percent Naphthenes-----	24 to 60	24 to 60
Vol. Percent Aromatics-----	7 to 12	9 to 15
Vol. Percent Others-----	0 to 2	0 to 2

Dehydrogenating Catalyst:
0.3 to 1.0 percent by weight Platinum
0.01 to 1.0 percent by weight Halogen
Support: Al₂O₃
Hydrothermal Catalyst:
2 to 6 Nickel
5 to 15 Molybdenum
2 to 7 Sulfur
Support: 70-90%:
7 to 14 Al₂O₃
28 to 81 SiO₂
0 to 44 BaSO₄

[Operating Conditions]

Reactor-----	R ₁	R ₂	R ₃
Vapor Inlet Temp. ° F-----	850 to 950	850 to 950	850 to 1,000
LHSV, V _n /hr./V _c -----	5 to 20	1.0 to 5	1.0 to 2
Pressure, p.s.i.g.-----	500 to 750	500 to 750	500 to 750
H ₂ to Naphtha mol Ratio-----	6 to 12	6 to 12	6 to 12
Overall LHSV, V _n /hr./V _{tc} -----	1.0 to 3.0		

V_n/hr./V_c—Volume of hydrocarbon per hour per volume of catalyst in the reactor.

V_n/hr./V_{tc}—Volume of hydrocarbon per hour per volume of catalyst in all reactors.

40 LHSV—Liquid Hourly Space Velocity.

Illustrative of suitable naphtha fraction for treatment in the method of the present invention are naphthas having the characteristics set forth in Table VI.

Table VI

	180° to 380° F. Fraction of Mid-Continent Naphtha	200° to 400° F. Fraction of Middle East Naphtha
50 Distillation, ASTM, ° F.:		
IBP-----	187	220
5% Volume-----	213	236
10% Volume-----	222	240
50% Volume-----	270	286
90% Volume-----	338	352
EBP-----	383	390
55 Bromine No. ASTM-----	0.3	0.3
Sulfur, p.p.m.-----	4	4
Chlorine, p.p.m.-----	2	0.2
Nitrogen, p.p.m.-----	0.2	0.8
Total Paraffins, Vol. Percent-----	47.0	61.2
Total Aromatics, Vol. Percent-----	7.5	11.9
Total Naphthenes, Vol. Percent-----	42.5	26.9
60 Total Others, Vol. Percent-----	3.0	0.0
	100.0	100.0
Octane Ratings Research, Clear-----	48.0	33.2
Research +3 cc. TEL-----	72.3	60.1
Motor, Clear-----	45.0	34.8
65 Motor, +3 cc. TEL-----	72.0	65.5

In general, the naphtha containing innocuous concentrations of sulfur, nitrogen, and arsenic (after hydro-decontamination in the presence of hydrogen and hydro-generating catalyst having capabilities of hydrodesulfurization, hydrodenitrogenation, and hydrodearsensation, if necessary) is contacted with particle-form solid platinum-group metal reforming catalyst in a naphthene dehydrogenation stage comprising one or more reaction zones and then is contacted with non-noble metal or sulfide cata-

lyst comprising sulfide of one or more of the metals, nickel, tungsten, and molybdenum as illustrated in the flowsheet FIGURE 2 of the drawings. On the other hand, the naphtha is fractionated, preferably after hydrodecontamination, to provide a light fraction having an end boiling point in the range of about 250° to 280° F. and a heavy fraction having a 10 percent point not lower than the 90 percent point of the light fraction and an end boiling point in the range of about 380° to about 420° F. The light fraction is contacted with particle-form solid platinum-group metal reforming catalyst to produce C₅+ reformat having an octane rating (Research +3 cc. TEL) in the range of about 94 to about 105 while the heavy fraction is contacted in the presence of hydrogen with non-noble metal catalyst described hereinbefore to produce C₅+ reformat having an octane rating (Research +3 cc. TEL) in the range of about 95 to about 100. The platinum group metal C₅+ reformat from the light fraction in whole or in part is blended with the whole or a part of the non-noble metal C₅+ reformat obtained from the heavy fraction to provide C₅+ blend having the target octane rating (Research +3 cc. TEL) in the range of about 95 to about 104.

