Dec. 1, 1959 C. E. SLYNGSTAD ET AL 2,915,458

REFORMING PROCESS WITH A PLATINUM CONTAINING CATALYST WITH TEMPERATURE REGULATION OF THE CATALYST BED

Filed May 18, 1954

FIG. 1

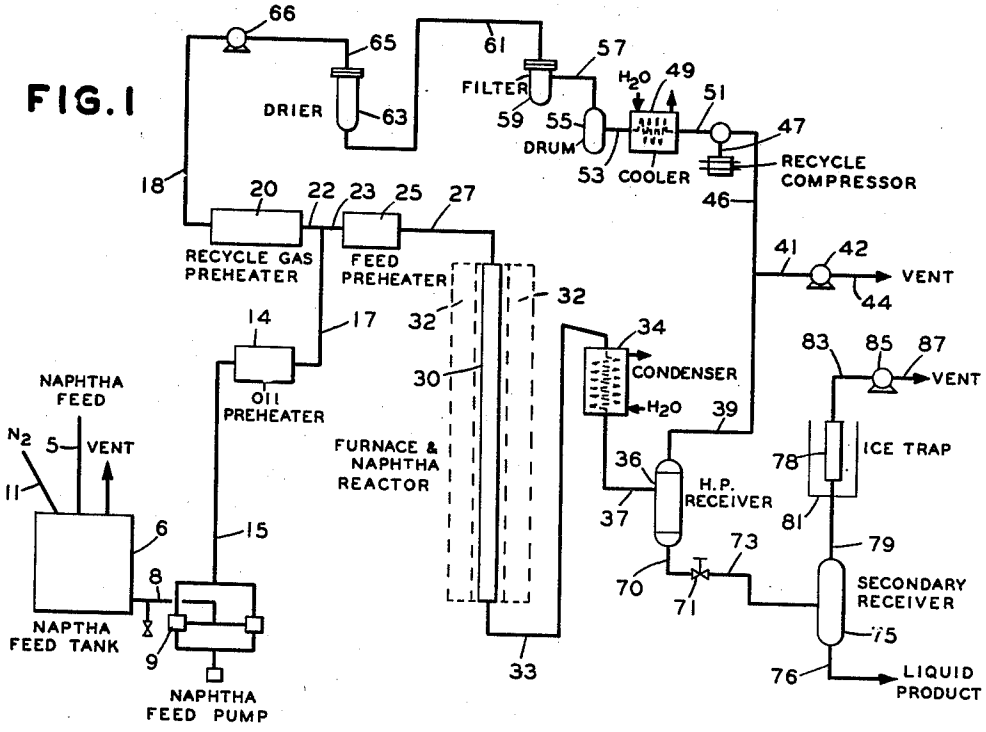
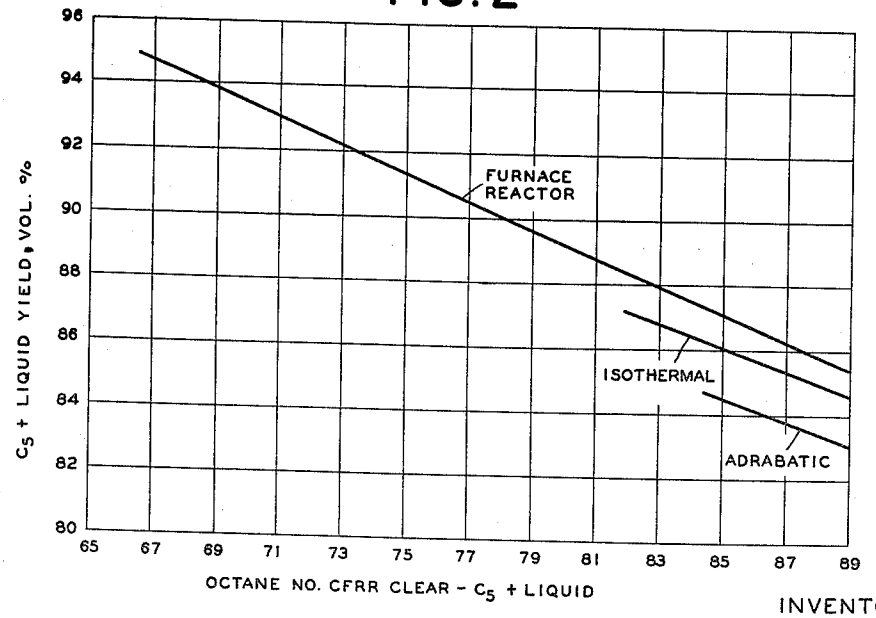


FIG. 2



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United States Patent Office 2,915,458 Patented Dec. 1, 1959

2,915,458

REFORMING PROCESS WITH A PLATINUM CONTAINING CATALYST WITH TEMPERATURE REGULATION OF THE CATALYST BED

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Application May 18, 1954, Serial No. 430,592

12 Claims. (Cl. 208—138)

This invention relates to an improved reforming process for light hydrocarbon oils, and more particularly, it pertains to a reforming process whereby a significantly high yield of high octane quality gasoline product is produced with a substantial reduction in catalyst requirements than previously known methods of operation.

