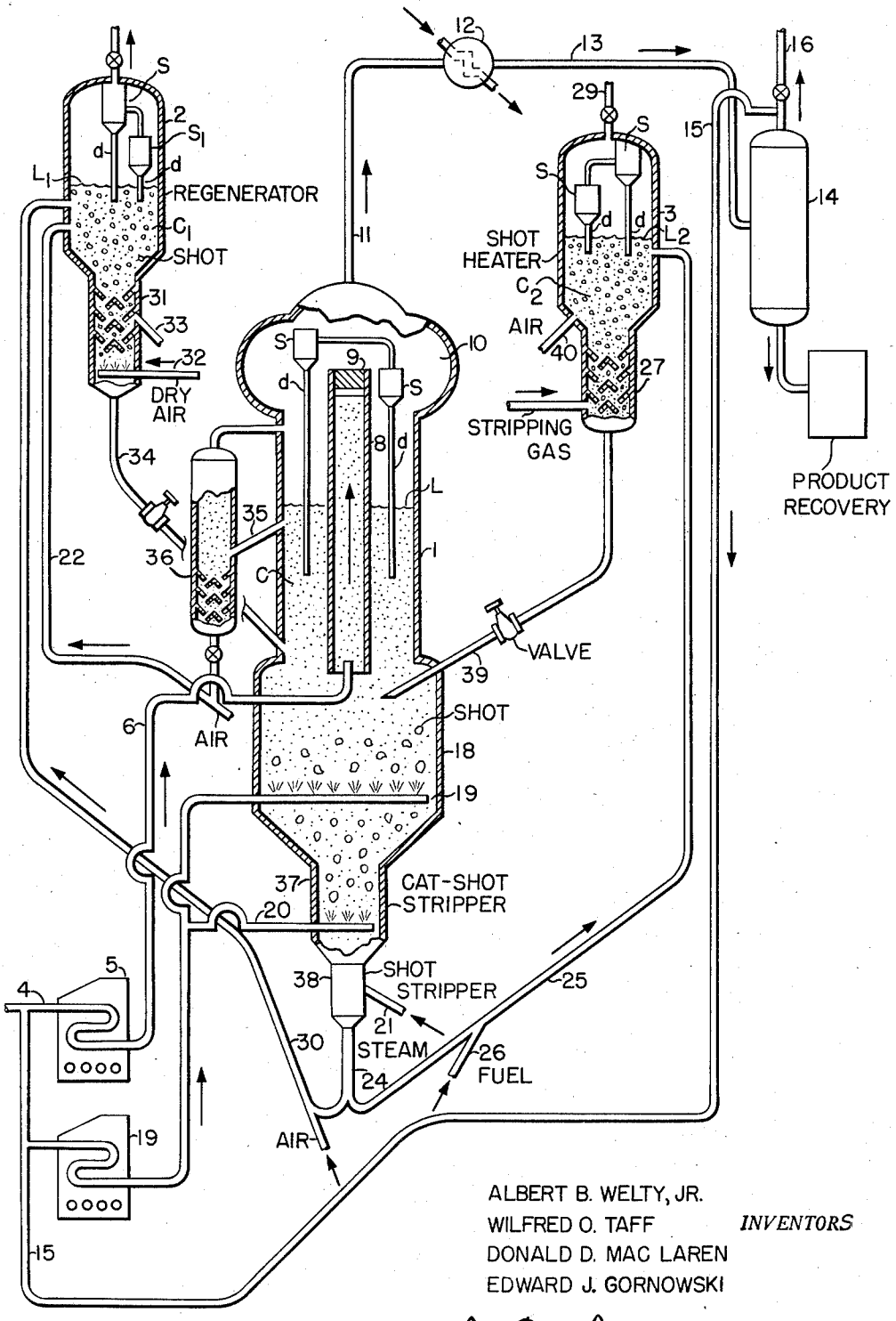
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HYDROFORMING WITH FLUIDIZED CATALYST AND INERT HEAT TRANSFER SOLIDS

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HYDROFORMING WITH FLUIDIZED CATALYST AND INERT HEAT TRANSFER SOLIDS

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The present invention relates to the catalytic conversion of hydrocarbon fractions containing naphthenes and paraffins. More particularly, it relates to the particular method of hydroforming gasolines and naphthenes in the presence of hydrogen and a platinum, aluminum catalyst.