Innocuous concentrations of sulfur, nitrogen, and arsenic as used herein are, for sulfur not more than 10 p.p.m.; for nitrogen not more than 1 p.p.m.; for arsenic not more than 2 p.p.b. i.e., 2/10⁹. Preferably the naphtha charged to the reactors containing particle-form solid platinum-group metal reforming catalyst is essentially free 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 C₅+ reformat having an octane rating of at least 100 (Research +3 cc. TEL), the yield of reformat, and the mechanical strength of the catalyst.

The flowsheet FIGURE 2 illustrates alternative embodiments of the present invention. In the preferred embodiment naphtha containing not more than innocuous (as defined herein) concentrations of sulfur, nitrogen and arsenic and having an end boiling point in the range 380° F. to 420° F. is dehydrogenated in the presence of platinum-group metal reforming catalyst and hydrogen (after start up recycle gas containing hydrogen) and hydroreformed in the presence of sulfide catalyst defined hereinbefore. In an alternative embodiment a light fraction having an end boiling point in the range 250° to 280° F. is dehydrogenated in the presence of platinum-group metal reforming catalyst while the heavy fraction having an end boiling point in the range 380° F. to 420° F. is hydroreformed in the presence of the aforesaid sulfide catalyst and hydrogen.

In the preferred embodiment as illustrated in FIGURE 2 the 180° to 380° F. fraction of naphtha containing at least 15 percent by volume of naphthenes is drawn from a source not shown through pipe 1 by pump 2. Pump 2 discharges the feed naphtha into pipe 3 at a pressure greater than the pressure in reactor 14 by at least the pressure drop between pump 2 and reactor 14. The feed naphtha flows through pipe 3 (valve 5 open; valve 115 closed) to pipe 4 and thence to indirect heat exchanger 6 where the feed naphtha is in heat transfer relation with the effluent of reactor 26 flowing from indirect heat exchanger 8 through conduit 28. From indirect heat exchanger 6 the feed naphtha flows through pipe 7 to indirect heat exchanger 8 where the feed naphtha is in heat transfer relation with the effluent of reactor 26 flowing therefrom through conduit 27. From indirect heat exchanger 8 the feed naphtha flows through conduit 9 (valve 10 open; valves 103 and 117 closed) to coil 11 in heater or furnace 12. At a point in conduit 9 intermediate to heater 12 and to heat exchanger 8 hydrogen-con-

taining gas, specifically reformer recycle gas after start-up, flowing from compressor 34 through conduit 35 at a pressure at least equal to that in conduit 9 is admixed with the feed naphtha or charge naphtha to provide a charge mixture having a hydrogen-to-naphtha mol ratio in the range set forth hereinbefore.

In furnace 12 the charge mixture is heated to a reforming temperature to provide at the vapor inlet of reactor 14 of the dehydrogenation stage a vapor inlet reforming temperature in the range set forth hereinbefore. The heated charge mixture flows from furnace 12 through conduit 13 to reactor 14. The heated charge mixture at reforming temperature flows downwardly through reactor 14 in contact with particle-form solid platinum-group metal reforming catalyst to the outlet of reactor 14. The effluent of reactor 14 flows therefrom through conduit 15 to coil 16 in furnace or heater 17. In heater or furnace 17 the first effluent is reheated to provide at the vapor inlet of reactor 19 a reforming temperature the same as, or higher than, or lower than, the vapor inlet temperature of reactor 14. The reheated first effluent flows from furnace 17 through conduit 18 to reactor 19. The reheated first effluent flows downwardly through reactor 19 in contact with particle-form solid platinum-group metal reforming catalyst to the outlet thereof. The effluent of reactor 19, i.e., the second effluent, having a concentration of naphthenes not greater than about 2 percent by volume of the naphthenes present in the feed naphtha to provide a C₅+ reformat having an octane rating (Research +3 cc. TEL) of 104 and not greater than about 10 percent by volume of the naphthenes in the feed naphtha to provide a C₅+ reformat having an octane rating (Research +3 cc. TEL) of 95 flows therefrom through conduits 20 and 22 to coil 23 in furnace or heater 24. (Valve 21 open; valves 109, 117 and 119 closed.) In heater 24 the second effluent is reheated to provide at the vapor inlet of reactor 26 a sulfide-reforming temperature in the range of about 850° to about 1,000° F. From heater 24 the reheated second effluent flows through conduit 25 to reactor 26. In reactor 26 the reheated second effluent flows downwardly in contact with the particle-form solid non-noble sulfide catalyst to the outlet thereof. The final effluent flows from reactor 26 through conduit 27 to indirect heat exchanger 8, conduit 28, indirect heat exchanger 6 and conduit 29 to cooler 120 (valve 122 open, valve 123 closed.) In cooler 120 the final effluent is cooled to a temperature at which at the existing pressure C₃ and heavier hydrocarbons are condensed. The cooled final effluent flows from cooler 120 through conduit 121 to liquid-gas separator 30. In separator 30 the uncondensed final effluent, designated reformer gas, comprising hydrogen, methane and ethane separates from liquid C₃ and heavier hydrocarbons. The reformer gas flows from separator 30 through conduit 31 to compressor 34. A portion of the reformer gas about equal to the gas made in reactors 14, 19 and 26, i.e., the make-gas is diverted through conduit 33 under control of valve 32 to the refinery fuel main, or to recovery or to conversion of the methane and ethane to salable products. The balance of the reformer gas, designated recycle gas, flows through conduit 31 to the suction side of compressor 34. Compressor 34 discharges the recycle gas into conduit 35 at a pressure at least equal to that in conduit 9. The compressed recycle gas flows through conduit 35 to conduit 9 to mix with the feed naphtha to form the charge mixture as previously described.

