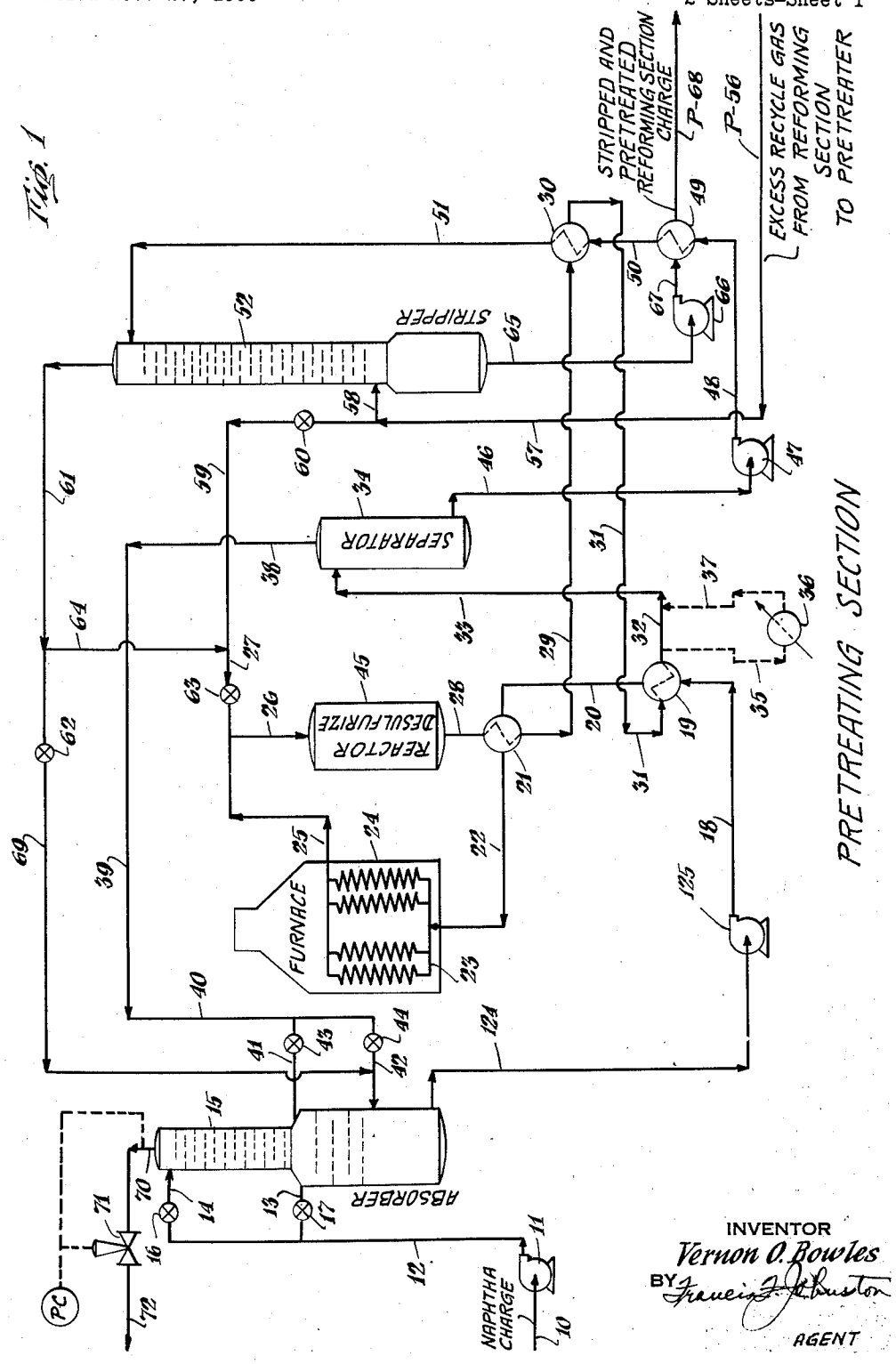
Sept. 8, 1959 V. O. BOWLES 2,903,415

INTEGRATED PRETREATING AND REFORMING OF THE PRETREATED NAPHTHA

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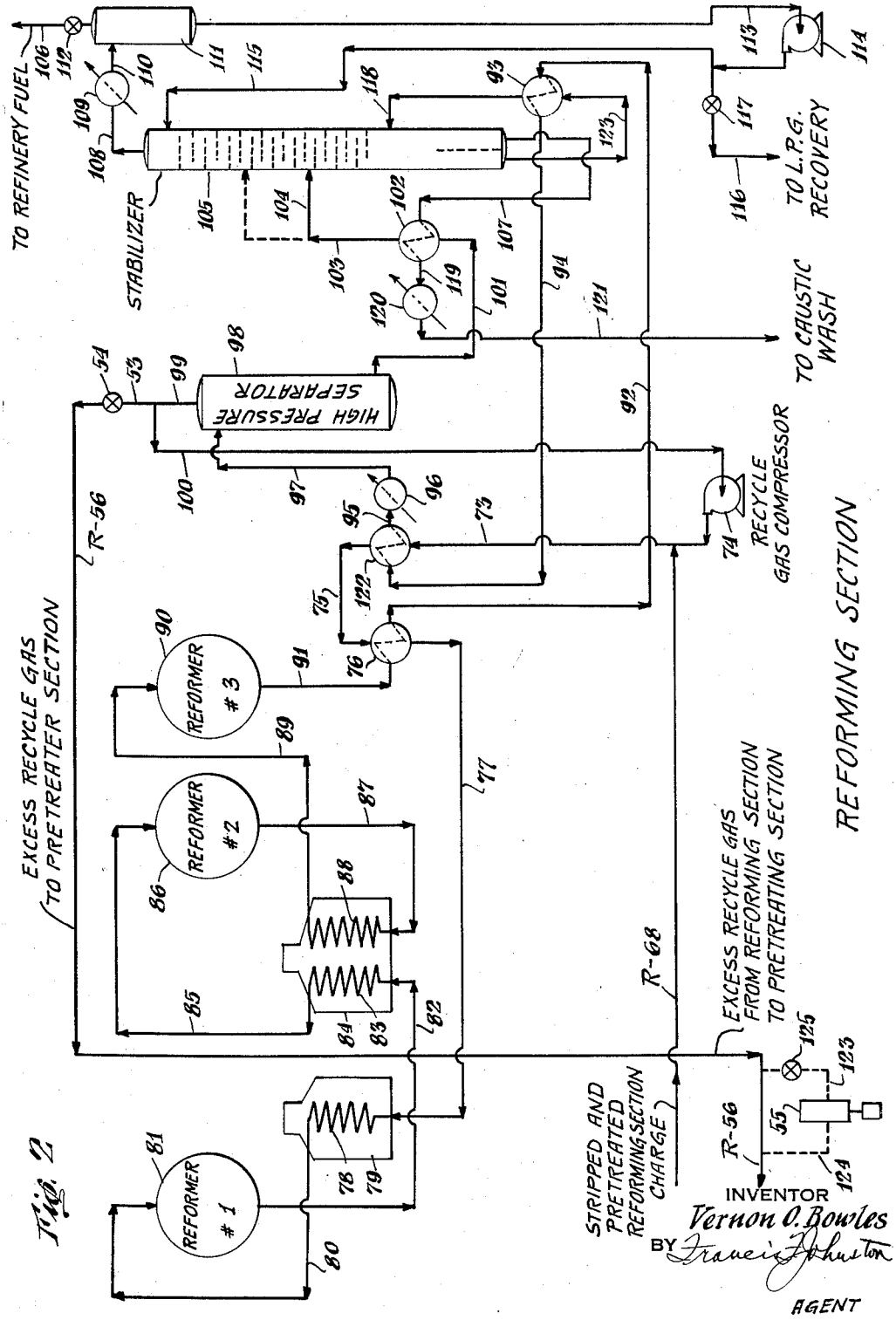