Two main systems for reforming naphthas are being investigated and/or commercialized at present, and these involve isothermal or adiabatic methods of operation. The isothermal operation is better than the adiabatic method from the standpoint of liquid product yield at a given octane number, however, the adiabatic technique is being commercialized for economical reasons. Both of these methods of operation appear to be satisfactory for the intended purpose, however, it is proposed by means of this invention to provide means for obtaining greater yields of reformed liquid product than these methods.

It is an object of this invention to provide an improved reforming process.

Another object of this invention is to provide a reforming process whereby the higher liquid product yields are obtained than heretofore known processes.

Still another object of this invention is to provide a method of reforming light hydrocarbon oils whereby a substantial saving in catalyst requirements is effected to accomplish a given result.

Other objects and advantages of this invention will become apparent from the following description and explanation thereof.

By means of this invention, a method of reforming a light hydrocarbon oil is proposed involving the steps comprising the passage of said oil feed at a temperature below the point of substantial thermal cracking to a heated zone containing a reforming catalyst under suitable reforming conditions including the presence of added hydrogen such that the resultant reaction product discharging from said zone is at a greater temperature than the inlet temperature of said oil feed thereto.

An essential part of the present invention resides in having a suitable reforming catalyst present in a heated zone such that heat is continuously supplied thereto at a rate sufficient to effect a temperature rise in the reactor effluent or reaction product over the inlet temperature of the feed. The heated zone can consist of various means for accomplishing this result, for example, a direct or indirectly fired furnace, a heat exchanger, etc. The rate of heat input to the catalyst bed in the heated zone can result in an initial drop in temperature, an isothermal effect, or a gradual rise in temperature throughout this initial portion of catalyst. This temperature pattern can exist in the region of up to about 50% by volume of the total catalyst in the heated zone. In this initial portion of catalyst the main reaction taking place is dehydrogenation, and it is highly endothermic in comparison with the other reforming reactions. In the preferred instance, the average temperature of the initial portion of catalyst will be either at the same or a lower level than the inlet temperature, because greater heat inputs may tend to deactivate the catalyst by reason that it may be necessary to maintain the metal equipment in contact with the catalyst at an undesirably high temperature for this purpose. A

temperature rise over the initial portion of the catalyst can be obtained in the case of processing a highly paraffinic feed, or one lean in naphthenes. The portion of catalyst having the temperature characteristic described above is primarily used in converting C_6 ring naphthenes to aromatics. This reaction tends to take place readily, consequently, the average temperature in the initial portion of the bed can be about 700° to 900° F., preferably, about 775° to 850° F. Lower temperatures make the task of supplying heat to the catalyst zone easier, and also there is less danger of deactivating the catalyst by reason thereof. In the case of the equipment being used to heat the catalyst, the metal surface in contact with the catalyst during the initial phase of the reaction or portion of catalyst should be maintained at about 850° to 1050° F., preferably, about 925° to 975° F. The volume of catalyst used for the dehydrogenation of C_6 ring naphthenes is not greater than about 50% of the total catalyst in the heated zone. Larger volumes of catalyst appear not to provide any advantage insofar as catalyst utilization is concerned.

Following the easily effected dehydrogenation reactions in the initial portion of heated catalyst, the temperature is permitted to increase to a level which is more favorable for the more difficult dehydrocyclization reactions. The reactions of next importance which occur in the heated zone are dehydrocyclization and isomerization. The C_5 ring naphthenes are converted to aromatics, the acyclic hydrocarbons or straight chain compounds are dehydrocyclized to produce aromatics and the straight chain compounds are isomerized to higher octane quality acyclic compounds. The temperature at which the aromatic producing reactions occur is substantially higher than the temperature used for dehydrogenation or isomerization. Following the passage of reactant material through the initial portion of heated catalyst, the temperature of the catalyst is increased until the final temperature of the outgoing reactant is greater than the inlet temperature. The average temperature in the second or final portion of catalyst in the heated zone is about 20 to 150° F., preferably, about 50° to 100° F. greater than the average temperature of the initial catalyst bed. This average temperature is about 850° to 930° F., preferably, about 875° to 925° F. The rate of heat input to this portion of catalyst can be gradual or rapid depending on how effectively this end can be achieved without damage to the catalyst. In view of catalyst deactivation, it is preferred to supply heat gradually to the second portion of catalyst.

The average temperature as intended herein is determined by employing the arithmetic average just so long as the temperature of the catalyst does not fall below the inlet temperature of the oil feed. Where any portion of the catalyst in the heated zone falls below the inlet temperature of the oil feed, the integrated average is employed for the temperature range falling below the oil feed inlet temperature.