The condensed final effluent comprising C₃ and heavier hydrocarbons and designated raw reformat flows through pipe 36 to the suction side of pump 37. Pump 37 discharges the raw reformat into pipe 38. The raw reformat flows through pipe 38 to indirect heat exchanger 39 where the raw reformat is in heat transfer relation with the bottoms, i.e., C₅+ reformat, of stabilizer 43 flowing from indirect heat exchanger 41 through pipe 47. From indirect heat exchanger 39 the raw

reformat flows through pipe 40 to indirect heat exchanger 41 where the raw reformat is in heat transfer relation with the C_5+ reformat flowing from stabilizer 43 through pipe 46. From indirect heat exchanger 41 the raw reformat flows through pipe 42 to stabilizer 43.

In stabilizer 43 a temperature is maintained at which C_4 and lighter hydrocarbons are volatile. Accordingly, an overhead comprising ethane and lighter hydrocarbons is taken through pipe 44 with suitable reflux (not shown), a side stream comprising C_3 and C_4 hydrocarbons is taken through pipe 45, and a bottoms comprising C_5 and heavier hydrocarbons flows from stabilizer 43 through pipe 46, indirect heat exchanger 41, pipe 47, indirect heat exchanger 39 and pipe 48 to storage, the addition of additives, blending and distribution.

Those skilled in the art will recognize that the single stabilizer of FIGURE 2 there can be employed a de-ethanizer, a de-propanizer, a de-butanizer and a de-pentanizer.

For the dehydrogenation of light naphtha, having an end boiling point in the range of 250° to 280° F., in the presence of hydrogen and particle-form solid platinum-group metal reforming catalyst and reforming of heavy naphtha, having an end boiling point in the range 380° to 420° F. in the presence of sulfide reforming catalyst the flow of liquids and gases is also illustrated in FIGURE 2. Thus, a light naphtha having an end boiling point in the range of 250° to 280° F. and containing not more than innocuous concentrations of sulfur, nitrogen and arsenic flows from a source not shown through pipe 101 to the suction side of pump 102. Pump 102 discharges the light fraction into pipe 103 at a pressure greater than the pressure in reactor 14. The light fraction flows through pipe 103 to indirect heat exchanger 104 where the light fraction is in heat transfer relation with the effluent of reactor 19 designated platinum reaction products, flowing from reactor 19 through conduit 20 (valve 21 closed; valve 109 open), indirect heat exchanger 106 and conduit 110 to indirect heat exchanger 104. From heat exchanger 104 the light fraction flows through pipe 105 to indirect heat exchanger 106 where the light fraction is in heat transfer relation with the platinum reaction products flowing from reactor 19 through conduit 20 (valve 109 open; valve 21 closed). From indirect heat exchanger 106 the light fraction flows through pipe 107 to conduit 9 (valve 108 open; valve 10 closed). In conduit 9 the light fraction is mixed with hydrogen-containing recycle gas (after start-up) flowing from compressor 34 through conduit 35 to form a light charge mixture. In furnace 12 the light charge mixture is heated to provide a vapor inlet reforming temperature at the vapor inlet of reactor 14 in the range set forth hereinbefore. The light charge mixture flows downwardly through reactor 14 in contact with particle-form solid platinum-group metal reforming catalyst. The effluent of reactor 14, designated first light effluent, flows from reactor 14 through conduit 15 to coil 16 in heater 17.

In heater 17 the first light effluent is reheated to a temperature to provide at the vapor inlet of reactor 19 a reforming temperature the same as, higher than, or lower than the vapor inlet temperature at reactor 14. The reheated first light effluent flows from furnace 17 through conduit 18 to reactor 19. In reactor 19 the reheated first light effluent flows downwardly in contact with particle-form solid platinum-group metal reforming catalyst. The effluent from reactor 19, designated final light effluent, flows from reactor 19 through conduit 20 (valve 21 closed; valve 109 open) to indirect heat exchanger 106, conduit 110, indirect heat exchanger 104 and conduit 111 to conduit 29 (valve 122 closed). The final light effluent flows through conduit 29 to cooler 120. In cooler 120 the final light effluent is cooled to a temperature at which C_3 and heavier hydrocarbons are condensed at the existing pressure. The cooled final light effluent flows from cooler 120 through conduit 121 to liquid gas separator 30.

In separator 30 the uncondensed final effluent comprising hydrogen, methane and ethane and designated reformer gas separates from the condensed final effluent designated raw light reformat. The reformer gas flows from separator 30 through conduit 31 to compressor 34 in amount sufficient to supply the requirements for hydrogen in reforming the light fraction in reactors 14 and 19 and the requirements for hydrogen in reactor 26. The balance of the reformer gas is diverted through conduit 33 under control of valve 32 to means for recovery of hydrogen and/or conversion of methane and ethane to other products, e.g., methane to acetylene and ethane to ethylene.

The raw light reformat flows from separator 30 through pipe 36 to the suction side of pump 37. Pump 37 discharges the raw light reformat into pipe 38. In pipe 38 the raw light reformat is mixed with the raw heavy reformat flowing from pump 130 through pipe 131. (Since from this point in the illustrative flow the flow of light raw reformat, admixed with heavy raw reformat, designated mixed raw reformat, is the same, the description of the illustrative flow of the heavy fraction, i.e., the fraction having an EBP in the range of about 380° to about 420° F. and the reaction products obtained therefrom will be described.)

The heavy fraction, i.e., the fraction having an end boiling point (EBP) in the range of about 380° to about 420° F. and an initial boiling point (IBP) not lower than about the 90 percent point of the light fraction of naphtha flows from a source not shown through pipe 112 to the suction side of pump 113. Pump 113 discharges the heavy fraction into pipe 114 (valve 115 open; valve 5 closed) at a pressure in excess of that in reactor 26. The heavy fraction flows through pipe 114 to pipe 4 and thence to indirect heat exchanger 6. In indirect heat exchanger 6 the heavy fraction is in heat transfer relation with heavy effluent flowing from indirect heat exchanger 8 through conduit 28. From indirect heat exchanger 6 the heavy fraction flows through pipe 7 to indirect heat exchanger 8 where the heavy fraction is in heat transfer relation with the heavy effluent flowing from reactor 26 through conduit 27. From indirect heat exchanger 8 the heavy fraction flows through conduit 9 (valve 10 closed; valve 117 open) to conduit 116 and thence to conduit 22 (valve 21 closed). At a point in conduit 116 intermediate to valve 117 and conduit 22, hydrogen-containing gas (reformer recycle gas after start-up) flowing from compressor 34 through conduits 35 and 118 under control of valve 119 is admixed with the heavy fraction to provide a heavy charge mixture containing hydrogen and naphtha in the range of mol ratios set forth hereinbefore, i.e., 6 to 12. The heavy charge mixture flows through conduit 116 to conduit 22 and thence to coil 23 in furnace or heater 24. In heater 24 the heavy charge mixture is heated to a temperature to provide at the vapor inlet of reactor 26 a reforming temperature in the range of about 850° F. to about 1,000° F.

The heavy charge mixture flows downwardly through reactor 26 in contact with sulfide catalyst described hereinbefore. The effluent of reactor 26, designated heavy effluent as stated hereinbefore, flows from reactor 26 through conduit 27, indirect heat exchanger 8, conduit 28 and indirect heat exchanger 6, and conduits 29 and 124 (valve 122 closed; valve 123 open) to cooler 125.

In cooler 125 the heavy effluent is cooled to a temperature at which C_3 and heavier hydrocarbons are condensed at the existing pressure. The cooled heavy effluent flows from cooler 125 through conduit 126 to gas-liquid separator 127.