Fig. 2

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2,903,415

INTEGRATED PRETREATING AND REFORMING OF THE PRETREATED NAPHTHA

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20 Claims. (Cl. 208—89)

The present invention relates to the hydrodesulfurization and reforming of naphtha to provide a gasoline of low sulfur content and high octane rating. More particularly, the present invention relates to an integrated unit for the hydrodesulfurization and reforming of naphthas in which the pressure in both the hydrodesulfurization or pretreating unit and the pressure in the reforming unit is controlled by the pressure maintained at the pretreater-absorber off-gas outlet. Furthermore, the pretreater unit operates at the pressure at which the hydrogen-containing gas enters the pretreater unit less the pressure loss due only to normal system pressure drop, substantially all, if not all of the hydrogen-containing gas being supplied by the reformer unit. Furthermore, the operation is characterized by a very high thermal efficiency, that is to say, substantially all or a large percentage of the external heat energy introduced into the pretreating section feed is recovered in the process or in the effluent flowing directly to the catalytic reforming circuit. For example, in a typical pretreating operation the naphtha feed is heated by heat exchange to about 660° F. and then by one or more fired heaters to about 780° F. The total heat introduced into the reactor feed including the hydrogen-rich gas is approximately 147M B.t.u./bbl. of naphtha charge and that introduced by the heater only is about 27M B.t.u./bbl. of naphtha charge. On the other hand, the total amount of heat rejected to cooling water is only 9M B.t.u./bbl. of naphtha charge while 21M B.t.u./bbl. of naphtha charge remains in the pretreated naphtha flowing to the catalytic reforming circuit. Thus, only about 6 percent of the total heat or about 33 percent of the fired heat is rejected to water in the pretreating system.

Since the pressure in both units is controlled by the pressure maintained upon the pretreater-absorber off-gas outlet, the total system pressure drop is minimized, and the hydrogen-rich off-gas is available at the highest possible pressure. Thus, there is a reduced demand for gas compressors with a concomitant saving in initial cost and operating utilities of hydrogenation and hydrotreating units which employ this hydrogen-rich off-gas at elevated pressure. Additionally, the pretreating-reactor pressure is maintained at the highest possible pressure frequently without the need of compressing off-gas from the catalytic reforming circuit before it enters the pretreating circuit.

By stripping the pretreat effluent wtih pressured hydrogen-containing gas at a pressure intermediate that of the reforming unit gas separator and that of the pretreating reactor and passing the stripped off-gas to the absorber either directly or through the pretreating reactor system, pressure drop is minimized and a smaller absorber of as little as 4 to 8 actual trays and of simple inexpensive design can be used to absorb from the pretreater gas valuable hydrocarbons and to strip water, oxygen compounds, and other heat exchanger deposit precursors from the pretreater feed.

Furthermore, through the control of pressure in both the pretreating and reforming sections of the integrated unit by control of the pressure on the pretreater-absorber off-gas, hydrogen-containing gas is available at relatively high pressure (400 p.s.i.g. or more) for other reactions requiring hydrogen carried out at higher pressures.

As a consequence of the integration of the two sections, i.e., pretreating and reforming into a unit the pressure of which is controlled primarily at a single point, there is no significant drop in pressure between the pretreater stripper and the pretreater absorber. This results in a minimum requirement of power to cause the naphtha feed to flow through the integrated unit and a minimum requirement of power to pump the off-gas hydrogen to other processes.

Under some conditions, it will be understood by those skilled in the art that it may be necessary to operate the pretreater at a higher pressure than the reformer gas separator pressure in order to obtain the desired conversion to, and removal of, water, hydrogen sulfide, arsines, and especially ammonia. In this case, compression between the reformer gas separator and the pretreating system would be required and the advantages of the afore-described technique involving minimum pretreater system pressure drop are apparent.

In addition, the heat requirement for the pretreater stripper is relatively small even through an excellent stripping function is performed and essentially all of the heat given up to the stripper overhead is captured in the process.

The present invention makes it possible to produce reformer feed of extremely low content of hydrogen sulfide, water, and other volatile materials such as ammonia and arsines which would interfere with the catalytic reforming reactions and with a minimum of pressure loss to the hydrogen-rich gas available from the catalytic reformer circuit.

Finally, although the absorber tends to absorb and retain in the system harmful agents formed and/or released in the pretreater reactor such as hydrogen sulfide, water, ammonia, arsines, and hydrochloric acid, (which latter material may cause platinum catalyst cracking activity to become excessively high), the stripper reduces the concentration of these materials to satisfactorily low values in the range of 0–20 parts per million, and although some system recycle of these materials does develop the conditions are so controlled that the desired result is achieved without excessive recycle of such materials. It should be recognized that if the reformer feed stock were not pretreated, then these volatile compounds, although not present in the feed per se, would be produced in the reforming reactor, as in the pretreating reactor and therefore would bring about the identical harmful effects as if they were not stripped properly from the reformer feed.

It will be recognized by those skilled in the art that particular advantages arise from the present invention when employing a platinum type reforming catalyst due to the purification of the feed to the reforming section. On the other hand, the greatly improved thermal and hydraulic efficiency provided by the present invention is advantageous regardless of the type of catalyst employed in the reforming section.