In general, it is also important to charge the light hydrocarbon oil feed to the heated catalyst zone at a temperature which is not conducive to thermal cracking. Thermal cracking causes lower liquid product yield, higher normally gaseous material and coke yields, and lower octane quality. Generally, the inlet temperature is below the point at which substantial thermal cracking takes place. This temperature falls in the range of about 600° to 900° F., preferably, about 750° to 850° F. Substantial thermal cracking is the production of at least 0.5% by weight of dry gas, basis feed, which is produced in the absence of catalyst, more usually 1–5%, on the same basis. Dry gas consists of hydrocarbons containing one to three carbon atoms. Adverse thermal cracking effects represent an additional reason for maintaining

a relatively low average catalyst temperature in either or both of the catalyst portions in the heated zone. The oil reactant should be brought into contact with the catalyst at a temperature which induces primarily the desired catalytic reaction with as little thermal cracking as possible. The temperature of the resultant reaction product leaving the heated zone is about 875° to 975° F., preferably, about 900° to 950° F. The outlet temperature of the treated product is about 25° to 200° F., preferably, about 60 to 150° F., greater than the inlet temperature. By maintaining an average catalyst temperature in the heated zone which is relatively low, the overall effect is to contact the oil reactant with catalyst under conditions resulting in substantially less thermal cracking and/or hydrocracking than an isothermal or adiabatic system. Consequently, in general, the oil reactant is treated in the heated zone at an overall average temperature of about 825° to 900° F., preferably, about 850° to 880° F. Consequently, in a heated zone, the temperature is regulated or controlled to provide optimum temperatures for effecting the desired reactions, and the overall average temperature is less than is used in other systems thus resulting in less thermal cracking effects. It is also preferred in the present invention that the reactant material to be processed in the heated zone be heated such that little or no thermal cracking effects take place prior to the reactant coming into contact with the catalyst. Accordingly, the adverse thermal cracking effects defined above as being substantial, i.e., at least 0.8% by weight of dry gas, basis feed, is produced, covers the total dry gas produced including that produced in heating the reactant to the desired temperature for passage to the heated zone as well as any which is formed in the heated zone as a result of thermal cracking.

The other reaction conditions in the heated catalyst zone can be maintained within suitable levels for reforming. In the case of a non-regenerative system, the pressure is maintained at least about 350 p.s.i.g., more usually, about 500 to 1000 p.s.i.g., at a hydrogen rate of at least about 1500 standard cubic feet, 60° F. and 760 mm. Hg, per barrel of oil feed, abbreviated as s.c.f.b., more usually, about 3500 to about 15,000 s.c.f.b. The weight space velocity, $W_o/hr./W_c$, varies from about 1 to about 15, more usually, about 2 to 12. A non-regenerative system is one which can be operated for at least 1500–2000 hours before regeneration, anything less is a regenerative process. In a regenerative system, the total pressure is at least about 50 p.s.i.g. to about 500 p.s.i.g., at a hydrogen rate of about 1000 to about 7500 s.c.f.b. The weight space velocity varies from about 0.5 to about 12, more usually, about 1.5 to about 6. In general, for either type of system, reforming is effected at a pressure of 50 to about 1000 p.s.i.g., a weight space velocity of about 0.5 to about 15, and a hydrogen rate of about 1000 to about 15,000 s.c.f.b.

The product material leaving the heated zone is at a temperature of about 875° to about 975° F. Ordinarily, this product material can have an octane number of at least about 60 CFRR clear. In the event that the reactant is treated further it is preferred that the octane number of the product leaving the heated zone be maintained at about 60 to about 85 CFRR, clear, because unusually severe conditions in the heated zone can result in rapid deactivation of the catalyst. Consequently, it is preferred that in the present invention, a second reactor be employed for the purpose of increasing the octane number of the reformed product to a level in the range of about 85 to about 110 CFRR clear. For this purpose, it is proposed by means of this invention to employ a second reactor operated under adiabatic conditions for the purpose of improving the octane quality of the product to a high level. In the practice of this invention, it is preferred that the heated zone contain about 5 to about 50% by weight of the total catalytic material employed in the complete or whole operation, preferably, about 15 to about 35% by weight, on the same basis. The adiabatic reactor contains the remainder of the catalytic material and it is operated at an average temperature of about 900° to about 950° F. In the event that the temperature at which the reaction product leaves the heated zone is not sufficient for optimum performance in the adiabatic zone, it is contemplated reheating the reaction product prior to charging the same to the adiabatic zone. The pressure of the adiabatic operation can vary within the same range as given above in connection with the operation of the heated zone. Generally, the pressure is maintained at about 50 to about 1000 p.s.i.g. and it can be varied to provide a regenerative or non-regenerative operation much in the same manner as discussed above in connection with the heated zone. The weight space velocity falls in the range of about 0.5 to about 15, more usually, about 1 to about 10. The hydrogen rate is about 1000 to about 15,000 s.c.f.b., more usually, about 1500 to about 7500 s.c.f.b. One method of operation involves employing conditions conducive to non-regenerative operations in the heated zone followed by a regenerative type of operation in the adiabatic zone in order to produce an unusually high octane quality product, e.g., at least 90 CFRR clear. Accordingly, the adiabatic reactor will be "shifted" with another adiabatic reaction in order that the operation is continuous. The regeneration of the catalyst can take place when there has been deposited thereon 2 to about 15% by weight of carbon and this regeneration is effected by the passage of an oxygen containing gas, e.g., air, oxygen or a diluted air stream containing about 0.5 to about 10% by volume of oxygen. The temperature of regeneration is maintained at about 500° to about 1050° F., and at a pressure of about 1 atmosphere to about 1000 p.s.i.g. The catalyst can be subjected to a mild regeneration treatment in which all of the carbonaceous material is removed from the catalyst under conditions tending to contact the catalyst with a minimum amount of water at the lowest temperature possible. The ideal condition is to remove essentially all of the water from the regeneration gas being supplied to the catalyst zone. Following the mild treatment of the catalyst for the removal of carbonaceous material, it is then treated under more severe conditions involving the use of a regeneration gas containing an oxygen partial pressure of about 5 to about 200 p.s.i.a., more usually, about 14.7 to about 100 p.s.i.a. This severe treatment is conducted at a temperature of about 850° to about 1050° F. and for a period of about 0.25 to about 30 hours, more usually, about 1 to about 8 hours.