In a copending application Serial No. 453,456, filed September 1, 1954, in the name of Frederick W. Steffgen, C. N. Kimberlin, Jr. and Fred J. Buchmann, there is described and claimed a method of hydroforming naphthas in the presence of a platinum group metal catalyst in fluidized state, the operation being conducted at relatively low pressures and relatively low recycle gas rates.

Hydroforming is a matter of record and commercial practice. The catalyst used in hydroforming comprises platinum group metals or metal oxides of the IV, V and VI periodic system, suitably supported. Other than platinum, the most commonly suggested catalyst is one containing molybdenum oxide on alumina. The principal reactions in the hydroforming of naphthas are (1) dehydrogenation of naphthenes to the corresponding aromatic, (2) isomerization of paraffins and (3) hydrocracking of the higher boiling paraffins.

The object of the present process is to very substantially increase the octane rating of the naphtha by the formation of aromatics, branched chain paraffins and aromatization of compounds such as normal heptene. It is, of course, important from the standpoint of economic feasibility to obtain as high a yield as possible of the desired high octane product.

Heretofore, and prior to the present invention, commercial operations employing a platinum catalyst have been conducted at high pressures, say, of the order of 300–800 p. s. i. g. and utilizing high "recycle gas" rates, that is to say, feeding with each barrel of oil to the reaction zone 4000 to 10,000 cubic feet of a hydrogen-containing gas. Such operations are characterized by two disadvantages (1) dehydrogenation is suppressed and hydrocracking increased so that yield octane relationships are poorer than at lower pressure; and (2) equipment is expensive because of the high pressure and large quantity of recycle gas which must be compressed, heated and cooled.

The present invention relates to a method of operating a hydroforming process using a platinum-containing catalyst under conditions of relatively low pressures, say, of the order of 50 p. s. i. g. and very low recycle gas rates, that is to say, feeding to the reaction zone with each barrel of oil, less than 1000 standard cubic feet of recycle gas, and preferably, from 150–500 standard cubic feet of hydrogen per barrel of oil.

Under these conditions maximum yields of high octane product are possible and equipment cost is considerably reduced due to the major reduction in recycle gas rate.

When operating under these conditions, three problems must be solved: (1) A unique method of supplying heat of reaction must be provided. This results from the very limited amount of recycle gas which is used; (2) a unique type of fluid reactor must be used due to the very high activity of the freshly regenerated catalyst which makes a conventional dense fluid bed too shallow for good reaction efficiency; and (3) a unique method of continuously reactivating the spent catalyst must be provided to maintain its high activity under conditions which cause rapid carbon lay down.

The object of the present invention is to provide a continuous method for hydroforming naphthas, utilizing a platinum-containing catalyst, under the conditions stated.

Another object of the present invention is to provide a hydroforming process adapted to operate continuously and to effect the maximum yield-octane number relationship.

Another object of the present invention is to provide a hydroforming process adapted to effect important economies with respect to the amount of gasiform material required to be compressed, heated and cooled.

Another object of the present invention is to adapt a hydroforming process using a platinum-containing catalyst to the fluidized catalyst technique, and thus to secure the advantages of that technique with respect to continuity of operation, uniformity of temperature in the catalyst bed and flexibility of operation.

In brief compass, the present invention relates to a method, as previously indicated, of operating the hydroforming process at pressures as low as 50 p. s. i. g. when recycling as little as 200 standard cubic feet of hydrogen per barrel of oil. These conditions are, of course, drastically different from the 300 to 800 p. s. i. g. and the 4000–10,000 standard cubic feet of recycle gas per barrel of oil that heretofore have been considered normal for hydroforming in the presence of a platinum catalyst. The change in both of these variables increases the rate at which the catalyst is deactivated. It also requires that heat of reaction be supplied by other means than feed and recycle gas, and that a unique reactor design be used.