Accordingly, it is an object of the present invention to provide an integrated process for the pretreating and reforming of naphthas in which the pressure in the pretreating section and the pressure in the reforming section is controlled at the pretreater-absorber off-gas outlet. It is another object of the present invention to provide an integrated method for the pretreating and reforming of naphthas in which the pretreating section of the unit is

operated at the pressure at which the hydrogen-containing recycle gas from the reforming section enters the pretreating section less pressure losses due only to the normal pressure drop in the pretreating section. It is a further object of the present invention to provide an integrated method of pretreating and reforming naphthas in which the pretreater stripper is operated at a pressure intermediate that of the pretreating section reactor and the pressure of the reforming section gas separator and at a stripper overhead temperature at which water, hydrogen sulfide, and other volatile components thereof such as ammonia, arsines, and hydrochloric acid, which tend to poison, inhibit, or otherwise adversely affect platinum type catalyst are rejected in the stripper overhead (and subsequently in the absorber off-gas) to produce a charge stock or feed to the reforming section substantially devoid of such volatile, harmful components. In an operation where the pretreating section must be operated at a higher pressure than the reforming section, it will be understood that the compressor required for boosting the pressure of the hydrogen-rich gas to the pretreating section pressure level is considered an integral part of the reforming section and that the aforementioned principles apply nonetheless. It is still another object of the present invention to provide an integrated method of pretreating and reforming naphthas in which the pressure and temperature under which the pretreater stripper operates is correlated with the amount of hydrogen-containing recycle stripper gas available from the reforming section. The present invention also provides an integrated method of pretreating and reforming naphthas in which the heat energy carried by the pretreater stripper overhead is not wasted to cooling water but carried directly to the pretreater absorber to heat the feed naphtha and/or to the reactor to supply at least a part of the reactor heat input. Additionally, the liquid-gas separator downstream of the pretreater reactor is operated at a sufficiently elevated temperature to minimize, or in some instances eliminate, loss of heat to water in the condenser just upstream of said liquid gas separator.

These and other objects and advantages will become apparent to those skilled in the art from the following description taken in conjunction with the drawings in which

Figure 1 is a flow diagram of the pretreating, or hydrodesulfurizing, section of the integrated method of hydrodesulfurizing and reforming naphthas, and

Figure 2 is a flow diagram of the reforming section of the integrated method of pretreating, or hydrodesulfurizing, and reforming naphthas.

The useful catalysts and reaction conditions for hydrodesulfurizing and hydrodenitrogenizing naphthas are well-known to those skilled in the art and are given here only to complete the description and not to exclude catalysts and conditions not enumerated hereinafter.

For the purpose of description and illustration the present invention will be discussed using a catalyst comprising a mixture of oxides of cobalt and molybdenum or alumina for hydrodesulfurizing and/or hydrodenitrogenizing and a platinum-on-alumina catalyst for reforming.

In general, the pressure in the pretreating section is substantially that in the reforming section, any difference in pressure being due to the normal pressure drop in the pretreating section. It is preferred to operate the reforming unit gas separator at about 250 to about 750 lbs. per square inch (p.s.i.g.) and usually at about 475 to 525 p.s.i.g. Consequently, the pretreating section reactor usually operates at about 475 p.s.i.g. In other words, the pretreating section operates at the reforming section gas separator pressure, usually about 500 p.s.i.g., less the pressure drop inherent in the pretreating section. The pretreating section reactor is operated in the temperature range of about 550 to about 850° F., a space velocity of about 1.0 to about 8.0, hydrogen-to-naphtha ratio at the reactor inlet of about 150 to about 2500 standard cubic feet per barrel (s.c.f./bbl.) dependent upon the activity of the catalyst and the severity necessary to reduce the sulfur and nitrogen content of the naphtha to a degree which does not poison, inhibit, or otherwise adversely affect the reforming catalyst and otherwise as those skilled in the art are aware. Under some conditions, it will be understood by those skilled in the art that it may be necessary to operate the pretreater at a higher pressure than the reformer gas separator pressure in order to obtain the desired conversion to, and removal of water, hydrogen sulfide, arsines, and especially ammonia. In this case compression of at least a portion of the reformer gas leaving the reformer gas separator and entering the pretreating system is required and the advantages of the afore-described technique involving minimum pretreating system pressure drop are apparent.

In the reforming section the reaction temperature is about 875 to about 975° F. and the space velocity about 0.5 to about 3 dependent upon the activity of the catalyst, the required increase in octane rating of the naphtha and other factors well-known to those skilled in the art when using a platinum type catalyst such as one containing about 0.1 to about 1.0 weight percent platinum, a concomitant amount (0.1 to 1.0 weight percent) of chlorine, with the balance being alumina to make 100 weight percent.

The flow diagram Figures 1 and 2 illustrates the flow of naphtha and the flow of gases through the integrated unit.

A charge naphtha, such as a straight run 180° F. to 380° F. boiling range, or a full (100° F.–380° F.) boiling range naphtha, or a mixture straight run and cracked naphtha flows from a source not shown through line **10** to the suction side of pump **11** and is discharged at pretreater pressure into line **12**. The charge naphtha containing sulfur and/or nitrogen, water, and deposit-forming precursor materials flows through line **12** and lines **13** and **14** to absorber **15**. In absorber **15** the charge naphtha is intimately contacted with gas flowing from separator **34** through lines **38**, **39**, **40**, **41**, and **42** and from stripper **52** flowing through lines **61**, **69** and **42**.

In the absorber two objects are achieved. Valuable C_{4+} hydrocarbons are absorbed from the gas and the gas strips water, oxygen and other deposit forming precursor materials from the charge naphtha. However, the amount of oil introduced into absorber **15** through lines **13** and **14** and the amount of gas introduced into absorber **15** through lines **41** and **42** must be controlled or there will be excessive absorption with a concomitant build-up of undesirable recycle, or there will be insufficient stripping of the oil. When a relatively large amount of gas flows through line **42** to absorber **15** and simultaneously a large amount of oil flows into absorber **15** through line **14**, there is likely to be a condition of over-absorption. Accordingly, the flow of oil through line **14** is controlled by valve **16** so that a portion of the charge naphtha enters absorber **15** through line **14** while the balance of the charge naphtha enters absorber **15** through line **13**. Simultaneously, the gas introduced into absorber **15** is regulated to introduce a portion through line **42** and the balance enters absorber **15** through line **41**. In other words, the introduction of oil into absorber **15** is balanced between lines **13** and **14** and the gas introduced into absorber **15** is balanced between lines **41** and **42** to provide optimum stripping of deleterious material from the charge naphtha and optimum absorption of C_{4+} hydrocarbons from the gas without undesirable build-up of recycle.

When desirable, the naphtha charge can be fractionated into a heavy naphtha and a light naphtha. The heavy naphtha is pumped separately to absorber **15** through line **14** and the light naphtha pumped separately to absorber **15** through line **13**.

Since the gas carries with it the heat absorbed in the

pretreater stripper 52 and the heat carried from the pretreater separator 34, the feed naphtha is heated as well as stripped of deleterious components in the absorber. The stripped heated feed naphtha flows from absorber 15 through line 124 to the suction side of pump 125. Pump 125 discharges into line 18 through which the stripped heated naphtha flows to heat exchanger 19 where it is in indirect heat exchange relation with pretreater reactor 45 effluent flowing through line 31.

From heat exchanger 19 the feed naphtha flows through line 20 to heat exchanger 21 where it is in indirect heat exchange relation with pretreater reactor 45 effluent flowing through line 28. From heat exchanger 21 the feed naphtha flows through line 22 to coils 23 in furnace 24. In coils 23 the feed naphtha is heated to temperatures of about 550 to about 850° F. depending upon the catalyst, the age thereof, the severity required, etc. The feed naphtha flows from furnace 24 through line 25 to line 26. In line 26 the feed naphtha is mixed with hydrogen-containing gas flowing wholly from stripper 52 through lines 61, 64 and 27, or in part directly from the reformer section through lines P–56, 57, 59 and 27 and in part from the stripper 52 through lines 61, 64 and 27 as more fully described hereinafter. The feed naphtha and hydrogen-containing gas are mixed in line 26 in the proportion of about 150 to about 2500 cubic feet of hydrogen per barrel of feed naphtha.

The naptha-hydrogen mixture flows through line 26 to pretreating reactor 45 at about reactor temperature. As noted hereinbefore, the hydrogen-containing gas supplies, except in rare situations, at least a part of the heat input to the reactor.

The reactor effluent comprising desulfurized and, if reaction conditions are severe enough, denitrogenized feed naphtha, light hydrocarbons, hydrogen and harmful agents in catalytic reforming including water vapor, hydrogen sulfide and frequently ammonia, arsines, and hydrochloric acid, flows from reactor 45 through line 28 to heat exchanger 21 where the pretreater reactor effluent is brought into indirect heat exchange relation with the feed naphtha flowing through line 20 as hereinbefore described.

The reactor effluent flows from heat exchanger 21 through line 29 to heat exchanger 30 where it is in indirect heat exchange relation with the liquid from separator 34 flowing in lines 46, 48 and 50 to line 51 and stripper 52.

From heat exchanger 30 the reactor effluent flows through line 31 to heat exchanger 19 where the reactor effluent is in indirect heat exchange relation with the feed naphtha as previously described hereinbefore. From heat exchanger 19 the reactor effluent flows thlrough lines 32 and 33 to separator 34 which operates at a pressure less than pretreating reactor pressure only by the normal pressure drop in the lines and heat exchangers therebetween.

It will be noted that a part of the reactor effluent flows from heat exchanger 19 through line 32 and 35 to cooler 36 and thence through line 37 to line 33. This provision for routing a portion of the reactor effluent is for removing the small amount of heat, if any, required to control the separator temperatures at a suitable level (usually about 175 to 225° F.) or for emergency. Generally, there is little loss of heat to water. In other words, generally a major volume of the reactor effluent bypasses the cooler. Occasionally, it may be necessary to channel an increased amount of reactor effluent through cooler 36 in order to maintain temperatures in separator 34 if exchangers become fouled, for example. However, the amount of heat so rejected to cooling water produces very small losses of heat energy from the system.

In separator 34 hydrocarbons mostly of less than four carbon atoms per molecule, together with hydrogen, hydrogen sulfide, water vapor, ammonia, etc. are largely uncondensed and are separated from the portion of the reactor effluent which is liquid at substantially reactor pressure and temperatures of the order of about 175° F. to about 225° F.

The uncondensed portion of the pretreater reactor effluent flows from separator 34 through lines 38, 39 and 40 to lines 41 and 42 under control of valves 43 and 44 respectively. As previously described, the distributing or proportioning of feed naphtha between lines 13 and 14 and the concomitant distributing or proportioning of gas between lines 41 and 42 must be controlled to provide optimum removal of water and deleterious materials from the feed naphtha with optimum absorption of C_{4+} hydrocarbons from gas without causing undesirably high build-up of recycle materials.

The portion of the pretreater effluent liquid at pretreater reactor pressure and about 175° to about 225° F. together with such gases as are dissolved therein, hereinafter designated separator liquid, flows from separator 34 through line 46 to the suction side of pump 47. Pump 47 discharges into line 48 through which the separator liquid flows to heat exchanger 49 where the separator liquid is in indirect heat exchange relation with the bottoms of pretreater stripper 52. From heat exchanger 49 the separator liquid flows through line 50 to heat exchanger 30 where the separator liquid is in indirect heat exchange with the total effluent from pretreater reactor 45. From heat exchanger 30 the separator liquid flows through line 51 to stripper 52.

In stripper 52 hydrogen, water vapor, hydrogen sulfide, ammonia, arsines, hydrochloric acid, etc. and hydrocarbons, mostly having less than four carbon atoms in the molecule, are stripped from the separator liquid at a pressure intermediate that of the pretreater separator and that of the reforming unit gas separator or the booster compressor if the reforming section operates at lower pressure than the pretreating section. In other words, the pressure in stripper 52 is that of the reforming unit gas separator (or the aforementioned compressor discharge) less the normal pressure drop due only to piping, heat exchangers and the like on the stripping gas system between the reforming unit gas separator and said stripper 52.

Stripping gas is obtained from the reforming section high pressure separator 98 which is operated at slightly lower pressure than reforming reactor #3. That is to say, the pressure in high pressure separator 98 is that of reformer reactor #3 less the pressure drop due only to the piping, heat exchangers and cooler interposed between reformer reactor #3 and separator 98.

The stripping gas flows from reforming section separator 98 through lines 99 and 53 under control of valve 54 to line R–56. From line R–56 the stripping gas flows into line P–56 of the pretreater section and thence to line 57. Dependent upon the amount of excess gas available at the reforming section and the temperature of the separator liquid entering the stripper 52 the stripping gas flow is split between lines 58 and 59 by means of valve 60. Illustrative of the relationship and the distribution of gas between lines 58 and 59 and 64 is the following tabulation:

Approximate flows of stripping gas (excess reformer recycle gas) required for:

Stripping Feed Temp., ° F.	Required Stripping Gas, s.c.f./b. Naphtha Charge
300–350	300–500
175–225	800–1200

Pretreating reactor requirement: 300–700 s.c.f./b. Naphtha feed.
Stripper Pressure: Intermediate, reformer separator (or booster compresser discharge) and pretreater separator.