Another method of operating the present invention is to employ either an isothermal reactor or a second catalyst heated zone following the initial heated zone or reactor. The second isothermal reactor or heated reactor can be operated under regenerative or non-regenerative operations, using the conditions specified hereinabove for regenerative and non-regenerative operations. In view of the high cost of operating an isothermal reactor, it is preferred, however, that the second reaction zone be operated adiabatically in the manner described hereinabove.

The feed material to be processed in accordance with this invention is a light hydrocarbon oil, e.g., gasoline, naphtha and/or kerosene. The light hydrocarbon oil contains an initial boiling point of about 70° to about 275° F. and an end point of about 300° to about 485° F. The feed material can be derived from a cracking operation, either thermal or catalytic, a straight run operation or it can be a combination of both types of feed material. In any event, the feed contains an olefin concentration range from about 0 to about 50 mol percent and an octane number ranging from about 0 to about 75 CFRR clear. The invention can be practiced using a feed material of varying paraffinic and naphthenic content. A method of designating the paraffinicity of a hydrocarbon

oil is the Watson characterization factor, and in this instance, the feed material can have a Watson characterization factor of about 11.0 to about 12.2. The sulfur concentration can vary over a wide range, for example, from about 0.01 to about 2% by weight of sulfur, however, in the case of a sulfur sensitive catalyst, it is preferred that the sulfur concentration be kept at a minimum in order to avoid the deactivating effects caused thereby. Since the catalytic material in the heated zone will be in close proximity to metal surfaces, any sulfur material present on such surfaces will tend to corrode the metal and then later evolve as sulfur compounds, e.g., SO_2, SO_3, during regeneration, and these have a serious deactivating effect upon sulfur sensitive reforming catalysts. This is particularly true in the case of the noble metals. Accordingly, it is preferred that the feed material contain a sulfur concentration of not more than about 0.01% by weight.

The catalytic material to be used in the heated zone for the purpose of this invention comprises any suitable reforming agent which is known to have hydrogenation and dehydrogenation properties or it has the ability to aromatize hydrocarbon materials. This includes a wide variety of materials, such as the compounds of metals of groups V and VI of the periodic table, the noble metals, the heteropoly acids, etc. The compounds of the metals of groups V and VI can be used singly or as mixtures on a carrier material. A particularly important class for reforming operations comprises the oxide and/or sulfide of the left hand elements of group VI, namely, molybdenum, chromium and/or tungsten. These catalytic elements, that is, the compounds of groups V and VI can comprise 0.1 to about 20% by weight of the total catalyst. The carrier material can be, for example, alumina, silica, kieselguhr, pumice, magnesia, activated charcoal, zinc spinel, silica-alumina, silica-magnesia, etc. The noble metals are, for example, platinum, palladium, etc. These metals are distributed or dispersed on any of the carrier materials enumerated above. The noble metal comprises about 0.01 to about 10% by weight of the total catalyst or usually about 0.1 to about 2% by weight, on the same basis. These catalysts are sulfur sensitive, consequently, it is preferred that the sulfur concentration of the feed material be maintained low. The other suitable class of catalysts comprises the heteropoly acids and they are, for example, those acids having chromium, molybdenum, tungsten and/or vanadium as the outer acid forming element and the central acid forming element can be, for example, phosphorus, silicon, germanium, plantinum, palladium, etc. Specific examples of these are phosphomolybdic acid, silicomolybdic acid, aluminomolybdic acid, silicotungstic acid, etc. The catalytic element is used alone or supported on a carrier material, e.g., any of those which are enumerated hereinabove. This catalytic element comprises about 1 to about 50% by weight of the total catalyst. Another suitable class of catalysts are those which exhibit an alkaline reaction. Such catalysts are prepared by the incorporation of an alkaline material such as, for example, compounds of the alkali and/or alkaline earth materials. Examples of such materials are the oxides of sodium, potassium, calcium, barium, etc. When used in the catalyst, the alkaline material comprises about 0.05 to about 10% by weight of the total catalyst. Specific examples are alkalized chromia, alkalized platinum, etc. While various types of catalysts can be used for the purpose of this invention, it should be understood that they are not equivalent for all purposes, but that under some conditions some are more desirable than others. Platinum catalysts represent an excellent material for this invention.