The increased rate of catalyst deactivation requires that the catalyst be regenerated more often. In other words, only short on-stream periods of, say, from 1 to 24 hours, can be tolerated while still maintaining a high yield-octane number relationship and high catalyst activity. This type of operation, of course, would not be very practical in a system utilizing a fixed bed of catalyst. It can, however, be readily adapted to a process utilizing fluidized solids provided that (1) a satisfactory reactivation procedure is used; (2) a means is provided for supplying heat of reaction; and (3) a suitable reactor design is provided to use the very high activity of the catalyst. This invention provides all of these necessary items.

In the accompanying drawing, there is set forth, diagrammatically, an apparatus design in which a preferred modification of the present invention may be carried out into effect.

Referring in detail to the drawing, **1** represents a hydroforming reactor which has expanded upper and lower portions; **2** represents a catalyst regenerator; and **3** represents a heater for shot, which is utilized in supplying heat to the endothermic reaction occurring in **1**. In operation, a mixture of recycle gas and naphtha is charged from line **4** to a furnace **5** wherein it is heated to a temperature of about 925° to 975° F., and then charged via line **6** to reactor **1**. It should be pointed out that the mixture in line **4** may be heat exchanged with hot product from reactor **1** before it is charged to furnace **5** in means not illustrated. It will be noted that reactor **1** contains a bed of catalyst C, which is in fluidized form and has an upper dense phase level L. The reactor **1** is provided with a draft tube **8** so that the circulation of catalyst is from the bed C into the bottom of draft tube **8**, thence upwardly admixed with the naphtha vapors and the recycle gas. It is in this draft tube that the reaction occurs. Use of this draft tube makes pos-

sible efficient use of the high activity catalyst. The upper portion of the draft tube is provided with veins **9** which enable a separation of catalyst from the gasiform material, which catalyst then descends toward the bed C. The expanded portion **10** of reactor **1** operates also to effect a substantial separation of catalyst from the gasiform material. The gasiform material then passes upwardly toward the top of reactor **1**, and before it is withdrawn from the reactor, it is forced through one or more cyclones S wherein catalyst still entrained in the gasiform material is removed and returned to the bed of catalyst C through one or more dip pipes *d*. The crude product admixed with hydrogen is withdrawn overhead from reactor **1**, through line **11**, thence passed through a condenser **12**, wherein it is cooled to a temperature of about 100° F., thence passed via line **13** into a separator **14**. The crude product is withdrawn from separator **14**, and delivered to a finishing still and other conventional equipment (not shown) to recover the desired hydroformate. Overhead from separator **14**, through line **15**, there is recovered a gasiform material which contains from 85–95% hydrogen, the remainder being light hydrocarbons. Because of its high hydrogen content this material is especially useful in other processes such as in hydrofining thermal or coker naphthas and/or sulfur bearing stocks. This hydrogen rich gas may be withdrawn from the present system for the uses just stated, via line **16**. A small portion of this material is recycled via line **15** to line **4** for reuse in the process.

Since under the severe conditions under which the present process operates, the catalyst C is rapidly contaminated with carbonaceous and other deposits, which deposits cause deactivation of the catalyst, it is necessary to regenerate the catalyst at frequent intervals. Toward this end, catalyst is withdrawn from reactor **1** via line **35** into stripper **36** where it is stripped with steam to remove occluded and/or adsorbed hydrocarbons and hydrogen. The catalyst is withdrawn from the stripper **36** and is transported in air via line **22** to the regenerator. Carrier air is limited in quantity to that which will not cause the catalyst temperature to exceed 1050° F. The catalyst is carried in suspension in said air stream into regenerator **2** and therein treated in the form of a fluidized bed C_1 under conditions more fully explained hereinafter. The bed C_1 has an upper dense phase level L_1 above which there is a dilute phase suspension of solids in gasiform material. Before the fumes are withdrawn from the regenerator, they are forced through one or more gas-solids separators to remove entrained catalyst, which is returned to the bed C_1 through one or more dip pipes *d*. The fumes are withdrawn overhead from the regenerator and they are passed through a hot oil scrubber (not shown) to recover whatever catalyst still persists in the said fumes. The regenerated catalyst, together with shot from the reactor, which serves to control regenerator temperature, then flows into a lower portion **31** of more restricted cross section than the main portion of the regenerator. In this portion the catalyst, substantially free of carbon, is treated with air for an extended period of time. This treatment serves to rejuvenate the catalyst, possibly by reducing the crystalline size of the platinum particles. Toward this end, the flow of air through the inlet pipe **32**, upwardly through the catalyst in the baffle section **31**, is continued for an extended period of time to reactivate the catalyst. Since the catalyst, preferably, contains a few weight percent of chlorine, and since this chlorine may be lost during the reaction and/or the regeneration process, additional chlorine may be added through line **33** to the catalyst in section **31**. The regenerated and reactivated catalyst is returned to reactor **1** via line **34**.

As previously mentioned, shot is used to supply the major portion of the heat of reaction. To this end, hot shot from burner vessel **3** enters the bottom expanded section **18** of reactor **1**. In this zone it gives up its heat and settles into stripper **37**. In zone **37** catalyst is stripped from the shot with recycle gas supplied via line **20**. The pure shot then passes into lower stripping zone **38** where occluded and/or adsorbed hydrogen and hydrocarbons are stripped from the shot with steam. The shot then passes downward into standpipe **24** and is split into two streams. One stream, as previously mentioned, is transported with air to the regenerator via line **30** where it serves to control temperature. The major portion of the shot is transported via line **25** to an elevated burner vessel **3**. The transport gas is formed by combustion of fuel supplied in the burner vessel via line **26**. The burner vessel is at such a height that with the reactor at 50 p. s. i. g. pressure, the burner is at essentially atmospheric pressure. The differential pressure is supplied by the dense standpipe of shot **39**. With this arrangement air at essentially atmospheric pressure can be fed to the burner vessel via **40**, thus affecting considerable savings in air compression. Air is charged to shot heater **3** via line **40** and burns the fuel supplied via line **25** with release of heat which is taken up by the shot. The shot is formed into a dense fluidized bed C_2 in heater **3** by controlling the superficial gas velocity, the bed having an upper dense phase level at L_2, above which there is a dilute phase extending from L_2 to the top of the vessel. Before the combustion fumes are withdrawn from the heater, they are forced through one or more solid gas separators S wherein entrained solids are removed and returned to the bed C_2 by one or more dip pipes *d*. The fumes emerge from the heater **3** through line **29** and their sensible and chemical heat may be recovered to preheat the feed oil to generate steam, drive the main air compressor turbine, or otherwise utilized. The heated shot is withdrawn through a baffled nipple **27** wherein it is treated with steam or other gas for the purpose of stripping out occluded or adsorbed oxygen. The heated shot is returned to reactor **1** via transfer line or standpipe **39**.

In prior practice where the fluidized catalyst technique has been employed with a hydroforming catalyst, or where a fixed bed of catalyst has been employed in hydroforming, over 50% of the heat required to support the endothermic hydroforming reaction has been supplied through the medium of the recycle gas. This recycle gas has a relatively low heat capacity, requiring 4000–8000 s. c. f./b. to supply the needed heat. Circulating this large quantity of gas is achieved only at great cost.

In the present process some heat is, of course, obtained as the heat content of the hot regenerated catalyst is returned from regenerator **2** to reactor **1**. Some heat is supplied by the combined feed and recycle gas stream entering the reactor. However, the total heat thus recovered is a minor fraction of that required in reactor **1**. To supply the major portion of the heat to the reaction zone, according to the present invention, an inert material such as mullite in the form of particles having a size of, say, from 400 to 500 microns, and commonly referred to as shot is heated in the burner **3**, and thence charged to reaction zone **1**. The shot is heated by burning fuel which can be the tail gas obtained from the product recovery system or any liquid fuel such as kerosene, etc.

It will be obvious that the apparatus layout depicted in the accompanying drawing sets forth merely the essentials of such an apparatus, and that in a commercial plant accessory apparatus would actually be employed to facilitate the operation; thus, automatic temperature and pressure control devices, temperature and pressure recording devices, pumps, additional valves, all well known to the skilled petroleum engineer, would obviously be included in a commercial plant. Also transfer lines and standpipes carrying solids may be provided with injected gas to facilitate the flow of solids. A detailed

showing and description of this additional equipment has been omitted in the interest of clarity and to focus attention on the improvements claimed herein.

In order to explain the invention further, the following specific example is set forth with the understanding that it is purely illustrative, but in no wise limitative.

EXAMPLE

A naphtha of the following inspection was treated according to the present invention under the following conditions with the results set forth below:

Inspection of feed

Boiling range, ° F	215 to 335
Vol. percent aromatics	10
Vol. percent paraffins	51
Vol. percent naphthenes	39
Octane number CFRR	51

Conditions in reactor 1

	Preferred	Range
Catalyst	½ wt. percent Pt on 99.5 wt. percent eta alumina, plus 2% Cl_2 based on tot. wt. of catalyst.	
Length of catalyst onstream period	8	1–12
Temperature, °F	900	875–975
Pressure, p. s. i. g	50	0–100
Oil Feed Rate, lbs. of oil fed/hr./lb. of catalyst in reactor	9	6–14
Standard cubic feet of hydrogen fed to reaction zone per barrel of oil	200	200–1,000
Concentration of hydrogen in recycled hydrogen gas	90	85–95
Reactor velocities, ft./sec.:		
Draft tube reaction zone	10	5–15
Bottom heating zone	0.25	0.2–0.5
Catalyst Particle Size, microns:		
0–44	5	0–20
44–74	43	30–50
74–104	47	35–55
104+	5	0–10

Inspection of product

Vol. percent C_5+ hydrocarbons based on feed	89.0
Vol. percent aromatics in C_5+	55
Vol. percent naphthenes in C_5+	2
Vol. percent paraffins in C_5+	43
Vol. percent C_4	2.6
Dry gas	4.3
Octane number	90

In the foregoing example in order to maintain catalyst activity, it was found necessary to regenerate every 8 hours. This was accomplished under the following conditions:

Conditions in regenerator

	Preferred	Range
Temperature, °F	1,100	1,000–1,125
Pressure, p. s. i. g	50	0–100
Residence time of catalyst in regenerator, minutes	15	5–30
Oxygen in flue gas, wt. percent	5	2–10

After the major portion of the carbonaceous and other deposits were removed, straight air was used for removing the remainder of the deposits from the catalyst. It was found, however, that this method did not completely restore the activity of the catalyst and, therefore, it was subjected to the following supplementary treatment in baffled portion 31 of regenerator 2, as set forth below:

Supplementary treatment of substantially carbon-free catalyst

	Preferred	Range
Temperature, °F	1,075	950–1,100
Pressure, p. s. i. g	50	0–100
Composition of treating gas	1% Cl_2+99% air (dry)	
Duration of treatment, hours	1	½–4

Following the treatment with the diluted gas, as set forth above, the catalyst was treated with air for a period of five minutes to one hour to flush out excess chlorine.

The experimental work upon which the present invention is in part based, clearly demonstrates that without the foregoing treatment of this substantially carbon-free catalyst with the chlorine-containing gas, that the activity of the platinum catalyst was not restored. In other words, under the very severe conditions of operation set forth above, the catalyst following regeneration must be treated with the chlorine-containing gas to restore its activity to that of fresh catalyst. This treatment with the chlorine gas need not be performed continuously, but should be utilized when the catalyst activity level drops as evidenced by a loss in octane number at constant conditions. A good indication of catalyst activity is determined by X-ray examination of the catalyst. A deactivated catalyst may have some 70 wt. percent of its platinum crystals in an average crystal size of 450 A. units as determined by such X-ray diffraction. On the other hand, a reactivated platinum catalyst has no crystals detectable by X-ray diffraction analysis.

To recapitulate briefly, the relatively low pressure and low recycle gas rate process, utilizing a fluidized bed of a platinum catalyst described above is a feasible process provided the foregoing reactivation technique of the deactivated catalyst is employed in conjunction with the on-stream process. Due to the rapid deactivation of the catalyst under the severe conditions of the present process, the catalyst must be regenerated and chlorine-treated at frequent intervals so that the residence time of the catalyst in the reaction zone is from 1 to 12 hours, whereupon it must be removed and reactivated. The fact that low pressures and low recycle gas rates are employed, effects important economies in the operation. For example, the reactor recycle gas compressor and associated heat exchange equipment are very considerably reduced in size.