In separator 127 the uncondensed heavy effluent comprising hydrogen, methane and ethane separates from the condensed heavy effluent comprising C_3 and heavier hydrocarbons. The uncondensed heavy effluent, designated excess gas flows from separator 127 through conduit 128 to means for the recovery of hydrogen, to the

refinery fuel main, to means for converting methane to acetylene and ethane to ethylene for example, or to other uses for which gas of this composition is suitable.

The condensed heavy effluent, designated raw heavy reformat, comprising C₃ and heavier hydrocarbons flows from separator 127 through pipe 129 to the suction side of pump 130. Pump 130 discharges the raw heavy reformat into pipe 131 through which the heavy reformat flows to pipe 38 for admixture with raw light reformat. The mixture of raw light reformat and raw heavy reformat comprising C₃ and heavier hydrocarbons designated mixed raw reformat, flows through pipe 38 to indirect heat exchanger 39 where the mixed raw reformat is in heat transfer relation with the bottoms, C₅+ reformat, flowing from indirect heat exchanger 41 through pipe 47. From indirect heat exchanger 39 the raw reformat flows through pipe 40 to indirect heat exchanger 41 where the mixed raw reformat is in heat transfer relation with the bottoms of stabilizer 43 flowing therefrom through pipe 46. From indirect heat exchanger 41 the raw reformat flows through pipe 42 to stabilizer 43. (Those skilled in the art are cognizant of the fact that the stabilization of the raw reformat can be carried out in one or in a plurality of fractionating columns.)

In stabilizer 43 ethane and lighter hydrocarbons are taken overhead (with suitable reflux not shown) through conduit 44 to the refinery fuel main, recovery of the hydrocarbons or conversion of the hydrocarbons into saleable products. A C₃ and C₄ fraction is taken (with suitable reflux not shown) as a side stream through pipe 45 to storage as "L.P.G." product, recovery as separate hydrocarbons, to conversion to other hydrocarbons, for example, propane to propylene, butane to butylene, and the like.

The bottoms product comprising C₅ and heavier hydrocarbons flows from stabilizer 43 through pipe 46, indirect heat exchanger 41, pipe 47, indirect heat exchanger 39 and pipe 48 to storage, blending, addition of additives, and/or distribution.

Those skilled in the art will recognize that when the treatment in the second stage is in the presence of sulfide catalyst as defined herein not only is there a capital saving of about \$350,000 for the reforming of 10,000 barrels of naphtha per day but in addition there is the increased production of L.P.G. which in some refineries provides increased revenue of about \$1,350 per day per 10,000 barrels of naphtha reformed.

As used herein "overall" liquid hourly space velocity is the ratio of the volume of hydrocarbon mixture contacted per hour with the total catalyst in any stage or the total catalyst in both stages as is evident from the context.

I claim:

1. A method of reforming naphtha containing naphthenes and paraffins which comprises in a first and dehydrogenation stage contacting dehexanized charge naphtha comprising naphthenes and paraffins having an IBP in the range of about 180° F. to about 200° F. and an EBP in the range of 380° F. to 420° F. in the presence of hydrogen with platinum-group metal reforming catalyst at naphthene-dehydrogenating conditions of vapor inlet temperature in the range of about 800° to about 1,050° F., of pressure in the range of about 500 to about 1,200 p.s.i.g., and of liquid hourly space velocity of at least about 0.5, obtaining dehydrogenation stage reaction products comprising hydrogen and C₁ and heavier hydrocarbons, the C₅ and heavier portion of the aforesaid C₁ and heavier hydrocarbons containing not more than about two to about ten percent of the naphthenes of the aforesaid dehexanized charge naphtha, in a second stage contacting substantially all of the aforesaid dehydrogenation stage reaction products with non-noble metal sulfide catalyst at a pressure in the range of about 500 to about 1,500 p.s.i.g., at a vapor inlet temperature in the range of about 800° to about 1,100° F., and at a liquid hourly

space velocity of at least 0.5, and recovering (1) reformer gas comprising hydrogen, (2) liquid petroleum gas comprising C₃ and C₄ hydrocarbons and (3) C₅ and heavier hydrocarbons having an octane rating at least 15 octane units higher than the octane rating (Research+3 cc. TEL) of said dehexanized charge naphtha of which C₅ and heavier hydrocarbons the C₅ to 220° F. (TBP) fraction has an octane rating about four octane numbers higher than the octane rating (Research+3 cc. TEL) of the C₅ to 220° F. (TBP) fraction of conventionally produced C₅ to 380° F. platinum reformat.

2. The method set forth in claim 1 wherein the non-noble metal sulfide catalyst is nickel-tungsten sulfide catalyst.

3. A method of reforming naphtha containing naphthenes and paraffins which comprises in a first and dehydrogenation stage contacting first naphtha having an end boiling point in the range of about 250° to about 280° F. in the presence of hydrogen with platinum-group metal reforming catalyst at naphthene-dehydrogenating conditions of vapor inlet temperature in the range of about 800° to about 1,050° F., of pressure in the range of about 500 to about 1,200 p.s.i.g., and the liquid hourly space velocity of at least about 0.5, obtaining dehydrogenation stage reaction products comprising hydrogen and C₁ and heavier hydrocarbons, the C₅ and heavier portion of the aforesaid C₁ and heavier hydrocarbons containing not more than about two to about ten percent of the naphthenes of the aforesaid first naphtha, separating said dehydrogenation stage reaction products into (1) reformer gas comprising hydrogen and (2) light reformat comprising C₃ and heavier hydrocarbons, in a second stage contacting second naphtha comprising naphthenes and paraffins having an IBP not lower than about the 90 percent point of said first naphtha and an EBP in the range of about 380° to about 420° F. with non-noble metal sulfide catalyst in the presence of hydrogen at a pressure in the range of about 500 to about 1,500 p.s.i.g., at a temperature in the range of about 800° to about 1,100° F., and at a liquid hourly space velocity of at least 0.5, obtaining second stage reaction products comprising hydrogen, and C₁ and heavier hydrocarbons, separating said second stage reaction products into (1) reformat and said heavy reformat to obtain mixed reformat comprising C₃ and heavier hydrocarbons, mixing said light reformat and said heavy reformat to obtain mixed reformat, separating said mixed reformat into (1) liquid petroleum gas comprising C₃ and C₄ hydrocarbons and (2) stabilized reformat comprising C₅ and heavier hydrocarbons, of said stabilized reformat the C₅ to 220° F. (TBP) fraction having an octane rating about four octane numbers higher than the octane rating (Research+3 cc. TEL) of the C₅ to 220° F. (TBP) fraction of conventionally produced C₅ to 380° F. platinum reformat.

4. The method set forth in claim 3 wherein the non-noble metal sulfide catalyst is nickel-tungsten sulfide catalyst.

5. The method set forth in claim 3 wherein the liquid hourly space velocity in the dehydrogenation stage is about 2.0 to about 4.0.

6. The method set forth in claim 1 wherein the dehydrogenation stage comprises at least two reaction zones, and wherein the liquid hourly space velocity in the first of said reaction zones in which the dehydrogenation of naphthenes occurs is in the range of about 10 to about 20 and the overall liquid hourly space velocity for the hydrogenation stage is in the range of about 2.0 to about 5.0.

7. The method set forth in claim 6 wherein the liquid hourly space velocity in the second stage is in the range of about 1.0 to about 3.0.

8. The method set forth in claim 6 wherein the second stage is charged with nickel-tungsten sulfide catalyst, and wherein the overall liquid hourly space velocity for the

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dehydrogenation stage and the second stage is in the range of about 1.0 to about 3.0.

9. The method set forth in claim 8 wherein the dehydrogenation stage comprises at least two reaction zones, wherein the liquid hourly space velocity in the first of said reaction zones is in the range of about 15, and wherein the overall liquid hourly space velocity for the dehydrogenation stage and the second stage is in the range of about 1.0 to about 3.0.

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References Cited by the Examiner

UNITED STATES PATENTS

2,758,062	8/56	Arundale et al.	208—65
2,909,477	10/59	Muller	208—65
2,944,005	7/60	Scott	208—109
3,017,344	1/62	Woodle	208—65
3,037,930	6/62	Mason	208—112

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,198,728

August 3, 1965

Louis P. Evans

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 13, for "94" read -- 95 --; column 12, lines 43 and 44, for "(1) reformat and said heavy reformat to obtain mixed" read -- (1) reformer gas comprising hydrogen and (2) heavy --; lines 66 and 67, for "hydrogenation" read -- dehydrogenation --.

Signed and sealed this 18th day of January 1966.

(SEAL)

Attest:

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