For the purpose of evaluating the present invention, reference will be had to the accompanying drawings which form a part of this specification.

Figure 1 is a schematic diagram of a pilot plant which was employed to demonstrate the furnace-reactor of the present invention; and

Figure 2 is a correlation showing the advantage in using the present invention over isothermal and adiabatic operations.

In Figure 1, naphtha feed is supplied from a source **5** and it is passed to a feed tank **6**. For the purpose of maintaining a steady flow of oil feed from feed tank **6** through line **8** and pump **9**, nitrogen pressure is imposed on the feed material in tank **6** by means of supply line **11**, which is connected to the top of feed tank **6**. The naphtha feed material is transported by means of pump **9** to an oil preheater **14** by means of line **15**. In the oil preheater **14**, the temperature was raised to about 650° to about 700° F. and thence it was discharged therefrom by means of line **17**. Recycle gas containing hydrogen in the amount of about 90 to 97% by volume is supplied from line **18**, and thence, the recycle gas is passed to a preheater **20** wherein the temperature is raised to about 650° to about 700° F. The heated recycle gas is discharged from preheater **20** by means of line **22**, and thereafter, it is combined with the preheated oil feed flowing through line **17** and the combined stream flows through line **23** prior to entering feed preheater **25**. In feed preheater **25**, the combined stream of recycle gas and oil feed is heated to a temperature which varied in the range specified in the experiments to be given hereinafter. The preheated reactants were discharged from the preheater **25**, and thence they were passed through a line **27** joined with the top of furnace-reactor **30**.

Furnace-reactor **30** consisted of a 1 inch schedule 40–304 standard stainless steel pipe. This reactor was 12 feet, 2 inches in length and the catalyst having a 1/16 inch diameter and approximately 1/8 inch long was placed in the reactor such that it occupied approximately 12 feet of the reactor length. The catalyst employed for the experiments to be reported hereinafter consisted of 0.6% by weight of platinum supported on alumina and the catalyst was prepared as extruded pellets. For the purpose of taking temperatures, two thermowells were situated concentrically within the reactor tube and these thermowells consisted of 1/4 inch O.D. tubing. By means of these thermowells, it was possible to take catalyst bed temperatures at a distance of 2 feet from the top, designated as "top catalyst temperature"; 6 feet from the top, designated as "middle catalyst temperature"; and 11 feet from the top, designated as "bottom catalyst temperature." The furnace proper was a vertical, cylindrical, direct-fired, gas furnace. Although not shown, the reactor tube **30** contained a metal shield around it in order to avoid direct flame impingement from the burners. The furnace proper is shown schematically as **32** in the drawing. Temperatures of the furnace were also taken for the purposes of this invention in order to show the heating pattern for this invention. In this connection, the top furnace temperature was taken over an initial two foot length, the middle furnace temperature was taken between 5 and 7 feet from the top and the bottom furnace temperature was taken between 9 and 12 feet from the top. In addition, skin temperatures were taken of the reactor tube. The top skin temperature was taken at a 2 foot distance from the top, the middle skin temperature was taken at a distance of 6 feet from the top and the bottom skin temperature was taken at a distance of 11 feet from the top. The reaction product was discharged from the reactor tube **30** by means of line **33**, and thence it was passed to a water cooled condenser **34**. As a result of cooling in condenser **34**, substantially all of the normally liquid product material was condensed, and thence the reaction product was passed from condenser **34** to a high pressure receiver **36** by means of line **37**. The pressure in the receiver was essentially reaction pressure. The normally gaseous product material is discharged from the top of receiver **36** by means of line **39**. The net production of normally gaseous product material was

discharged from the system by means of a vent line **41** in which there was situated a gas flow meter **42** for the purpose of measuring the amount of normally gaseous product material produced in the system. After measurement of the gas in meter **42**, it was vented therefrom by means of line **44**. The portion of normally gaseous product material earmarked for recycle to the furnace-reactor was passed through line **46**. This gaseous product material was recompressed by means of compressor **47**, and thence it was passed to a water cooler **49** by means of line **51**. The cooled compressed gaseous material was discharged from the cooler by means of line **53**, and thence it was passed to a separating drum **55** wherein any condensate was separated from the compressed gaseous material. The gaseous material was discharged from the top of separating drum **55** by means of line **57**, and then it was passed to a filter **59** wherein any solid material contained in the gaseous material was removed therefrom. The filtered gaseous material was discharged from the top of the filter **59** by means of line **61**, and then it was passed to a dryer **63**. A substantial part or all of the moisture contained in the recycle gas was removed therefrom by means of suitable desiccant material contained in dryer **63**. The dried recycle gas was discharged from the top of dryer **63** by means of line **65**, and then it was passed to a gas meter **66** whereby the recycle gas rate was measured. The measured recycle gas was then discharged from the gas meter and passed to line **18**, which has been previously mentioned.