Available Excess Recycle Gas from Reforming Section, s.c.f./b.	Flow Through Line 64	Valves			Stripper Temp., ° F.
		Closed	Full Open	Partly Open	
300–500	From 61 to 27	60, 62	63		300–350
500–700	From 61 to 27	62	63	60	300–350
700–1,000	From 61 to 27			60, 62, 63	300–350
1,000–1,300	From 27 to 61			60, 62, 63	300–350
1,000–1,300	From 61 to 27	60 or nearly.		62, 63	175–225

Stripper **52** operates entirely on the heat captured in heat exchangers **30** and **49** with stripping gas available from the reforming unit. Thus, with 300–500 s.c.f. of stripping gas per barrel of feed naphtha available from the reformer, and a stripper temperature of 300°–350° F. all of the stripping gas will flow from line **57** through line **58**, through stripper **52** and line **61** to and through lines **64** and **27** to pretreater reactor **45**. On the other hand, when 700 s.c.f./b. of stripping gas is available from the reformer and the stripper is operating at 300° to 350° F. about 400 s.c.f. of stripping gas per barrel of feed naphtha flows through line **58** and the balance through line **59**. Under these conditions when the pretreater reactor required 500 s.c.f. of gas per barrel of feed naphtha all of the gas flowing through line **59** will flow through line **27** and in addition about 200 s.c.f. of gas per barrel of feed naphtha flowing through line **61** will flow through lines **64** and **27** by proper manipulation of valves **63** and **62**. Similarly, when say 1300 s.c.f. of stripping gas per barrel of feed naphtha is available at the reforming section (line R–**56**) and the stripper **52** is operating at 225° F. about 1100 s.c.f. of stripping gas per barrel of feed naphtha flows from line **57** through line **58** to stripper **52** while the balance (200 s.c.f.) flows through line **59** to line **27**. When the pretreater reactor requires 700 s.c.f. per barrel of feed naphtha under these conditions then all of the gas in line **59** flows into line **27** and about 500 s.c.f. per barrel of feed naphtha flows from line **61** through line **64** to line **27**. Accordingly, in general, valves **62** and **63** are primarily used to obtain the desired quantity of hydrogen-rich gas for the pretreating reactor from the pretreater stripper or the reformer directly or vice versa, and to provide for recovery of all heat picked up by the hydrogen-rich, stripping and treating gas by causing it to flow to absorber **15** where it is heat-exchanged by direct contact with the naphtha feed flowing through said absorber.

It is to be noted that when stripping gas is available at the reforming section (line R–**56**) in amounts of 1000 s.c.f. or more per barrel of feed naphtha both heat exchangers **30** and **59** can be almost entirely bypassed or possibly eliminated completely.

The separator liquid introduced into stripper **52** through line **51** flows countercurrently downwardly therethrough in intimate contact with the stripping gas introduced into stripper **52** through line **58**. The intimate contact of the stripping gas with the separator liquid at temperatures of 175° to 350° F. at the separator pressure (generally 475±25 p.s.i.g.) strips the separator liquid of any hydrogen sulfide dissolved therein, water, C_1 to C_4 hydrocarbons, and volatile potential reformer catalyst poisons such as ammonia, arsines, hydrochloric acid, and the like.

The stripped and pretreated stripper bottoms of stripper **52** is the feed to the reforming section. The stripper bottoms flow from stripper **52** through line **65** to the suction side of pump **66**. Pump **66** discharges into line **67** through which the stripper bottoms flow to heat exchanger **49** in which the stripper bottoms is in indirect heat exchange relation with the separator liquid flowing from line **48**. The stripper bottoms flow from heat exchanger **49** through line P–**68** to line R–**68** and provide the pretreated reformer feed substantially devoid of water, hydrogen sulfide, and volatile potential catalyst poisons such as ammonia, arsines, hydrochloric acid and the like.

Returning to stripper **52**, the overhead from stripper **52** comprising stripping gas plus hydrogen sulfide, water C_1 to C_4 hydrocarbons and potential catalyst poisons stripped from the separator liquid in stripper **52** flows through line **61**. Dependent upon the total amount of hydrogen-containing gas in excess of that required for the reforming reaction available in line R–**56**, the amount of stripping gas passed through stripper **52**, and the amount of gas required by the pretreater reactor, valves **62** and **63** are adjusted to regulate the flow of gas from line **61** to line **69** and lines **64** and **27**. The flow of gas in line **59** to line **27** or line **64** is likewise regulated for the same purposes as discussed hereinbefore by adjusting valves **62** and **63**. Accordingly, the mixture of stripper overhead and recycle gas or stripper overhead only flows through line **27** to line **26** and is mixed with the feed naphtha in line **26** as previously described. The balance of the stripper overhead, if any exists, flows through line **69** to line **42** and in admixture with gas flowing from separator **34** through lines **38**, **40** and **42** is introduced into absorber **15**.

The stripper overhead gas, if any, the gas from separator **34** and excess recycle gas from lines **57** and P–**56**, if any, at reforming section pressure (or booster compressor pressure) less pressure drop due only to the piping, etc, pass upwardly through absorber **15** in countercurrent flow to the feed naphtha flowing downwardly through absorber **15**. In the intimate contact of the relatively cold feed naphtha and the relatively warm separator gas or separator gas and stripper overhead, the heat of both gas streams is captured while the valuable hydrocarbons in the gases are absorbed by the feed naphtha and while water and heat exchange deposit precursors are stripped from the feed naphtha by a portion of the gas. The stripped feed naphtha leaves absorber **15** through line **16** as previously described. The absorber off-gas now of greatly reduced C_{4+} hydrocarbon content but containing hydrogen sulfide, hydrogen, water vapor, ammonia, arsines, hydrochloric acid, etc., stripped from the feed naphtha leaves absorber **15** at reforming section pressure less only the normal pressure drop due to the piping, etc. between the reforming section and the absorber outlet. With the reforming unit gas separator operating at about 500 p.s.i.g. the pressure at the absorber outlet will be about 450 to about 475 p.s.i.g. The absorber off-gases leave absorber **15** through line **70** under control of pressure regulating valve **71**. The absorber off-gases flow through line **72** to the plant fuel system or to other processes requiring hydrogen.

Description of the flow of gas through the reforming section or even inspection of the drawings by one skilled in the art brings the realization that the present invention provides a notable advantage in that the pressure on the entire unit, i.e., the reforming section, as well as the pretreating section, can be controlled and regulated by pressure control valve **71**, and that any loss in pressure between the high pressure separator **98** or the booster compressor **55** of the reforming section and pressure control valve **71** is inherent and solely due to normal system pressure drop concomitant with the equipment employed. Furthermore, the hydrogen-containing gas in available at pressures of the order of 400 p.s.i.g. or greater at valve **71**. Thereby compression is eliminated when using the absorber off-gas in other processes at pressures of about 400 p.s.i.g. or less and smaller compressors are required for the use of the absorber off-gas in processes requiring hydrogen at pressures above about 400 p.s.i.g. than are required when the hydrogen-containing gas is available at reduced pressure. In the situation where it is desirable and necessary to operate the pretreating section at a higher pressure than the reforming section pressure then the application of the principles illus-

trated and discussed hereinbefore will result in minimum compression horsepower requirement to cause the hydrogen-rich gas to flow from the reforming section to the pretreating section operating at a higher pressure level.

Furthermore, by preserving the reforming section pressure level to about 450 to 475 p.s.i.g. through the pretreater absorber a much smaller, simpler, inexpensive absorber is required. Thus, a simple absorber with 4 actual trays and a maximum of 8 actual trays has been found to provide satisfactory and flexible absorption of the gas for light hydrocarbon recovery and stripping the feed naphtha of objectionable exchanger deposit precursors.

Returning to line P–68 through which the stripped and pretreated reforming section charge flows to line R–68 of the reforming section of the integrated unit, the stripped and pretreated reforming section charge containing little water, say less than 25 and usually less than 15 parts per million of water, and substantially devoid of hydrogen sulfide, ammonia, arsines, hydrochloric acid, and other volatile catalyst poisons or reatcion inhibitors flows through line R–68 to line **73** which is the line receiving the discharge of recycle gas compressor **74**. The pressure in line R–68 and the pressure in line **73** are substantially the same and of the order of about 550 to about 650 p.s.i.g. The stripped pretreated reforming section feed, hereinafter designated pretreated reformer feed, is mixed with the hydrogen-containing recycle gas in the ratio of about 2 to about 15 mols of recycle gas or about 2 to about 10 mols of hydrogen per mol of pretreated reformer feed to form a reformer charge mixture.

The reformer charge mixture flows through line **73** to heat exchanger **122** where the charge mixture is in indirect heat exchange relation with cooled reformer reactor #3 effluent flowing through line **94** as hereinafter described.

From heat exchanger **122** the warmed charge mixture flows through line **75** to heat exchanger **76** where the charge mixture is in indirect heat exchange relation with reformer reactor #3 effluent flowing directly from reformer reactor #3 through line **91**.

From heat exchanger **76** the warmed charge mixture flows through line **77** to coil **78** in heater **79**. In coil **78** the charge mixture is heated to a reforming reaction temperature dependent upon the reforming catalyst employed, the age thereof (activity), the required octane of the reformed product and other variables known to those skilled in the art upon which the temperature of the reaction is dependent. When using a platinum type catalyst, the temperatures are usually of the order of 850° to 1000° F.

From coil **78** the heated charge mixture flows through line **80** to reformer reactor #1 wherein there is a temperature drop dependent upon the extent to which the heat requirements of the endothermic reactions exceed the heat supplied by the exothermic reactions taking place in reformer reactor #1. Usually, there is a temperature drop of the order of 25 to 150° F. Consequently, the partially reformed charge mixture must be reheated to reaction temperature after flowing from reformer reactor #1 when a simple adiabatic reactor is used. Of course, a more complicated isothermal reactor can be used and maintenance of reaction temperature substantially constant in the reactor substituted for external heating of the reformer reactor #1 effluent.

From reformer reactor #1 the effluent partially reformed pretreated reformer feed, reaction products, and recycle gas flow through line **82** to coil **83** in heater **84**. In coil **83** the reformer reactor #1 effluent is again heated to reaction temperature dependent upon the variables enumerated hereinbefore and usually about 850° to 1000° F.

From coil **83** the heated reformer reactor #1 effluent flows to reformer reactor #2 (**86**) through line **85**. From reformer reactor #2 (**86**) the further reformed pretreated reformer feed together with reaction products flows through line **87** to coil **88** in furnace or heater **84**. When reformer reactor #2 is an adiabatic reactor there is usually a temperature drop of lesser magnitude than the temperature drop to which the contents of reformer reactor #1 are subjected. Nevertheless, the effluent of reformer reactor #2 is usually also heated to reaction temperature dependent upon the variables enumerated hereinbefore and for a platinum type catalyst of about 850°–1000° F.

From coil **88** the reformer reactor #2 effluent flows through line **89** to reformer reactor #3 (**90**) wherein the reforming reaction is completed. The reformer reactor #3 effluent comprising C_{1+} hydrocarbons and hydrogen, flows through line **91** to heat exchanger **76** where the reformer reactor #3 effluent is in indirect heat exchange relation with the charge mixture flowing through line **75** as described hereinbefore. From heat exchanger **76** the cooled reformer reactor #3 effluent flows through line **92** to heat exchanger **93** in which the cooled reformer reactor #3 effluent is in indirect heat exchange relation with the bottoms of stabilizer **105** flowing therefrom through line **123**.

From heat exchanger **93** the heat exchanged reformer reactor #3 effluent flows through line **94** to heat exchanger **122** where the heat exchanged reformer reactor #3 effluent is in indirect heat exchange relation with the charge mixture flowing through line **73** as hereinbefore described.

From heat exchanger **122** the reformer reactor #3 effluent flows through line **95** to cooler **96** where the cooling of the #3 reactor effluent to a temperature at which most C_{4+} hydrocarbons condense at the pressure of reformer reactor #3 less line pressure drop and at a temperature of about 80° to about 120° F.

From cooler **96** the cooled reformer reactor #3 effluent flows through line **97** to separator **98**. In separator **98** the uncondensed hydrogen and C_{1+} hydrocarbons separate from the condensed hydrocarbons and flow from separator **98** through line **99**. A portion of the uncondensed reformer reactor #3 effluent now designated recycle gas dependent upon the recycle gas requirements for reformer reactors #'s 1, 2 and 3 flows through line **100** to recycle gas compressor **74**. The balance, designated excess recycle gas, under control of valve **54** flows through line **53** to line R–56 and thence through line P–56 (Figure 1) to the pretreating section of the integrated unit.

When the pretreating section is operated at a pressure in excess of that of the reforming section a part or all of the excess recycle gas can flow through line **123** under control of valve **125** to the suction side of compressor **55**. Compressor **55** raises the pressure on all or a part of the excess recycle gas to the pressure necessary to provide the desired pretreating section pressure. The compressed, excess recycle gas flows through line **124** to line R–56.

The condensed hydrocarbons flow from separator **98** through line **101** to heat exchanger **102** where the condensed reformer reactor #3 effluent is in indirect heat exchange relation with the bottoms of stabilizer **105** flowing through line **107**.

From heat exchanger **102** the condensed reformer reactor #3 effluent flows through line **103** to line **104** and thence to stabilizer **105**.

In stabilizer **105** entrained or dissolved hydrogen, and C_1 to C_4 hydrocarbons are taken overhead through line **108** to cooler **109** where the overhead is cooled and reflux is condensed. The cooled and condensed overhead flows from cooler **109** through line **110** to accumulator **111**.

In accumulator **111** the condensed hydrocarbons separate from the uncondensed overhead. The uncondensed overhead leaves accumulator **111** through line **106** under control of valve **112** to flow to the refinery fuel system.

The condensed overhead flows from accumulator **111** through line **113** to the suction side of pump **114** which discharges into line **115**. A portion of the condensed overhead flows from line **115** through line **116** under

control of valve **117** to the liquefied petroleum gas recovery system. The balance flows through line **115** to stabilizer **105** to serve as a reflux. The amount of condensed stabilizer overhead flowing to stabilizer **105** to serve as reflux is determined by the reflux ratio required to provide the desired separation in the stabilizer.

The bottoms or unvaporized condensed reformer reactor #3 effluent in stabilizer **105** flows in part through line **123** to heat exchanger **93** where the stabilizer bottoms are heated to a temperature at which a portion of the hydrocarbons are vaporized by indirect heat exchange with the reformer reactor #3 effluent as described hereinbefore. The heated and partly vaporized stabilizer bottoms flow from heat exchanger **93** through line **118** to stabilizer **105**.

The balance of the stabilizer bottoms flow through line **107** to heat exchanger **102** where the stabilizer bottoms give up at least a portion of its heat to the condensed reformer reactor #3 effluent (the stabilizer **105** feed) flowing through line **101**. From heat exchanger **102** the cooled stabilizer bottoms flow through line **119** to cooler **120** and thence through line **121** to gasoline blending.

It will be noted that very little of the heat energy input to the oil is lost to water in the pretreating section of the present integrated unit. Thus, in the said pretreating section where the incoming charge naphtha, for example, has a temperature of about 100° F., only a very small amount of heat is lost to water in cooler **36**, and under some conditions none, and none is lost to water elsewhere. Incidentally, it will be noted that heat is lost to water in the reforming section in cooling the reformer #3 effluent to about 150° F. in cooler **96** and again in cooling the stabilizer bottoms in cooler **120** to about 100° F.

Those skilled in the art will understand that instead of three adiabatic reactors only one can be used or the number of reactors can be greater than 3 without losing the advantages attendant upon the combination of controlling the pressures in the pretreating section and in the reforming section by means of a valve on the pretreater absorber off-gas; of operating the pretreater stripper and absorber in cascade flow with no significant drop in pressure therebetween; of capturing the pretreater stripper overhead and separator vapor heat, of producing pretreated reformer feed with minimum pressure loss; of rejecting hydrogen sulfide, water and other volatile materials, e.g., arsines and ammonia which tend to inhibit or poison platinum type catalysts and hydrochloric acid which increases excessively platinum catalyst cracking activity, and accordingly the production of C_3 and C_4 hydrocarbons; of the use of a small, simple, inexpensive absorber of 4 to 8 actual trays.

I claim:

1. In the method of catalytically hydrotreating a petroleum fraction in a pretreating section in a hydrotreating zone in the presence of hydrogen and hydrogenation catalyst to produce pretreated reformer charge stock and catalytically reforming said pretreated reformer charge stock in a reforming section in a reforming zone in the presence of hydrogen and reforming catalyst under reforming conditions with the production of hydrogen in excess of the hydrogen required in said reforming zone, said hydrogen in excess of that required in said reforming zone being designated excess hydrogen hereinafter, wherein the hydrotreating zone effluent is separated into a hydrogen-containing gaseous fraction and a liquid effluent fraction containing a deleterious concentration of at least one harmful agent, wherein the aforesaid hydrogen-containing gaseous fraction is vented substantially continuously, wherein said liquid effluent fraction only is contacted with at least a part of said excess hydrogen in a stripping zone to provide a stripping zone off-gas and a liquid effluent fraction having an innocuous concentration of harmful agent, wherein said liquid effluent fraction having an innocuous concentration of harmful agent flows to a reforming section and is reformed in a reforming zone in said reforming section in the presence of hydrogen and reforming catalyst with the production of said excess hydrogen, wherein in a reformer separation zone a reforming zone effluent is separated into a hydrogen-rich gaseous fraction substantially devoid of said harmful agents and a liquid fraction, wherein a portion of said gaseous fraction is recycled to said reforming zone, and the balance of said gaseous fraction, designated excess hydrogen, is passed to a pretreating section including said hydrotreating zone and said stripping zone, and wherein gas is released from both said pretreating sections and said reforming section through one release valve only, the improvement which comprises passing at least a portion of said excess hydrogen at substantially the aforesaid reformer separation zone pressure less only line loss to the aforesaid pretreating section without the aid of gas pressuring means between said reformer separation zone and said pretreating section, and controlling the pressure at said release valve to maintain the pressure in said pretreating section at the pressure at which said excess hydrogen enters said pretreating section less pressure loss due only to normal pressure drop through said treating section.

2. The improvement as set forth and described in claim 1 wherein the petroleum fraction is contacted prior to catalytic hydrotreating with at least the gaseous fraction of the pretreating zone effluent in an absorber to remove valuable hydrocarbons from said gaseous fraction and to provide stripped gas and to transfer water and heat exchanger deposit precursors to said stripped gas and said stripped gas is released through said release valve.

3. The improvement as set forth and described in claim 1 wherein all of said excess hydrogen flows through said stripping zone and at least a part of the stripping zone off-gas flows through said hydrotreating zone.

4. The improvement as set forth and described in claim 1 wherein a portion of said excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone and the balance flows to said hydrotreating zone.

5. The improvement as set forth and described in claim 1 wherein a portion of the excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone and the balance flows directly to said hydrotreating zone.

6. The improvement as set forth and described in claim 1 wherein a portion of the excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone, the balance of said excess gas flows to said hydrotreating zone, a portion of the stripping zone off-gas flows to the hydrotreating zone, and the balance of the stripping zone off-gas is contacted with petroleum fraction to be pretreated in an absorber prior to hydrotreating.

7. The improvement as set forth and described in claim 1 wherein a portion of the excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone, a portion of the stripping zone off-gas flows to said hydrotreating zone, the balance of said off-gas is contacted with petroleum fraction to be pretreated in an absorber prior to hydrotreating, and the balance of said excess hydrogen flows directly to said hydrotreating zone.

8. The improvement as set forth and described in claim 1 wherein a portion of the excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone, the balance of said excess hydrogen flows directly to said hydrotreating zone, a portion of the stripping zone off-gas is contacted with petroleum fraction to be pretreated in an absorber together with the gaseous fraction of the hydrotreating zone effluent prior to hydrotreating and the balance flows to said hydrotreating zone.