The present process may be carried out at conventional hydroforming temperatures, but the pressure and recycle gas rate may be considerably lower. For example, pressure may vary within the limits of from 0 to 100 p. s. i. g. and the recycle gas rate from 200 to 1000 standard cubic feet of hydrogen fed to the reaction zone per barrel of oil feed. The catalyst may contain from 0.5 to 1.5 wt. percent platinum carried on an active form of alumina. A minor percentage of silica may be included in the catalyst composition, and it is also desirable to have a minor percent of chlorine associated with the catalyst composition. Palladium may be used in place of platinum, but the amount of palladium should be about three times that of platinum as set forth above, since palladium is not as active a catalyst.

The chlorine treatment of the substantially carbon-free catalyst should be carried out under essentially dry conditions. Thus, if the chlorine treatment is carried out in the regenerator shown in the drawing, it is necessary to supply dry air to the bottom section of the regenerator. It is within the compass of the present invention to use a separate vessel to treat the catalyst following the normal regeneration for the supplementary treatment of the catalyst with the chlorine-containing gas. In this supplementary treatment, the partial pressure of chlorine admixed with air may vary from 0.1 to 1 atmosphere. Good results are obtained in this chlorine treatment when operating at a pressure of about 50 p. s. i. g., using dry air to dilute the chlorine, and operating at temperatures at about 950°–1100° F. for a period of 30 minutes to 4 hours. In order to add the necessary heat to support the endothermic hydroforming reaction, the present invention proposes the use of hot shot, which shot is charged to the reaction zone wherein it mixes with the catalyst therein, giving up its heat, is withdrawn from the bottom of the reaction zone and returned to a heater where it is heated in the presence of a burning fuel.

Many modifications of the present invention will be apparent to those who are familiar with the present art.

What is claimed is:

1. The method of hydroforming naphthas which comprises charging said naphtha and hydrogen to the bottom of a confined, elongated reaction zone of restricted cross-sectional area causing said naphtha and hydrogen to flow upwardly therein, the said reaction zone being positioned within and extending above a second zone, the latter providing an annular zone surrounding the said reaction zone, maintaining a fluidized bed of catalyst particles comprising a supported platinum group metal in said annular zone, inducing flow of catalyst from the bottom of said annular zone into the bottom of said reaction zone by the upwardly flowing naphtha vapors and hydrogen in said reaction zone, maintaining hydroforming conditions of temperature and residence time in said reaction zone, withdrawing raw product and catalyst from the top of said reaction zone and permitting it to flow into an expanded catalyst disengaging space wherein catalyst is separated from the product vapors and hydrogen and gravitated toward the said annular zone, causing catalyst to flow from said annular zone into a heating zone disposed immediately below the annular zone, adding hot inert solids of larger size than said catalyst particles to the heating zone and causing hydrogen to flow upwardly in said heating zone and said annular zone to maintain the catalyst in both zones in a fluidized state, permitting solids to flow from the heating zone into an elutriating zone immediately below said heating zone, which elutriating zone is of more restricted cross-sectional area than said heating zone, whereby catalyst is separated from the said inert solids, withdrawing said inert solids from the bottom of said elutriating zone and transferring them to a heating zone, reheating said withdrawn inert solids in said heating zone by burning a fuel in said heating zone with air at substantially atmospheric pressure, recycling the said heated inert solids to the heating zone to supply by heat exchange with catalyst the major portion of the heat required for the endothermic reaction of hydroforming, withdrawing fouled catalyst from the annular zone and charging it to a catalyst regeneration zone where it is treated with oxygen-containing gas to burn off carbonaceous deposits and thereafter returning the regenerated catalyst to the reaction zone, the process being further characterized in that the hydroforming is conducted at a pressure of from about 0 to 100 p. s. i. g. in said reaction zone, in that 200 to 1000 s. c. f. of hydrogen, per barrel of naphtha feed, is fed to the reaction zone and maintaining a superficial velocity of vaporiform material in said reaction zone of from about 5 to 15 feet per second.

2. The process defined by claim 1 in which said withdrawn solid inert particles are heated in an extraneous heating zone while maintaining the particles as a fluidized bed by passage of air and feed through said fluidized bed.

3. The process defined by claim 1 in which said withdrawn solid inert particles are subjected to a stripping step prior to introduction to said heating zone.

4. The process defined by claim 1 in which said withdrawn catalyst particles are subjected to a stripping step prior to introduction to said reactivation zone.

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