The normally liquid product material contained in high pressure receiver **36** was then discharged from the bottom thereof by means of line **70**. Line **70** contained a control valve **71** whereby the liquid product material was depressured to essentially atmospheric pressure, and thence it was passed to line **73**. As a result of releasing the pressure on the liquid product, normally gaseous product material was desorbed therefrom and the mixture of liquid and gaseous material was passed to a secondary receiver **75**. The liquid product was discharged from the bottom of receiver **75** by means of line **76**; whereas the normally gaseous material was discharged overhead therefrom, and thence passed to an ice trap **78** by means of line **79**. The ice trap **78** was surrounded by a vessel **81** wherein an ice bath was situated for cooling purposes. The cooled normally gaseous product material was discharged overhead from trap **78** by means of line **83**, and thence it was measured in gas meter **85** prior to being vented from the system by means of line **87**.

The feed stock used for the evaluation of the furnace-reactor is given below.

TABLE I

API° gravity	54.4
ASTM distillation, ° F.:	
I.B.P.	238
5	262
10	270
20	280
30	286
40	294
50	301
60	308
70	318
80	328
90	342
95	255
E.P.	400
Aniline point, ° F.	138
Octane No., CFRR clear	33.6
Paraffins, vol. percent	58.6
Naphthenes, vol. percent	32.9
Aromatics, vol. percent	8.5
Sulfur, wt. percent	.002
Watson factor	11.97
Molecular weight	128

The results obtained by means of the apparatus shown in Figure 1 are given in Table II below.

TABLE II

Run No.	1	2	3	4
Length of Run, Hrs	12	12	12	12
Pressure, Inlet, p.s.i.g	522	525	522	509
Pressure, Outlet, p.s.i.g	472	473	471	487
Space Vel., $W_o/hr./W_c$	9.94	9.95	9.97	5.96
H_2 rate, s.c.f.b	5,100	5,000	5,000	5,000
Temperatures:				
Oil inlet, ° F	757	848	850	849
Furnace, Top, ° F	1,032	1,100	1,120	1,065
Furnace, Mid., ° F	1,038	1,041	1,101	1,013
Furnace, Bot., ° F	1,018	972	981	964
Skins, Top, ° F	837	954	970	942
Skins, Mid., ° F	921	948	974	950
Skins, Bot., ° F	969	974	974	972
Catalyst, Top, ° F	768	825	828	818
Catalyst, Mid., ° F	801	868	878	888
Catalyst, Bot., ° F	881	921	933	946
Catalyst, Ave., ° F	804	861	869	872
Yields, Output Basis, Vol. percent:				
C_5+ Liquid	94.6	91.2	90.6	85.6
Butanes	0.7	2.2	2.3	4.5
Dry Gas (Wt. percent)	2.3	4.0	4.5	7.1
10# RVP Liquid	107.9	104.0	102.4	96.2
H_2 Product (s.c.f.b.)	701	792	833	882
Octane No., CFRR clear:				
C_5+ Liquid	65.6	74.8	79.2	88.5

A three reactor adiabatic system was operated using the same catalyst as employed in the furnace-reactor as well as the same feed material. The data obtained from the adiabatic operation are reported in Table III below.

TABLE III

Adiabatic data

Run No.	1	2	3
Length of run, hrs	291	20	1,113
Temperatures, ° F.:			
Inlet #1 reactor	960	970	971
Outlet #1 reactor	850	844	844
Inlet #2 reactor	940	945	945
Outlet #2 reactor	909	912	907
Inlet #3 reactor	914	920	920
Outlet #3 reactor	903	908	904
Pressure, p.s.i.g	502	516	510
Space Vel., $W_o/hr./W_c$	2.96	2.1	2.01
Recycle H_2, s.c.f.b	5,030	4,738	4,974
Percent H_2 in Recycle, Vol. percent	84.9	87.0	84.7
Yields, Output Basis, Vol. percent:			
C_5+ Liquid	84.2	83.3	83.7
Butanes	5.0	5.5	4.6
Dry Gas (Wt. percent)	8.3	8.9	9.0
Octane No., CFRR clear:			
C_5+ Liquid	86.0	88.2	87.2

The data for an isothermal operation involving the same feed material and catalyst as employed for the furnace-reactor and adiabatic operation are reported in Table IV below.