9. The improvement as set forth and described in claim 1 wherein substantially all of the excess gas flows through the stripping zone, substantially all of the stripping zone off-gas flows to the hydrotreating zone, and the gaseous fraction of the hydrotreating zone effluent is contacted with petroleum fraction to be pretreated in an absorber prior to hydrotreating.

10. In the method of catalytically hydrotreating a mixture of hydrocarbons boiling in the boiling range of reformer feed to reduce the concentration of agents harmful to a reforming catalyst which agents form gaseous hydrogen derivatives in the presence of hydrogenating catalyst and hydrogen to produce a treated reformer feed and reforming the treated reformer feed wherein raw reformer feed is contacted in an absorber with at least one of pretreater effluent gas and stripper off-gas, wherein said raw reformer feed is heated to hydrodecontaminating temperature, wherein said heated raw reformer feed is contacted in a pretreating zone with hydrogenation catalyst and hydrogen-containing pretreater gas to provide a pretreating zone effluent, wherein said pretreating zone effluent is separated into a pretreater effluent gas and a pretreater liquid fraction, wherein said pretreater effluent gas is vented continuously through said absorber, wherein said pretreater liquid fraction only is contacted in a stripping zone with hydrogen-containing stripping gas to obtain a treated reformer feed containing innocuous concentrations of the aforesaid agents harmful to reforming catalyst, and stripper off-gas containing gaseous hydrogen derivatives of the aforesaid agents harmful to reforming catalyst, wherein said treated reformer feed is contacted in a reforming zone with reforming catalyst to produce a reformer effluent, wherein in a reformer separator said reformer effluent is separated into a reformer gas comprising hydrogen substantially devoid of the aforesaid hydrogen derivatives of the aforesaid agents harmful to reforming catalyst and a liquid reformate, wherein said liquid reformate is recovered, wherein a portion of said reformer gas, designated excess hydrogen, passes to a pretreating section comprising the aforesad absorber, pretreating zone, pretreater separator, and pretreater stripping zone, and the balance of said reforming gas is pressured to a pressure in excess of reforming zone pressure and recycled to said reforming zone, wherein the aforesaid stripping gas comprises at least a portion of said excess hydrogen, and wherein said pretreater gas comprises at least one of the aforesaid excess hydrogen, and at least a portion of the aforesaid stripper off-gas, the improvement which comprises passing all gas to be vented from the aforesaid pretreating section through said absorber and through a single release valve, controlling the pressure at said release valve to maintain a pressure in said pretreating section the same as the reformer separator pressure less only line loss to flow the aforesaid excess hydrogen from said reformer separator through said pretreating section without gas pressuring means between said reformer separator and said pretreating section, and recovering in the process substantially all of the external heat introduced into said feed.

11. The improvement as set forth and described in claim 10 wherein the petroleum fraction is contacted prior to catalytic hydrotreating with at least the gaseous fraction of the pretreating zone effluent in an absorber to remove valuable hydrocarbons from said gaseous fraction and to provide stripped gas and to transfer water and heat exchanger deposit precursors to said stripped gas and said stripped gas is released through said release valve.

12. The improvement as set forth and described in claim 10 wherein all of said excess hydrogen flows through said stripping zone and at least a part of the stripping zone off-gas flows through said pretreating zone.

13. The improvement as set forth and described in claim 10 wherein a portion of said excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone and the balance flows to said pretreating zone.

14. The improvement as set forth and described in claim 10 wherein a portion of said excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone and the balance flows directly to said pretreating zone.

15. The improvement as set forth and described in claim 10 wherein a portion of the excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone, the balance of said excess gas flows to said pretreating zone, a portion of the stripping zone off-gas flows to the pretreating zone, and the balance of the stripping zone off-gas is contacted with petroleum fraction to be pretreated in an absorber prior to hydrotreating.

16. The improvement as set forth and described in claim 10 wherein a portion of the excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone, a portion of the stripping zone off-gas flows to said pretreating zone, the balance of said off-gas is contacted with petroleum fraction to be pretreated in an absorber prior to hydrotreating, and the balance of said excess hydrogen flows directly to said pretreating zone.

17. The improvement as set forth and described in claim 10 wherein a portion of the excess hydrogen sufficient to reduce the concentration of harmful agent to an innocuous concentration flows through said stripping zone, the balance of said excess hydrogen flows directly to said pretreating zone, a portion of the stripping zone off-gas is contacted with petroleum fraction to be pretreated in an absorber prior to hydrotreating and the balance flows to said pretreating zone.

18. The improvement as set forth and described in claim 10 wherein substantially all of the excess gas flows through the stripping zone, substantially all of the stripping zone off-gas flows to the pretreating zone, and the gaseous fraction of the pretreating zone effluent is contacted with petroleum fraction to be pretreated in an absorber prior to hydrotreating.

19. In the reforming of naphtha containing in deleterious amounts agents harmful to satisfactory operation in catalytic reforming which agents form gaseous hydrogent derivatives in the presence of a hydrogenating catalyst and hydrogen wherein a charge naphtha is hydrotreated in a pretreating zone in a pretreating section in the presence of hydrogen-containing gas delivered to the aforesaid pretreating section from a reformer separator, wherein the deleterious concentration of the aforesaid agents harmful to satisfactory operation in catalytic reforming is reduced to innocuous concentration by contact of the liquid portion only of the effluent of the aforesaid pretreating zone in a stripping zone in the aforesaid pretreating section with at least a portion of the hydrogen-containing gas delivered to the aforesaid pretreating section to produce a pretreater section liquid effluent containing innocuous concentration of the aforesaid agents and stripper off-gas containing hydrogen derivatives of the aforesaid agents, wherein the aforesaid pretreater section liquid effluent is reformed in a reforming zone in a reforming section comprising the aforesaid reforming zone, a reformer separator, and a reformer gas compressor, to produce a reforming zone effluent, separating said reforming zone effluent in a reformer separator into reformer gas and reformer zone liquid effluent, pressuring said reformer gas to a pressure in excess of reforming zone pressure, and recycling at least a portion of said pressured reformer gas to said reforming zone, the improvement which comprises pressuring only a portion of the aforesaid reformer gas to a pressure in excess of reforming zone pressure, recycling said

pressured portion of the reformer gas to the reforming zone, flowing the balance of said reformer gas at reformer separator pressure less line loss to said pretreating section, releasing substantially all gases vented from both the aforesaid pretreating section and the aforesaid reforming section through a single absorber and a single release valve, and controlling the pressure at the aforesaid single release valve to maintain the pressure in the aforesaid pretreating section at the pressure of said reformer separator less pressure drop due only to normal pressure drop between said reformer separator and the aforesaid absorber.

20. The impovement as set forth and described in claim 19 wherein less than 10 percent of the total heat introduced into the charge naphtha is rejected to a coolant.

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