

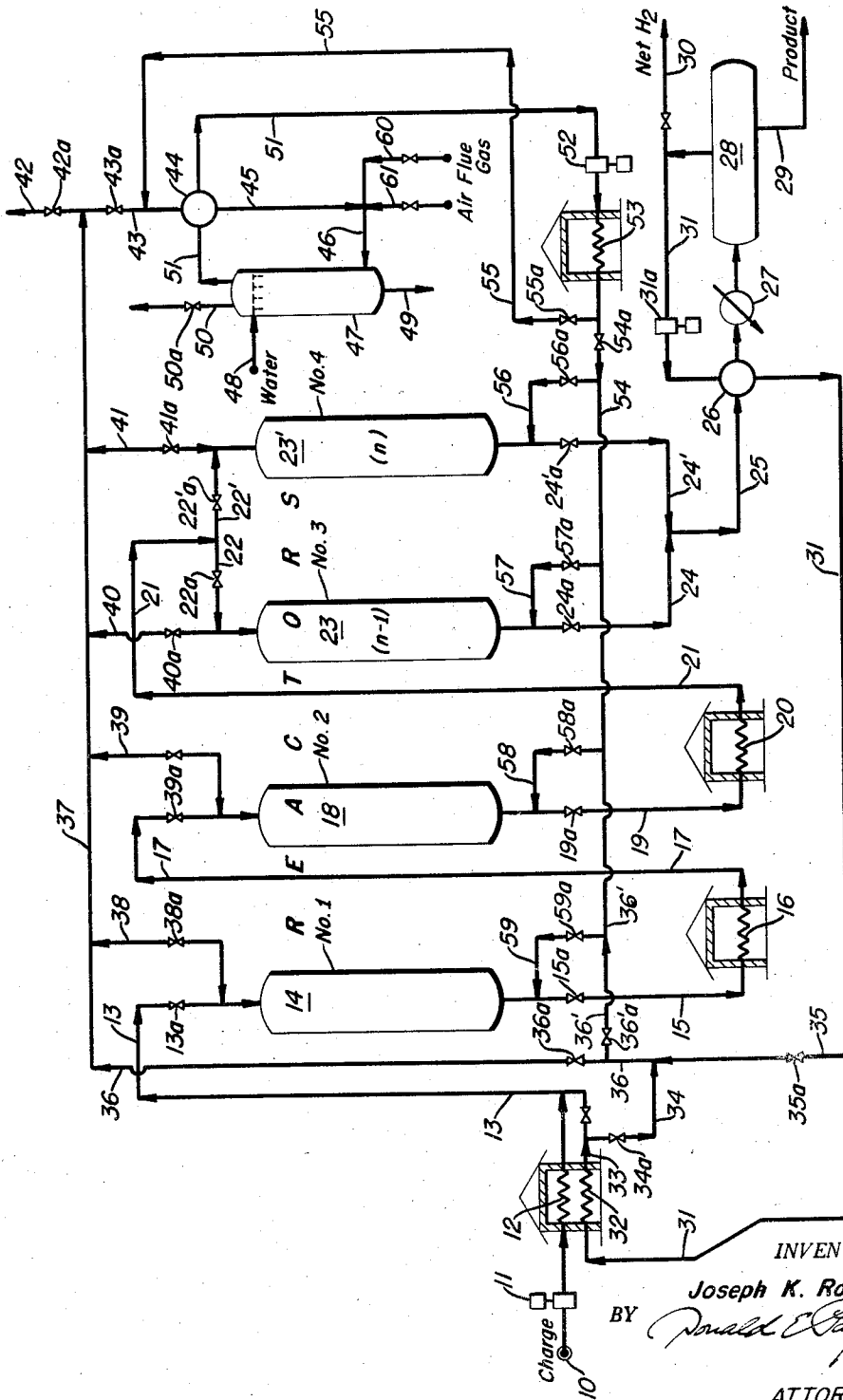
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REGENERATIVE PLATINUM HYDROFORMER SYSTEM

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REGENERATIVE PLATINUM HYDROFORMER SYSTEM

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2 Claims. (Cl. 196—50)

This invention relates to an improved regenerative platinum-on-alumina hydroformer system for producing maximum yields of high octane number motor fuel.

Non-regenerative platinum-on-alumina hydroforming systems (e. g. U. S. 2,654,694) offer the advantage of low initial investment cost but are subject to the serious disability that they cannot be operated for long periods of time to produce high octane number products, i. e. products having an octane number in the range of about 93 to 100; furthermore these non-regenerative systems, exemplified by the platforming process, usually require operating pressures in the range of about 500 to 750 p. s. i. g. in order to obtain a reasonable run length and these high pressures result in a loss of about 2 to 5 percent or more of potential gasoline yield. The original ultraforming process, as described in The Petroleum Engineer, volume XXVI (April 1954), page C-35, and claimed in U. S. Patent 2,773,014, enabled hydroforming with platinum-on-alumina catalyst at the low pressures required for obtaining markedly increased yields of higher octane number products from a given charging stock but, at the same time, required an increased capital investment because of the additional connecting lines, valves and regeneration equipment. The object of this invention is to provide an improved regenerative hydroforming process which will retain the advantages of the ultraforming process but markedly decrease initial investment costs. In other words, the object is to combine the low initial cost advantage of the non-regenerative system with the advantage of maximizing yields of increased octane number gasoline obtainable with the ultraforming process. Other objects will be apparent as the detailed description of the invention proceeds.

In practicing the invention at least three reactors are connected in series with a preheater ahead of the first reactor and reheaters between the first and second and between the second and third reactors, respectively. For some charging stocks and for obtaining very high octane number products of the order of 96 to 100, it may be necessary or desirable to have four or five reactors connected in series with reheaters between the third and fourth and between the fourth and fifth. In any event, an alternate reactor is provided to operate in parallel with the final or tail reactor of the series so that during periods when no regeneration is required, the alternate reactor may be operated in parallel with the tail reactor and so that one of these last two reactors may be regenerated while the other remains on-stream. By operating all but the tail reactors under properly controlled conditions, the catalyst therein may remain on-stream for a period of about four months to two years without requiring regeneration, i. e. until such time as it is desirable for a plant shutdown to insure that all parts thereof are in proper condition. However, the tail reactors, i. e. those in which the product octane number is increased to the final high value in the range of about 93 to 100 octane number, when operated under the relatively low pressures of 100 to 350 p. s. i. g. required

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for obtaining high yields of such high octane number products, necessarily require periodic regeneration and/or rejuvenation. In this invention, such regeneration and/or rejuvenation can be effected without interrupting onstream flow.

When the average catalyst temperature in the first reactor is maintained in the range of about 800 to 875° F. and the catalyst bed in the second reactor is maintained at an average temperature substantially below 900° F. but usually above 850° F., both of these reactors may be operated with proper charging stocks from four months to two years without requiring regeneration. The octane number obtainable from the second reactor effluent in this case usually does not exceed about 85 octane number and, in order to obtain products in the 93 to 100 octane number range, it is usually necessary to operate the tail reactors at an average temperature substantially above 900° F. under which conditions carbonaceous deposits are formed on the catalyst and periodic regeneration is required. Whenever after the inlet temperature to the tail reactor has been increased to the maximum extent permissible (about 960–970° F.) the effluent from one of the tail reactors has suffered an octane number decrease of the order of 1 to 3 octane numbers, i. e. about 2 octane numbers, the catalyst in that reactor should be regenerated. At this time the parallel operation of the tail reactors is discontinued, the temperature of the stream entering the remaining tail reactor is preferably raised at least about 10° F. in order to compensate for the doubled space velocity and on-stream flow is continued through only one of the tail reactors while catalyst in the other is being regenerated and rejuvenated. When the freshly regenerated and rejuvenated bed goes on-stream, the inlet temperature should be lowered since the desired octane number can be produced under normal operating conditions with the regenerated reactor while the other tail reactor is undergoing regeneration. Thereafter, both tail reactors are again operated in parallel until further regeneration is required.

It is important that the charging stock be substantially free from catalyst poisons and when such charging stocks contain large amounts of sulfur, nitrogen and other deleterious components, it is preferably subjected to a hydrofining pretreatment either with a platinum-on-alumina catalyst or a so-called sulfur-immune catalyst such as a mixture of cobalt and molybdenum oxides on activated alumina. To insure removal of all nitrogen compounds, the preliminary hydrofining operation may be effected in the presence of a halide which, in turn, may be a component of the hydrofining catalyst or may be introduced as a component of the hydrofining charge. With a properly selected and/or pretreated charge, the regenerative hydroforming system herein described may remain on-stream for a year or more in the production of 93 to 100 octane number products in much larger yields than could be produced in non-regenerative systems.

The invention will be more clearly understood from the following description of a specific example read in conjunction with the accompanying drawing which forms a part of the specification and which is a schematic flow diagram of the improved hydroforming system.

The naphtha charge in this example is a virgin Mid-Continent naphtha having a boiling range of about 200 to 360° F., containing about 50 percent paraffins, 42 percent naphthenes and 8 percent aromatics, having a research octane number of about 45 and being substantially free from sulfur and nitrogen compounds, the sulfur content being preferably not more than .01 percent and the nitrogen content not more than 1 or 2 parts per million. In order to remove sulfur, nitrogen and other deleterious components from the charging stock, it may be pretreated, for example, by hydrofining with a

platinum-on-alumina catalyst or with a so-called sulfur-immune catalyst containing an oxide or sulfide of a group VI metal such as molybdenum or tungsten combined with an oxide or sulfide of a group VIII metal such as nickel or cobalt on an alumina support. The hydrofining or hydrodesulfurization conditions should be selected to effect removal of nitrogen as well as sulfur. The charge is preferably stripped and/or fractionated after the preliminary hydrofining step as described in greater detail in U. S. Patent 2,800,428.

The naphtha charge from source 10 is pumped by pump 11 to a pressure of about 300 p. s. i. g. and passed through preheater coil 12 wherein it is vaporized and heated to about 900° F. and then introduced through line 13 to reactor 14 together with about 4,000 to 8,000 cubic feet per barrel of hot recycled hydrogen so that the inlet temperature to reactor 14 is in the range of about 900 to 950° F., the temperature being in the lower part of this range at the beginning of the operation and being raised as the operation proceeds. For a plant processing about 10,000 barrels per day of charge, reactor 14 may contain about 10 to 12 tons (about 400 to 500 cubic feet) of platinum-on-alumina catalyst in the form of 1/8 inch diameter pellets. Such catalyst may be prepared as described in U. S. 2,659,701 or by any other method known to those skilled in the art and, since no novelty is claimed in the catalyst per se, it will not be described in further detail. The catalyst may contain a small amount of halogen such as fluorine or chlorine but it should be substantially free from sodium, iron and molybdenum.

The conversion in reactor 14 is highly endothermic and the average temperature in the catalyst bed in this first reactor is in the range of 800 to 875° F. Initially the effluent temperature may be as low as 750° F. but during continued operation the effluent temperature increases to about 800° F. and even to 850° F. This effluent is passed by line 15 to reheater 16 wherein it is reheated to a temperature in the range of about 900 to 950° F. and introduced by line 17 to reactor 18 which may contain approximately the same amount of the same type of catalyst as is employed in reactor 14. In this system, however, it is possible to employ different amounts of catalyst in reactors 14 and 18; reactor 14 may contain only 8 tons and reactor 18 may contain 12 tons of the defined catalyst. The average temperature in the catalyst bed in reactor 18 is usually above 850 and below 900° F., the effluent leaving this reactor at a temperature of at least about 825 but below 900° F., the temperature usually increasing within this range as the run proceeds.

Effluent from reactor 18 is passed by line 19 to reheater 20 wherein it is heated to a temperature in the range of about 920 to 980° F. and then passed by line 21 and lines 22 and 22' to reactors 23 and 23' which are connected to operate in parallel. In a four reactor system these reactors are referred to as the final or tail reactors. It should be understood that an additional number of reactors may be employed, each preceded by a preheating step, use of additional reactors being desirable in systems for producing 97 to 100 octane number product. In this example reactors 23 and 23' each contain the same amount of the same type of catalyst which is contained in reactor 14. At the beginning of an on-stream period charge may be introduced into these tail reactors at a temperature of about 920° F. but as the run proceeds the inlet temperature is raised. The average catalyst bed temperature in the tail reactors is in the range of 900 to 950° F. and the effluent from the tail reactors at a temperature of at least about 900° F. is withdrawn through lines 24 and 24', line 25, heat exchanger 26 and cooler 27 to separator 28 wherein hydrogen is separated from condensed hydrocarbons at a temperature not substantially higher than 100° F.

The condensed hydrocarbons are withdrawn through line 29 to any known type of product recovery system; in this example the product will require depropanizing but will not require rerunning. The net hydrogen produced

is withdrawn through line 30 usually to a suitable absorber for recovering hydrocarbons therefrom. The remainder of the hydrogen is recycled by compressor 31a through line 31 and heat exchanger 26, most of the hydrogen passing through heating coil 32 and lines 33 for admixture with charging stock vapors in transfer line 13.

A part of the heated hydrogen may be withdrawn through line 34 in amounts controlled by valve 34a for admixture with another part of the recycled hydrogen withdrawn from line 35 in amounts controlled by valve 35a. This hydrogen mixture may be passed by line 36 which communicates with line 37 to any selected reactor by branch lines 38, 39, 40 and 41. Line 37 also serves as a regeneration gas line from which gases may be vented to a stack by line 42 in amounts controlled by valve 42a. By closing valve 42a and opening valve 43a regeneration gases may be circulated by line 43 through heat exchanger 44, line 45 and line 46 to the base of scrubber 47 wherein the gas is cooled and scrubbed by water or alkaline aqueous medium introduced through line 48 and withdrawn through line 49. Excess gas may be vented from the top of scrubber 47 through line 50 in amounts controlled by valve 50a. Cooled gas from the top of scrubber 47 may be passed by line 51 through heat exchanger 44 and then compressed by compressor 52 and heated to the desired temperature in heater 53 for return through line 54. A by-pass line 55 containing valve 55a provides for recycling heated gas to scrubber 47. Line 54 communicates with each of the reactors through lines 56, 57, 58 and 59, respectively.

After the on-stream operation above described has been in progress for a number of days or weeks, there will be a decline in catalyst activity, particularly in the tail reactors. When after increasing the inlet temperature to about 960° F. the octane number of the effluent leaving reactor 23 drops from about 96 to 94 it is usually desirable to regenerate and rejuvenate the catalyst in this reactor. At this time valve 22a is closed and the reactor contents are purged from the reactor by introducing hydrogen from lines 36 and 37 through line 40 by opening valve 40a. When reactor 23 is thus taken off-stream by closing valve 22a it is preferred to increase the reheat temperature of the inlet stream to reactor 23' by at least about 10° F., e. g. to about 975° F., in order to avoid undue octane number decline in the final effluent. After hydrocarbons have been purged from reactor 23 with hydrogen introduced through line 40, valves 34a and 35a are closed and valve 42a is set to depressure the reactor and vent the hydrogen to a stack, valves 24a and 43a being closed. Meanwhile, flue gas produced in an external source (not shown) is introduced by line 60 and line 46 and is being circulated by line 51 to compressor 52 and heater 53 and thence back by line 55. When reactor 23 has been depressured, valve 54a and 57a are opened and valve 55a is closed so that the flue gas passes upwardly through reactor 23 for purging hydrogen therefrom. After the flue gas purge of the hydrogen is complete valve 42a is closed, valve 43a is opened and the pressure in reactor 23 is gradually raised to about 200 to 300 p. s. i. g. by continued introduction of flue gas with heater 53 discharging at a temperature of about 700° F. When the desired regeneration pressure has been reached, the introduction of flue gas through line 60 is discontinued and air is introduced through line 61 to give about a 1 percent oxygen concentration in the circulating flue gas entering the reactor which effects combustion of carbonaceous deposits on the catalyst in a combustion zone which traverses the catalyst bed in reactor 23. The amount of oxygen is controlled to prevent the bed temperature from exceeding about 1050° F. The net flue gas produced by the combustion is vented from the system through line 50 and valve 50a which may now be set to hold the desired back pressure.

When the catalyst is completely regenerated by burning combustible deposits thereon, the introduction of air

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is continued through line 61 but heater 53 is set to heat the recycled gas to a temperature of about 1050° F. and the catalyst is thus given a treatment with a gas having a high oxygen partial pressure for effecting rejuvenation. Thereafter the introduction of air is discontinued, valve 50a is set for pressure reduction and the oxygen-containing gas is purged from the system through line 50. To complete this purge, flue gas is again introduced through line 60, valve 42a is opened and 43a is closed and all oxygen is removed from the system by flue gas. Thereafter the regeneration system is shut down. Valve 54a is closed and hydrogen is introduced at the base of the reactor by opening valve 36'a (valve 36a being closed), line 36' and line 57. The temperature of the hydrogen thus introduced by line 36' is controlled by regulating valves 34a and 35a. As soon as all of the flue gas has been eliminated from the reactor system through lines 40, 37 and 42, valve 42a is set for repressuring to required on-stream pressure; during this period valve 36a may be opened and valves 36'a and 57a may be closed and when the reactor reaches the desired pressure, valve 24a may be opened, valves 36a and 40a closed and inlet charging stock stream is reintroduced by opening valve 22a. Instead of the regeneration and rejuvenation system herein described, the regeneration system taught and claimed in co-pending application Serial No. 416,072 may be used.

When reactor 23 is returned on-stream (with an inlet temperature of about 920° F.) the catalyst in reactor 23' may be regenerated and rejuvenated in a similar manner. Such regeneration and rejuvenation may only require about 12 to 24 hours and when reactor 23' is again placed on-stream, both of the tail reactors may be operated in parallel until the effluent stream from one of them has an octane number below about 94. Obviously, the amount of stream introduced through line 21 may be introduced into reactors 23 and 23' in any desired proportions by controlling valves 22a and 22'a. The inlet temperature of the stream entering the tail reactors may be increased from about 920 to 960° F. to maintain the desired octane number and, after a period of parallel operation, it is desirable to further increase the inlet temperature by at least about 10° F. in the single reactor which is on-stream while the other tail reactor is undergoing regeneration.

By employing the conditions in the earlier reactors hereinabove set forth, these reactors may be operated for from 4 to 24 months without requiring regeneration. By that time it is usually desirable to shut down the entire plant for inspection and repair and the catalyst in reactors 14 and 18 can be regenerated while the plant is thus shut down, using the same sequence of operations described above for reactor 23. The plant and operation herein described requires a much lower capital investment than the hydroforming system wherein an alternate reactor is connected to be operated in parallel with each and all of the reactors in the system. Still further savings in capital investment may be effected by limiting the regeneration to the tail reactors and replacing the catalyst in the first two reactors during the shut-down period. At the same time the advantages of ultraforming are obtained, i. e. the increased yields of high octane number motor fuel in the range of 93 to 100 octane number, better utilization of catalyst activity and greater flexibility than could possibly be obtained with a non-regenerative system. While maximum advantages are obtainable by operations with on-stream pressures in the range of 100 to 350 p. s. i. g., the apparatus and process features herein described may likewise be used in systems wherein the on-stream pressures are substantially higher, i. e. 400 to 750 p. s. i. g. or more, at least in the stages preceding the tail reactors.

I claim:

1. In a regenerative process for hydroforming naphtha with platinum-on-alumina catalyst in a system operated

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at about 100-350 p. s. i. and containing four reactors, the method of operation which comprises preheating the naphtha and recycled hydrogen, contacting the preheated naphtha and hydrogen in a first reactor at an average temperature in the range of about 800 to 875° F., reheating the effluent from the first reactor and contacting the reheated effluent in a second reactor at an average temperature at least about 850° F. but below 900° F., reheating the effluent from the second reactor and passing it in parallel through third and fourth reactors while maintaining an average temperature in the third and fourth reactors in the range of about 900 to 950° F., periodically passing all reheated effluent from the second reactor through the third reactor while regenerating catalyst in the fourth reactor and passing all reheated effluent from the second reactor to the fourth reactor while regenerating catalyst in the third reactor, increasing the amount of heat supplied to the effluent leaving the second reactor and the average temperature in the third reactor while the fourth reactor is undergoing regeneration and regenerating catalyst in the first and second reactors only during periods when no reactors are on-stream.

2. In a process for converting a low octane number naphtha into a naphtha boiling range product having an octane number in the range of about 93 to 100 octane number in a regenerative hydroforming system employing platinum-on-alumina catalyst at a pressure in the range of 100 to 350 p. s. i. in n reactors where n is at least 4, the improved method of operation which comprises preheating said low octane number naphtha and recycled hydrogen and introducing the preheated mixture into the first reactor at a temperature of about 900 to 950° F., withdrawing effluent from the first reactor at a temperature in the range of 750 to 850° F. so that the average first reactor temperature is in the approximate range of about 800 to 875° F., reheating the first reactor effluent to a temperature in the range of 900 to 950° F. and passing it through a second reactor to obtain a second reactor effluent having a temperature of at least 825° F. but below 900° F., the average temperature in the second reactor being at least about 850° F. but below 900° F., reheating effluent to be introduced to the final n and $n-1$ reactors to a temperature in the range of 920 to 980° F. and passing said last named reheated effluent in parallel through the final reactors to obtain reactor effluents having a temperature at least about 900° F., continuing the parallel operation of the final reactors until there is an octane number decline in effluent leaving one of said final reactors of approximately 2 octane numbers, then diverting all of the finally reheated effluent to the other of said final reactors while catalyst is regenerated in the one final reactor, increasing the inlet temperature to the final on-stream reactor at least about 10° F. while catalyst in the alternate final reactor is undergoing regeneration after a period of parallel operation, and regenerating catalyst in the first and second reactors only during periods when no reactor is on-stream.

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