TABLE IV

Isothermal data

Run No.	1	2
Length of run, hrs	20	20
Temperature, ° F	891	890
Pressure, p.s.i.g	500	504
Space Vel., $W_o/hr./W_c$	3.2	3.1
H_2 rate, mol/mol feed	5.5	5.8
Yields:		
C_5+ Liquid, Vol. percent	84.7	87.2
Butanes	4.6	3.5
Dry Gas (Wt. percent)	8.2	7.1
10# RVP Liquid	95.5	98.6
H_2, s.c.f.b	881	821
Octane No., CFRR clear:		
C_5+ Liquid	88.8	82.3

The data obtained by the three methods of operation form the basis of Figure 2 in the accompanying drawings. In this figure, the C_5+ liquid yield was correlated against the octane number of this product material. It is to be noted that in the case of the fired reactor, the yield of product material at a given octane number was significantly higher than the yields obtained in the adia-

batic and isothermal operations. It is also significant to note by means of a comparison of the data reported in Tables II, III and IV that a significantly smaller amount of catalyst is required for the furnace tube reactor. This is clearly illustrated by means of the space velocities used to obtain the results reported. On the basis of the comparison between the direct-fired reactor, isothermal operation and adiabatic operation, it is quite apparent that distinct advantages lie with the use of a direct-fired furnace or a heated reactor.

Having thus provided a description of our invention, it should be understood that no undue limitations or restrictions are to be imposed by reason thereof, but that the scope of the invention is defined by the appended claims.

We claim:

1. A process for reforming a light hydrocarbon oil which comprises passing said oil at a temperature below the point of substantial thermal cracking to a heated zone containing a fixed bed of platinum reforming catalyst, contacting said oil with catalyst under suitable reforming conditions and supplying heat to the catalyst during said contact of the oil with the catalyst such that the average temperature in the initial portion of the catalyst bed is between about 700° F. and about 900° F. and the average temperature in the remaining portion of the catalyst bed is between about 20° F.° and about 150° F. greater than the temperature in said initial portion whereby the temperature of the resultant product is greater than the inlet temperature of the oil being fed to said heated zone and producing a reformed product having an octane number of at least about 60.

2. A process for reforming a light hydrocarbon oil which comprises passing said oil having an inlet temperature of about 600° F. to about 900° F. to a heated zone containing a fixed bed of platinum reforming catalyst under reforming conditions and supplying heat to the catalyst during contact of the oil with the catalyst such that the average temperature in the initial portion of the catalyst bed is between about 700° F. and about 900° F. and the average temperature in the remaining portion of the catalyst bed is between about 20° F. and about 150° F. greater than the temperature in said initial portion whereby the temperature of the resultant reaction product is about 25° F. to about 200° F. greater than said inlet temperature and producing a reformed product having an octane number of at least about 60.

3. A process for reforming a light hydrocarbon oil which comprises passing said oil feed at a temperature below the point of substantial thermal cracking to a heated zone containing a fixed bed of platinum reforming catalyst under reforming conditions, not more than 50 percent by volume of said catalyst is used mainly for dehydrogenation of naphthenes, supplying heat to the catalyst during contact of the oil with the catalyst such that the average temperature in the initial portion of the catalyst bed is between about 700° F. and about 900° F. and the average temperature in the remaining portion of the catalyst bed is 20° F. to 150° F. greater than the temperature in said initial portion whereby the resultant reaction product has a temperature greater than the temperature of the oil feed, and converting said oil in the presence of added hydrogen to a reformed product having an octane number of at least about 60.

4. A process for reforming a light hydrocarbon oil which comprises passing said oil feed at a temperature below the point of substantial thermal cracking to a heated zone containing a fixed bed of platinum reforming catalyst under suitable reforming conditions, supplying heat to the catalyst during contact of the oil with the catalyst, the rate of heating said catalyst being sufficient to provide that the initial portion thereof comprising not more than 50 percent by volume be maintained at an average temperature of about 700° F. to about 900° F. and the remaining portion of catalyst is at an average temperature which is about 20° F. to about 150° F. greater than the said initial portion, and thus converting said oil feed in the presence of added hydrogen such that the temperature of the resultant reaction product is greater than the temperature of the oil feed and producing a reformed product having an octane number of at least about 60.

5. A process for reforming a light hydrocarbon oil which comprises passing said oil feed at a temperature below the point of substantial thermal cracking to a heated zone containing a fixed bed of platinum reforming catalyst in contact with metal surfaces under suitable reforming conditions, heating said catalyst during contact of the oil with the catalyst at a rate such that the skin temperature of the metal surface is about 850° F. to about 1050° F. and the average temperature in the initial portion of the catalyst bed is between about 700° F. and about 900° F. and the average temperature in the remaining portion of the catalyst bed is about 20° F. to about 150° F. greater than the temperature in said initial portion and converting the oil feed in the presence of added hydrogen to a product having a temperature greater than the temperature of the oil feed and an octane number of at least about 60.

6. A process for reforming a light hydrocarbon oil which comprises passing said oil feed at an inlet temperature of about 600° F. to about 900° F. to a heated zone containing a fixed bed of platinum reforming catalyst under suitable reforming conditions, supplying heat to the catalyst during contact of the oil with the catalyst such that the average temperature in the initial portion of the catalyst bed is between about 700° F. and about 900° F. and the average temperature in the remaining portion of the catalyst bed is about 20° F. to about 150° F. greater than the temperature in said initial portion and converting the oil in the presence of added hydrogen to a reformed product having an octane number of at least about 60 and a product temperature of about 875° F. to about 975° F., said product temperature between about 25° F. to about 200° F. greater than the inlet temperature of the oil feed.

7. A process for reforming a light hydrocarbon oil which comprises passing the oil feed at an inlet temperature of about 600° F. to about 900° F. to a heated zone containing a fixed bed of platinum reforming catalyst under suitable reforming conditions, supplying heat to the catalyst during contact of the oil with the catalyst at a rate such that the initial portion constituting not more than 50 percent by volume of the catalyst bed is maintained at an average temperature of about 700° F. to about 900° F. and the remaining portion of the catalyst bed is heated at a rate to provide an average catalyst temperature of about 850° F. to about 930° F., said average catalyst temperature in the remaining portion being about 20° F. to about 150° F. greater than the temperature in the initial portion of the catalyst in the heated zone, and thus converting the oil feed under suitable reforming conditions to a reformed product having an octane number of at least about 60.

8. A process for reforming a light hydrocarbon oil which comprises passing said oil containing not more than about 0.01 percent by weight of sulfur at a temperature below the point of substantial thermal cracking to a heated zone containing a fixed bed of platinum reforming catalyst, contacting said oil with catalyst under suitable reforming conditions and supplying heat to the catalyst during said contact of the oil with the catalyst such that the average temperature in the initial portion of the catalyst bed is between about 700° F. and about 900° F. and the average temperature in the remaining portion of the catalyst bed is about 20° F. to about 150° F. greater than the temperature in said initial portion whereby the temperature of the resultant product is greater than the inlet temperature of the oil being fed to the heated zone

and the octane number of the resultant product is at least about 60.

9. A process for reforming a light hydrocarbon oil which comprises passing said oil at a temperature below the point of substantial thermal cracking to a heated zone containing a fixed bed of platinum reforming catalyst under suitable reforming conditions, heat being supplied to said catalyst during contact of the oil with the catalyst at a rate such that the average temperature in the initial portion of the catalyst bed is between about 700° F. and about 900° F. and the average temperature in the remaining portion of the catalyst bed is about 20° F. to about 150° F. greater than the temperature in said initial portion whereby the temperature of the resultant product is greater than the inlet temperature of the oil and the octane number of the resultant product is at least about 60, passing the product from the heated zone to a second zone containing a platinum reforming catalyst and operated under suitable adiabatic reforming conditions such that a high octane quality reformed product is produced.

10. The process of claim 9 wherein the heated zone contains about 5 to about 50 percent of the total catalyst which is contained in the adiabatic and heated zones.

11. A process for reforming a light hydrocarbon oil which comprises passing said oil at a temperature below the point of substantial thermal cracking to a heated zone containing a fixed bed of platinum reforming catalyst under suitable reforming conditions such that the operation is substantially non-regenerative, supplying heat to the catalyst in the heated zone during contact of the oil with the catalyst to provide an average temperature in the initial portion of the catalyst bed between about 700° F. and about 900° F. and an average temperature in the remaining portion of the catalyst bed between about 20° F. and about 150° F. greater than the temperature in said initial portion whereby a reformed product having an octane number of at least about 60 is obtained at a temperature greater than the temperature of the oil feed, passing the product from the heated zone to a second zone containing platinum reforming catalyst under suitable adiabatic reforming conditions such that the operation is regenerative, and thereby producing a reformed liquid product having an octane number between about 85 to about 110.

12. A process for reforming a light hydrocarbon oil containing not more than about 0.01 percent by weight of sulfur which comprises passing said oil at a temperature in the range of 600° F. to 900° F. to a heated zone containing a fixed bed of platinum reforming catalyst under suitable reforming conditions, supplying heat to said catalyst during contact of the oil with the catalyst to provide an average temperature in the initial portion of the catalyst bed between about 700° F. and about 900° F. and an average temperature in the remaining portion of the catalyst bed between about 20° F. and about 150° F. greater than the temperature in said initial portion whereby the oil is converted in the presence of added hydrogen to a reformed product having an octane number between about 60 and about 85, said reformed product having a temperature between about 875° F. and about 975° F. which temperature is between about 25° F. and about 200° F. greater than the inlet temperature of the oil feed, passing the product from the heated zone to a second reforming zone containing a platinum reforming catalyst under adiabatic reforming conditions and thereby producing a reformed product having an octane number between about 85 and about 110.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,915,458 December 1, 1959

Charles E. Slyngstad et al.

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

Column 5, line 50, for "plantinum" read -- platinum --; line 60, for "materials" read -- metals --; column 9, line 27, for "20° F.°" read -- 20° F. --.

Signed and sealed this 10th day of January 1961.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents