This invention relates to the catalytic conversion of hydrocarbon fractions boiling within the motor fuel boiling range of low knock rating into high octane number motor fuels and particularly to a process and apparatus whereby such a conversion is effected by the fluidized solids technique.

Catalytic cracking of hydrocarbon oils by the fluidized solids technique is a well known and widely practiced process today. In such cracking processes, the conversion as well as the catalyst revivification or regeneration is effected substantially at atmospheric pressure. Moreover, the deactivation and regeneration of cracking catalysts does not effect any important change in the chemical nature of the catalyst components.

It has been generally suggested in numerous patents specifically directed to catalytic cracking by the fluidized solids technique that the process there disclosed is applicable to other catalytic conversions including reforming or hydroforming of naphtha or hydrocarbon fractions boiling in the motor fuel range. Fluid hydroforming, if properly conducted, should have several fundamental advantages over fixed bed hydroforming of heavy virgin naphtha for octane improvement.

A partial list of the advantages of fluidized solids operation for hydroforming are: (1) the operations are continuous, (2) the vessels and equipment can be designed for single rather than dual functions, (3) the reactor temperature is constant and simulates isothermal fixed bed operations, and (4) the regeneration is readily controlled.

When it was attempted to carry out the hydroforming of petroleum fractions boiling in the motor fuel range in accordance with the fluidized solids technique, it was found that numerous problems peculiar to this process are encountered. In the first place, hydroforming is effected at elevated pressure of approximately 100 to 500 lbs. per sq. in. rather than at atmospheric pressure creating several problems. In the second place regeneration of catalyst particles deactivated by carbonaceous deposits by burning off the latter effects a change in the chemical nature of the catalyst component. In the case of molybdenum oxide-containing catalysts, burning off the carbonaceous deposits on spent catalyst may oxidize the catalytically active form to a relatively inactive form. When such regenerated catalyst is contacted with hydrogen-containing gas such as process gas or the like, the inactive form is converted to an active form by an exothermic reaction which, particularly at the pressure and temperature obtaining in the reaction system is difficult to control and may lead to permanent deactivation of the catalyst.

It is the object of this invention to provide a process whereby hydrocarbon fractions boiling within the motor fuel range may be hydroformed by the fluidized solids technique.

It is also an object of this invention to provide an apparatus or reaction system in which hydrocarbon fractions boiling within the motor fuel range may be hydroformed by the fluidized solids technique.

These and other objects will appear more clearly from the detailed specification and claims which follow.

In the drawing:

Figs. 1 and 1a illustrate a schematic flow plan for a system for hydroforming hydrocarbon fractions boiling within the motor fuel boiling range using the fluidized solids technique in accordance with the present invention.

The feed or charging stock, which may be a virgin naphtha, a cracked naphtha, Fischer-Tropsch naphtha or the like, is introduced through line 11, pump 12 and line 13 through preheater 14 (Fig. 1a) wherein it is passed in indirect heat exchange with hot reaction product vapors. The preheated charging stock is then passed through line 15 to combination furnace 16 wherein it is heated substantially to reaction temperature. The preheated feed stock is then conducted through line 17 to the bottom of a large reactor 18 above grid member 18a. The feed stock is preferably added through a plurality of tubes or nozzles as shown into the bottom portion of the catalyst bed 19 presently to be described.

The reactor is charged with a mass of finely divided hydroforming catalyst above grid member 18a. Suitable catalysts include group VI metal oxides, such as molybdenum, chromium or tungsten oxide or mixtures thereof upon a carrier such as activated alumina, zinc aluminate spinel or the like. Other suitable catalysts or carriers may be used. The catalyst particles are for the most part between 200 and 400 mesh in size or about 0 to 500 microns in diameter with a major proportion between 20 and 80 microns. A stream of hot hydrogen-containing gas containing the catalyst suspended therein is introduced into the bottom of the reactor below the grid 18d which serves to distribute the catalyst and gas uniformly over the full cross-sectional area of the reactor. In starting up the process for the first time, the hydrogen-containing gas may be supplied from an extraneous source. The
process, however, normally evolves hydrogen which may be recycled to the reactor. The naphtha vapors and hydrogen-containing gas are passed as a mixture up through the reaction zone at a superficial velocity of about 0.2 to 0.9 ft. per second at reactor conditions depending upon the pressure. For example, the velocity should be below 0.6 ft. per second in the pressure range of 200–250 lbs. per sq. in. gauge. The velocity should be sufficient to maintain a dense turbulent liquid-simulating bed 15 of solids and gas having a level 23 with a dilute phase suspension of gas and solids 23′ thereabove. Lower linear gas velocities are used for higher pressures to obtain dense fluidized beds. If desired the reactor 13 may be provided with horizontally arranged perforated baffles spaced vertically therein or vertically arranged and spaced baffles to improve contacting between the hydrocarbon vapors and catalyst.

A vertical internal conduit 21 is provided in the reactor 18, for the withdrawal of catalyst directly from the dense bed 15. The upper end of the conduit 21 extends above the level 20 and has openings or ports 21′ at one or more points along its length to permit flow of catalyst from the dense bed into the conduit. As the catalyst and hydrocarbon vapors are introduced at the lower end of reactor 13 and product vapors are removed overhead and catalyst is removed near the top of the catalyst bed 15, there is a general concurrent flow of hydrocarbon vapors and catalyst in the reactor 18. The port 21′ may be located in the upper portion of bed 15 to obtain maximum concurrent flow of the catalyst and oil vapors up through the bed 15. However, the port should be sufficiently below the level 20 to take care of any normal fluctuations in the level 20. More than one orifice or port may be provided at different levels in conduit 21 and each port may be provided with valves to control the flow of catalyst into the conduit 21.

Steam or an inert gas such as nitrogen, nitro gas or mixtures thereof are supplied to conduit 21 through line 22 near the base of conduit 21 to dilute, strip off or desorb hydrogen, hydrocarbon reactants or reaction products flowing into conduit 21 with the catalyst, the stripping gas being passed upwardly through conduit 21 countercurrent to downflowing catalyst. The superficial velocity of the stripping gas should be equal to or higher than the superficial velocity of the vapors and gases passing upwardly through reactor 13.

The stripping gas and stripped-out constituents are discharged from the top of conduit 21 into the dilute phase 20′ and are combined with reaction product vapors leaving the dense bed 19 and the mixture is passed through one or more cyclone separators 21a or the like to remove entrained catalyst particles and then withdrawn through line 23 to suitable heat and product recovery equipment described below. The stripping of the catalyst decreases the amount of combustible material which must be burned during the regeneration of the catalyst as later described. If desired, a separate external stripping vessel may be used for the stripping step with the stripping gas and stripped-out material leaving the stripper being conducted to the reactor outlet line 23 or being separately treated to recover hydrocarbons therefrom.

The lower end of conduit 21 is necked down or reduced in diameter as at 23c and forms standpipe 23b having a smaller diameter than conduit 21. This standpipe serves to develop additional pressure necessary to overcome the pressure drop through the regeneration system. The catalyst flowing from the enlarged section 21 into the reduced section 23b will carry entrained or trapped gas with it in an amount sufficient to maintain it in freely flowing fluid condition and this condition should be maintained during passage of the catalyst through the reduced section standpipe section 23b. If necessary some additional gas may be added at one or more spaced points in the standpipe section 23b. However, as the process is carried out under an elevated pressure of 100 lbs. per square inch or higher, and is much higher than the pressure drop through the regeneration system, the amount of pressure built up by the standpipe is relatively small compared to the pressure in the process, consequently there is less compression of the gas entering the top of section 23b as the solids move down therein, so that in most cases there is no need for adding additional aerating gas to section 23b. This is particularly true if in section 23b the rate of downflow of solids in the standpipe is relatively high, so as to prevent the catalyst from being desorbed. By making the diameter of the standpipe relatively small as compared with the stripping section the velocity through the standpipe section will be increased thus reducing the tendency to desorb the catalyst.

The standpipe 23b at its lower end is provided with a valve 23c to control the rate of withdrawal of stripped catalyst from the standpipe.

Catalyst from the base of standpipe 23b is discharged into conduit 24 wherein the catalyst is picked up by a stream of air or other carrier gas supplied through line 25 and conveyed to regenerator 26 where carbonaceous deposits are burned from the catalyst. It has been found that the rate of burning of the carbonaceous deposits from hydroforming catalysts of the type described is much faster than the rate of burning of carbonaceous deposits from conventional cracking catalysts such as silica-alumina gel. This rapid burning of the carbonaceous deposits may cause overheating of the catalyst during passage through the line 24 unless special precautions are taken. This can be avoided by introducing a part or all of the air for regeneration into the regenerator through a separate line 27 and using only a portion of the air for regeneration or an inert gas for transporting the catalyst through the line 24 into the regenerator. About 15 to 40% of the total air required for regeneration may be used to convey the stripped spent catalyst to the regenerator without overheating the catalyst. The remainder of the air or about 60 to 85% may be passed through line 27 directly to the regenerator. Both lines 24 and 27 discharge into regenerator 23 below grid member 21a. While line 27 is shown as having a single outlet within the regenerator, it will be understood that this line may be extended above grid 27a into the regenerator and provided with a plurality of outlets at vertically spaced points within the regenerator in order to insures uniformity of temperature throughout the body of catalyst undergoing regeneration.

The velocity of the gas passing upwardly through the regenerator is controlled to maintain a lower dense, highly turbulent fluidized bed 27′ and an upper dilute suspension of catalyst and gas having a level or line of demarcation 27b. To accomplish this the superficial velocity of the regenerating gas in the regenerator 26 may
range between 0.3 to 1.5 feet per second depending upon the pressure, for example, below 1.0 at a regeneration pressure of about 200–250 lbs. per sq. in. The conduit 23 extends through the dense bed 21 of catalyst and through grid member 18a through the bottom of regenerator 23. The regenerated catalyst is withdrawn from the regenerator through a conduit 23 having an enlarged upper stripping section within the vessel and a reduced standpipe section 23b which is constructed and operated in the same manner as conduits 21 and 23b in withdrawing catalyst from the reactor. Stripping of the regenerated catalyst through inlet line 29 in order to strip entrained or adsorbed regeneration gases from the regenerated catalyst.

Standpipe 23b is provided at its lower end with a valve 23c for controlling the rate of withdrawal of catalyst from the standpipe section 23b. Catalyst from the lower end of standpipe 23b is discharged into line 30 where it is picked up by hot recycle gas later to be described to form a dilute suspension and the dilute suspension is introduced into the bottom of the reactor 18 below grid member 18a providing conduit 23 for conduit 23 through liquid line 29 in order to entrain or stripped gases from the standpipe section 23b. When the freshly regenerated catalyst substantially at regenerator temperature and pressure is contacted with hydrogen or a hydrogen-containing recycle gas in line 30 an exothermic reaction, which is difficult to control and which may deactivate the catalyst unless special precautions are taken. This will be avoided by making the transfer line 30 connecting the regenerator standpipe 23b with reactor 18 as extremely short and maintaining a adequately dilute suspension of the catalyst in the gas in this line.

By giving the regenerated catalyst a limited treatment with the hydrogen-containing gas before contacting the naphtha vapor, the catalyst may be restored to the desired valence so that the activity and selectivity of the catalyst may be better maintained. Various manual or automatic control means may be used for maintaining the desired conditions of operation. One of such control means is shown in the drawing but the invention is not to be restricted thereto. A level controller 28d is provided for detecting the liquid control valve 28c in standpipe 23b. A temperature responsive means 24a is located in transfer line 24 and means 24a is interconnected with valve 23c in standpipe 23b for controlling valve 23c. If for some reason the temperature in line 24 rises, the temperature responsive means 24a will operate to open valve 23c thereby allowing more catalyst from standpipe 23b to enter line 24 and as this catalyst from this reactor is cooler than that during regeneration, the temperature in line 24 is reduced to the desired design figure. By putting more catalyst 23d and 25 there is a temporary rise in the level of catalyst in the regenerator and the level controller 25d comes into action to open valve 23c to a lower withdrawal of catalyst from the regenerator to maintain the desired level.

Control of the temperature in the regeneration zone is effected by cooling coils 31 located within regenerator through which a cooling medium is circulated. An advantageous method for controlling bed temperatures in regenerator 28 is to arrange about 50 to 75% of the cooling surface in closely spaced relation near the lower portion of the bed. This section may serve to remove a fixed amount of heat at all times. The remainder of the cooling surface is arranged in more widely spaced relation in the upper portion of the regenerator. Any desired part of this cooling surface can be immersed in the bed by raising or lowering the level of the dense bed within the regenerator. The drawing illustrates equipment in which the heat liberated in the regenerator is used to generate steam. All of the coils should be wet tubes, that is there should be a film of liquid water on the interior of the tubes, the temperature control being effected by varying the amount of heat exchange surface immersed in the dense bed. The heat transfer coefficient of the dense bed is considerably greater than the dilute suspension above the bed. This arrangement is particularly effective in the present process since the regenerator contains a relatively small amount of catalyst as compared to the reactor so that variations in the level in the regenerator will not seriously affect the level of the dense bed in the reactor. The temperature in the regenerator may be automatically controlled by having the temperature in the regenerator actuate the valve 23c at the base of conduit 23 to change this height.

Regeneration gases are taken overhead from regenerator 21 through one or more cyclone separators 22e which remove entrained catalyst. The gas then passes through a pressure reducing valve 23d and is passed to stack 32. In order to control the amount of catalyst in the system special provisions are made for introducing and removing catalyst as follows. Hot catalyst may be withdrawn from the regenerated catalyst standpipe 23b through line 33, the withdrawn catalyst being passed through reactor cooler 34. The pressure on the catalyst in stages by passing it through fixed orifices 35. The depressurized catalyst is then discharged through line 36 into the catalyst storage hopper 37. Fresh catalyst received in hopper cars or the like is discharged into dump pit 38 and transferred into conduit 39 by means of a pump or the like and conveyed to fresh catalyst storage hopper 40 or to catalyst storage hopper 37 by a suitable gas stream. Cyclone separators (not shown) may be used to recover catalyst from gases leaving the hoppers 37 and 40. The catalyst in hoppers 31 and 40 is placed under adequate pressure to feed it into the system by the introduction of high pressure air through lines 41, 42 and 43. The catalyst to be added is withdrawn from hopper 37 or 40 and transported by high pressure air into a slurry tank 44 where it mixed with a portion of naphtha feed introduced through line 45. The catalyst naphtha slurry is pumped by pump 45 through pressure control valve 46 and line 47 into the reactor 18. The slurry is preferably introduced into the reactor above conduit 26 through one or more nozzles similar to the addition of fresh feed to the reactor. Lines 46 and 47 connect the bottom of the hoppers 40 and 37 respectively to conduit 51 through which catalyst for starting up the reactor system is transported into the system by a dry stream of high pressure gas such as air.

Returning again to the reactor 18, the reaction products as stated above are taken overhead from the reactor after passing through one or more internal cyclone separators which remove most but not all of entrained catalyst, and passed through line 52 to drum 53 (see Fig.1a). A heavy quenching oil which may be formed in the process is sprayed into line 25 from line 52.
The amount of quenching oil introduced into the vapors should be sufficient to cool the vapors below the vaporization temperature of the quenching oil. The resulting mixture comprising small oil droplets of gaseous and vaporous reaction products passes through some catalyst which is then passed tangentially into drum 52 where the liquid droplets and catalyst particles are separated from the gases.

The quenching oil is higher boiling than the naphtha feed and comprises essentially high boiling constituents of the gases or vapors formed during hydroforming although an entraining oil is used in the initial operation. A slurry of oil and catalyst is withdrawn from the bottom of the drum by pump 54. A portion of this slurry is passed through a cooler 55 and then recycled through line 53 and injected into line 12 as a quenching medium.

The remaining portion of the slurry stream is taken off through line 56, passed through a further cooler 57 and then introduced into a filter 58 for removing the catalyst; and portion of the clarified filtrate is passed through line 59 which merges with line 53 for admixture with the quench oil. The filter 58 is periodically backwashed with feed naphtha if it is desired to recover and reuse the catalyst. In this event the slurry of residual naphtha is passed through line 60 and line 41 and into the reactor. If the catalyst is to be discarded, it is backwashed with water and discarded through line 61.

Excess clarified oil may be withdrawn from the system at 59. Instead of drum 52 a bubble tower may be used for removing entrained catalyst from the vapors and also to fractionate and separate higher boiling polymer oil formed in the process.

The stream of gaseous and vaporous reaction products is taken overhead from drum 52 through line 62 and a portion may pass through exchanger 14 for preheating fresh naphtha feed and another part may be passed through heat exchanger 63 for preheating the hydrogen-containing recycle gas later described. The partially cooled stream of gaseous reaction products is then passed via line 65 through condenser 56 which serves to condense the hydroformate. Products from condens 56 pass to a receiver 57 in which liquid hydroformate separates from uncondensed gases. The liquid hydroformate is withdrawn from the bottom of separator 57 and passed through line 58 to stabilizing and rerun equipment not shown. The uncondensed gases which contain a high percentage of hydrogen is taken overhead from separator 57 through line 66, passed through knock out drum 10 to remove any entrained liquid. The gas relatively free of liquid is further compressed in compressor 11 and thence passed through line 72 to heat exchanger 63 wherein it is preheated by indirect heat exchange with heat of reaction products passing through line 62 as already described. The preheated gas which is recycled to the process is then passed through coils 73 in furnace 16 wherein the gas is heated sufficiently above the reaction temperatures to supply the additional heat required over and above that supplied by hot regenerated catalyst and preheated feed. Excess process gas from line 63 is drawn off through line 69 as tail gas.

A method of starting up and operating the reactor system in accordance with this invention is as follows:

Catalyst is transferred from the storage hopper 31 or 40 to the reactor and regenerator through line 51 by means of a stream of air. When the reactor and regenerator are charged or loaded with catalyst, inert gas generated in an inert gas generator 74' (Fig. 1) is passed through line 11 to reactor 16. Simultaneously hot air which may be heated by coil 13 of the furnace 16 during the starting up operation is passed through the regenerator until the regenerator temperature reaches about 800° F.

After removal of air from the reactor is complete and the regenerator is at about 800° F., passage of air through the furnace 16 is discontinued, oil is then burned in the regenerator to further heat the catalyst and circulation of catalyst is begun. Refinery fuel gas is supplied to the recycle gas circuit 12 and 14 for purging the recycle heating coil 73 and is then used for transportating catalyst from the base line 280 to the reactor 16 through line 33. Catalyst circulation is continued until the reactor reaches about 850° F. When this happens the feed of naphtha is begun.

As soon as sufficient carbon is produced on the catalyst, the catalyst on burning in the regenerator is sufficient to maintain heat balance, oil feed to the regenerator should be cut off and the naphtha feed rate is gradually increased and the plant brought up to operating pressure.

The naphtha feed stock, preferably a virgin naphtha, supplied to the system has a boiling range of about 175° F. to 450° F., preferably 200° F. to 350° F. and is preheated in indirect heat exchange with the product vapors in exchanger 14 to about 500° to 600° F. and then further heated in the combination furnace to 800° to 1000° F., preferably about 950° F. The naphtha preheat should be as high as possible while avoiding thermal degradation thereof by limiting the time of residence in the reactor 27.

The recycle gas which should contain 50 to 70 volume per cent of vaporous reaction products is taken overhead from drum 52 through line 62 and a portion may pass through exchanger 14 for preheating fresh naphtha feed and another part may be passed through heat exchanger 63 for preheating the hydrogen-containing recycle gas later described. The partially cooled stream of gaseous reaction products is then passed via line 65 through condenser 56 which serves to condense the hydroformate. Products from condenser 56 pass to a receiver 57 in which liquid hydroformate separates from uncondensed gases. The liquid hydroformate is withdrawn from the bottom of separator 57 and passed through line 58 to stabilizing and rerun equipment not shown. The uncondensed gases which contain a high percentage of hydrogen is taken overhead from separator 57 through line 66, passed through knock out drum 10 to remove any entrained liquid. The gas relatively free of liquid is further compressed in compressor 11 and thence passed through line 72 to heat exchanger 63 wherein it is preheated by indirect heat exchange with heat of reaction products passing through line 62 as already described. The preheated gas which is recycled to the process is then passed through coils 73 in furnace 16 wherein the gas is heated sufficiently above the reaction temperatures to supply the additional heat required over and above that supplied by hot regenerated catalyst and preheated feed. Excess process gas from line 63 is drawn off through line 69 as tail gas.

A method of starting up and operating the reactor system in accordance with this invention is as follows:

Catalyst is transferred from the storage hopper.
It is preferred to operate at a catalyst to oil ratio of 1 since ratios above 1 to 1.5 result in excessive carbon formation from the naphtha. Increased catalyst circulation rates resulting from higher catalyst to oil ratios tend to carry more hydrogen into the regenerator unless excessive stripping is carried out. Hydrogen is held rather tenaciously by the catalyst so some is transferred from the reactor to the regenerator. Higher circulation rates of catalyst not only increases the amount of naphtha converted to carbon but also considerably increases the cost of heat exchange surface necessary to remove the heat and the air which must be compressed.

The catalyst to oil ratios may be as low as 0.5. At higher pressures the catalyst to oil ratio may be increased, a ratio of 3:1 being suitable at a pressure of about 500 lbs. per sq. inch. Space velocity is defined as pounds of feed per hour per pound of catalyst in the reactor. Space velocity in the reactor depends somewhat upon the age or activity level of the catalyst. Space velocity for a molybdenum oxide on alumina gel catalyst may vary, for example, from about 1.5 wt./hr./wt. (lb. feed/hr./lb. catalyst) to about 0.15 depending on the catalyst activity, the desired octane number of the product and the characteristics of the feed. The temperature in the regenerator should be maintained between about 1050 and 1200 °F.

The following table summarizes the results obtained when operating under a given set of conditions in accordance with the present invention.

**Example 1**

Feed stock... 200–430 °F. heavy virgin naphtha 1 Catalyst... Gel type 2

**Operating conditions:**

- Reactor temperature ° F. 900
- Reactor top pressure, p. s. i. g. 200
- Catalyst-oil ratio by weight 1.2
- Space velocity, w./hr./w. 0.27
- Carbon on regenerated catalyst, wt. percent Less than 0.05
- Recycle gas rate, std. cu. ft./bbl. fresh feed 3575
- Percent Hs in recycle gas 65.4

**Yields:**

C1+ gasoline, volume percent 83.3
Total C1 volume percent 7.4
Total C6, volume percent 8.2
Dry gas, weight percent 13.6
Carbon, weight percent 0.8
Hydrogen, std. cu. ft./bbl. fresh feed 602

**C1 gasoline inspections:**

- CFR research octane number, clear 96.5
- ASTM octane number, clear 85.4
- Reid vapor pressure, p. s. i. g. 9.3
- Gravity, ° API 50.4

1 Feed stock inspections:
- Gravity, ° API 59.3
- Octane number 51.0
- CFR research, clear 43
- ASTM, clear 38.8
- Aniline point 7
- Sulfur, weight percent 0.11
- ASTM distillation:
  - 10% at ° F. 292
  - 50% 282
  - 80% 246
- Hydrocarbon type analysis, volume percent:
  - Aromatic 8
  - Paraffins 48
  - Naphthenes 40
  - Olefins 0
- Remaining (not analyzed) 4

2 The catalyst, contained about 8.5% molybdenum trioxide on alumina gel prepared by coprecipitation of the molybdenum and alumina.

3 The specifications for a fluid hydroforming process will now be given for a commercial unit adapted to process 14,400 barrels of heavy virgin naphtha per stream day. The reactor is a cylindrical internally insulated vessel 18 feet in diameter and 85 feet high (straight side dimension). The regenerator is a cylindrical vessel 7.5 feet in diameter and 26 feet (straight side dimension) high with a refractory liner. In the regenerator, heat in excess of that used for supplying heat to the reactor is utilized for producing 200 p. s. i. g. steam.

The naphtha feed is preheated in the heat exchangers to about 575 °F. and then to about 960 °F. in the combination furnace. The heated feed under a pressure of from 100–500 pounds per square inch is then passed through line 17 to the bottom of fluidized catalyst bed 16 in reactor 18. At this feed temperature the time of passage of the oil through the line should be controlled to avoid thermal cracking and degradation. Line 17 has an internal diameter of 6 inches. The reactor is maintained at a temperature of about 900 °F.

The recycle gas is heated to a temperature of about 1150 °F. The amount of recycle gas containing about 70 mol percent hydrogen is about 30,000 standard cubic feet per minute. The thus heated recycle gas passing through the reactor 18 is mixed with hot regenerated catalyst at a temperature of about 1150 °F. discharged from standpipe 28b to form a dilute suspension which is passed through line 30 into the bottom of the reactor 18 below grid 16a. The time of residence of the catalyst in the transfer line 30 should be less than about 5 seconds to prevent overheating and degradation of the catalyst before it is contacted with the naphtha vapors in reactor 18. Line 30 is about 26 inches in diameter.

The average residence time of catalyst in the reactor may be of the order of from 3 to 4 hours whereas the residence time of catalyst in the regenerator may be from 3 to 15 minutes.

The superficial velocity of the upflowing gas–inert material in reactor 18 is about 0.5 feet per second and the density of the fluidized bed is about 30 lbs./cu. ft. The density of the fluidized bed 27c in the regenerator 28 is about 26 lbs./cu. ft. The regenerator is at a pressure of about 205 p. s. i. g. and at about 1150 °F.

The product vapors pass overhead from reactor 18 through line 23 at a temperature of about 900 °F., are cooled to about 800 °F. by quench oil introduced at a temperature of about 500 °F. at 84. The product vapors are then cooled down to about 105 °F. to separate hydroformate product from recycle gas. About 13,500 barrels per standard day of raw hydroformate will be produced.

The stripper conduit 21 in reactor 18 is about 2 feet in diameter and at its lower end it is necked down to a 7 inch tube to form standpipe 22b. The standpipe effluent height of 25b is about 25 feet. Superheated steam is introduced from the bottom of stripping conduit 21 at the rate of about 2940 lbs. per hour. This steam flows upwardly for the most part through the stripper 21 countercurrent to downflowing catalyst but some steam and gas are entrapped in the catalyst flowing into standpipe 22b.

The stripper conduit 25 in regenerator 26 is about 2 feet in diameter and at its lower end is necked down to about 7 inches to form standpipe 22b. The effective standpipe height of 22b is about 50 feet. The amount of inert gas used
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for stripping in conduit 28 in the regenerator is 4900 lbs. per hour. The line 24 leading from standpipe 23b to regenerator 28 is about 8 inches in diameter and line 21 is about 4 inches in diameter.

For the size plant described about 260 tons of catalyst will be needed and about 250 tons will be in the reactor, about 9 tons will be in the regenerator and the rest in the lines leading to and from the reactor and regenerator.

The density of the catalyst mixture in standpipes 23b and 28b is about 44 lbs. per cu. ft. but may be about 38 to 44 lbs. per cu. ft.

What is claimed is:

1. A method of converting naphtha into a high anti-knock motor fuel by hydroforming which comprises passing naphtha vapors and separately introduced hot hydrogen-containing process gas through a dense fluidized bed of finely divided hydroforming catalyst in a reaction zone at a temperature of 850-925°F. and at a pressure of 100-500 lbs. per sq. inch at a catalyst to oil ratio by weight of from 0.5 to 3.0, withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from the reaction zone, withdrawing a stream of catalyst particles directly from the dense fluidized bed in said reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, regenerating the stripped catalyst particles by burning off carbonaceous deposits in a dense fluidized bed in a regeneration zone in the ratio of 1000 to 4000 cu. ft. per barrel of naphtha feed stock at a temperature of 1150-1200°F. and recycling the same to the reaction zone, separating residual catalyst material entrained with the stream of reaction products, passing fresh naphtha feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated naphtha feed to 800-1000°F. preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150-1200°F. and recycling the same to the reaction zone.

2. A method of converting naphtha fractions into high anti-knock gasoline which comprises passing vaporized hydrocarbon materials and separately introduced hot hydrogen-containing process gas through a dense fluidized bed of finely divided hydroforming catalyst in a reaction zone in the ratio of 1000 to 4000 cu. ft. per barrel of naphtha feed stock at a temperature of 850-925°F. and at a pressure of 100-500 lbs. per sq. inch at a catalyst to oil weight ratio of from 0.5 to 3.0, and at a space velocity of 0.15 to 1.5 (lbs. of hydrocarbon feed per hour per lb. of catalyst in the reactor), withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from said reaction zone, withdrawing a stream of catalyst particles directly from the dense fluidized bed in said reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, regenerating the stripped catalyst particles by burning off carbonaceous deposits in a dense fluidized bed in a regeneration zone, controlling the temperature of the catalyst undergoing regeneration to about 1200°F., withdrawing catalyst particles from the regeneration zone and recycling the same to the reaction zone, separating residual catalyst material entrained with the stream of reaction products, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800-1000°F. preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150-1200°F. and recycling the same to the reaction zone.

3. A method of converting hydrocarbon fractions boiling within the motor fuel range into high anti-knock motor fuels which comprises passing vaporized hydrocarbon materials and separately introduced hot hydrogen-containing process gas through a dense fluidized bed of finely divided hydroforming catalyst in a reaction zone at a temperature of 850-925°F. and at a pressure of 100-500 lbs. per sq. inch at a catalyst to oil weight ratio of from 0.5 to 3.0, withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from said reaction zone, withdrawing a stream of catalyst particles directly from the dense fluidized bed in said reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, regenerating the stripped catalyst particles by burning off carbonaceous deposits in a dense fluidized bed in a regeneration zone, controlling the temperature of the catalyst undergoing regeneration to about 1200°F., withdrawing catalyst particles from the regeneration zone and recycling the same to the reaction zone, separating residual catalyst material entrained with the stream of reaction products, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800-1000°F. preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150-1200°F. and recycling the same to the reaction zone.

4. A method of converting hydrocarbon fractions boiling within the motor fuel boiling range into high anti-knock motor fuels which comprises passing vaporized hydrocarbon materials and separately introduced hot hydrogen-containing process gas through a dense fluidized bed of finely divided hydroforming catalyst in a reaction zone in the ratio of 1000 to 4000 cu. ft. per barrel of hydrocarbon feed stock at a temperature of 850-
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925°F and at a pressure of 100-500 lbs per sq. inch at a catalyst to oil weight ratio of from 0.5 to 3.0, and at a space velocity of 0.15 to 1.5 lbs. of hydrocarbon feed per hour per lb. of catalyst in the reactor), withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from this reaction zone, withdrawing a stream of catalyst particles directly from the dense fluidized bed in said reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, conveying the stream of catalyst to a regeneration zone with at most about 40% of the air necessary for regeneration, adding the remainder of the regeneration air directly to the regeneration zone maintaining the catalyst particles in the regeneration zone as a dense, fluidized bed by the passage of regeneration air therethrough, controlling the temperature of the catalyst undergoing regeneration to about 1200°F, separating residual catalyst material entrained with the stream of reaction products, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800-1000°F preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150-1200°F, withdrawing a stream of catalyst particles directly from the dense, fluidized bed of catalyst in the regeneration zone, stripping the withdrawn catalyst substantially free of regeneration gases, discharging the stripped regenerated catalyst particles into a rapidly moving stream of said heated gaseous constituents, discharging the mixture of gaseous constituents and regenerated catalyst into the bottom of the reaction zone at such a rate that the regenerated catalyst particles are in contact with said stream of hot gaseous constituents for at most about 5 seconds before being discharged into the dense fluidized bed in the reaction zone.

5. A method of converting hydrocarbon fractions boiling within the motor fuel boiling range into high anti-knock motor fuels which comprises passing vaporized hydrocarbon feed and separately introduced hot hydrogen-containing process gas through a dense fluidized bed of finely divided hydroforming catalyst in a reaction zone at a temperature of 850-925°F and at a pressure of 100-500 lbs per sq. inch at a catalyst to oil weight ratio of from 0.5 to 3.0, withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from the reaction zone, withdrawing a stream of catalyst particles directly from the dense fluidized bed in the reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, regenerating the stripped catalyst particles by burning off carbonaceous deposits in a dense fluidized bed in a regeneration zone, controlling the catalyst undergoing regeneration to a temperature of about 1200°F, withdrawing catalyst particles from the regeneration zone and recycling the same to the reaction zone, separating residual catalyst material entrained with the stream of reaction products and higher boiling materials formed in the process by spraying a relatively high boiling hydrocarbon oil into said stream to effect separation of liquid oil and catalyst particles, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800-1000°F preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150-1200°F, withdrawing a stream of catalyst particles directly from the dense, fluidized bed in the reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, conveying the stream of catalyst to a regeneration zone with at most about one third of the air necessary for regeneration, adding the remainder of the regeneration air directly to the regeneration zone maintaining the catalyst particles in the regeneration zone as a dense, fluidized bed by the passage of regeneration air therethrough, controlling the temperature of the catalyst undergoing regeneration to about 1200°F, separating residual catalyst material entrained with the stream of reaction products and higher boiling materials formed in the process by spraying a relatively high boiling hydrocarbon oil into said stream to effect separation of oil catalyst particles, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800-1000°F preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150-1200°F, withdrawing a stream of catalyst particles directly from the dense, fluidized bed of catalyst in the regeneration zone, stripping the withdrawn catalyst substantially free of regeneration gases, discharging the stripped regenerated catalyst particles into a rapidly moving stream of said heated gaseous constituents, discharging the mixture of gaseous constituents and regenerated catalyst into the bottom of the reaction zone at such a rate that the regenerated catalyst particles are in contact with said stream of hot gaseous constituents for at most about 5 seconds before being discharged into the dense fluidized bed in the reaction zone.

6. A method of converting hydrocarbon fractions boiling within the motor fuel range into high anti-knock motor fuels which comprises passing vaporized hydrocarbon feed and separately introduced hot hydrogen-containing process gas through a dense fluidized bed of finely divided hydroforming catalyst in a reaction zone at a temperature of 850-925°F and at a pressure of 100-500 lbs per sq. inch at a catalyst to oil weight ratio of from 0.5 to 3.0, withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from the reaction zone, withdrawing a stream of catalyst particles directly from the dense fluidized bed in the reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, conveying the stream of catalyst to a regeneration zone with at most about one third of the air necessary for regeneration, adding the remainder of the regeneration air directly to the regeneration zone maintaining the catalyst particles in the regeneration zone as a dense, fluidized bed by the passage of regeneration air therethrough, controlling the temperature of the catalyst undergoing regeneration to about 1200°F, separating residual catalyst material entrained with the stream of reaction products and higher boiling materials formed in the process by spraying a relatively high boiling hydrocarbon oil into said stream to effect separation of oil catalyst particles, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800-1000°F preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150-1200°F, withdrawing a stream of catalyst particles directly from the dense, fluidized bed in the reaction zone, stripping the withdrawn catalyst substantially free of regeneration gases, discharging the stripped regenerated catalyst particles into a rapidly moving stream of said heated gaseous constituents, discharging the mixture of gaseous constituents and regenerated catalyst into the bottom of the reaction zone at such a rate that the regenerated catalyst particles are in contact with said stream of hot gaseous constituents for at most about 5 seconds before being discharged into the dense fluidized bed in the reaction zone.
weight ratio of from 0.5 to 3.0, withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from the reaction zone, withdrawing a stream of catalyst particles directly from the dense fluidized bed in the reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, regenerating the stripped catalyst particles by high-temperature combustion deposits in a dense fluidized bed in a regeneration zone, controlling the temperature of the catalyst undergoing regeneration to below about 1200°F, withdrawing a stream of catalyst particles directly from the dense, fluidized bed of catalyst in the regeneration zone, stripping the withdrawn catalyst substantially free of regenerated catalyst particles, discharging the mixture of gaseous and condensed catalyst into the bottom of the reaction zone at such a rate that the regenerated catalyst particles are in contact with said stream of hot gaseous constituents for at most about 5 seconds before being discharged into the dense fluidized bed in the reaction zone.

9. A method of hydroforming hydrocarbon fractions to produce high octane number motor fuels which comprises passing hot hydrogen-containing gas, separately introduced hydrocarbon vapors and finely divided hydroforming catalyst through a reaction zone at a temperature of 850–925°F and at a pressure of 100–500 lbs. per sq. inch, withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from said reaction zone, withdrawing stripped catalyst particles directly from the dense fluidized bed in the reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, conveying the stream of catalyst to a regeneration zone at about 1200°F, separating residual catalyst material entrained with the stream of reaction products and higher boiling materials formed in the method by spraying a hydrocarbon oil higher boiling than naphtha into said stream to effect separation of oil and catalyst particles, withdrawing a slurry of catalyst particles in oil, separating catalyst particles from oil and recycling the clarified oil to said spraying system, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800–1000°F preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150–1200°F, withdrawing a stream of catalyst particles directly from the dense, fluidized bed of catalyst in the regeneration zone, stripping the withdrawn catalyst substantially free of regenerated catalyst particles into a rapidly moving stream of said heated gaseous constituents, discharging the mixture of gaseous constituents and regenerated catalyst into the bottom of the reaction zone at such a rate that the regenerated catalyst particles are in contact with said stream of hot gaseous constituents for at most about 5 seconds before being discharged into the dense fluidized bed in the reaction zone.

8. A method of converting hydrocarbon fractions boiling in the motor fuel range into high anti-knock motor fuels which comprises passing vaporized hydrocarbon materials and separately introduced hot hydrogen-containing process gas through a dense fluidized bed of finely divided hydroforming catalyst in a reaction zone at a temperature of 850–925°F and at a pressure of 100–500 lbs. per sq. inch, at a catalyst to oil weight ratio of from 0.5 to 3.0, withdrawing a stream of reaction products containing small amounts of residual entrained catalyst overhead from the reaction zone, separating catalyst particles directly from the dense fluidized bed in the reaction zone, stripping adsorbed hydrocarbon material from the stream of catalyst, conveying the stream of catalyst to a regeneration zone at about 1200°F, separating residual catalyst material entrained with the stream of reaction products and higher boiling materials formed in the method by spraying a hydrocarbon oil higher boiling than naphtha into said stream to effect separation of oil and catalyst particles, withdrawing a slurry of catalyst particles in oil, separating catalyst particles from oil and recycling the clarified oil to said spraying system, passing fresh hydrocarbon feed in indirect heat exchange relation to the stream of reaction products to remove some of the heat therefrom, further heating the preheated hydrocarbon feed to 800–1000°F preparatory to introducing the same into the reaction zone, further cooling the stream of reaction products to condense hydroformate, separating hydroformate from gaseous constituents of the reaction products stream, heating said gaseous constituents to temperatures of 1150–1200°F, withdrawing a stream of catalyst particles directly from the dense fluidized bed in the reaction zone, recycling the same to the reaction zone.
reaction zone, stripping adsorbed hydrocarbon material from the withdrawn catalyst with steam at substantially reaction zone temperature, regenerating the stripped catalyst particles by burning off carbonaceous deposits in a dense fluidized bed in a regeneration zone, controlling the temperaturer of the catalyst undergoing regeneration to below about 1200° F., withdrawing catalyst particles from said regeneration zone, suspending the withdrawn catalyst substantially at regeneration temperature in hydrogen-containing gas as a dilute suspension, the gas being heated to a higher temperature than the regenerated catalyst, passing the dilute suspension of regenerated catalyst and hydrogen-containing gas through a short conduit into said reaction zone at such a rate that the regenerated catalyst particles are in contact with said stream of hot hydrogen-containing gas for at most about 5 seconds before being discharged into the dense, fluidized bed in the reaction zone.

11. A method of hydroforming naphthas which comprises passing naphtha vapors and separately introduced hydrogen-containing gas through a dense bed of hydroforming catalyst in a reaction zone under hydroforming conditions such that the reaction zone temperature is about 300° F. and the pressure is about 200 lbs./sq. in. and at a catalyst to oil weight ratio of about 1.0, withdrawing reaction products from said reaction zone, withdrawing catalyst from said dense bed of catalyst and stripping it, regenerating the stripped catalyst in a regeneration zone wherein the temperature is maintained below about 1200° F., withdrawing regenerated catalyst from the regeneration zone and returning it to said reaction zone in suspension in hot hydrogen-containing process gas at such a rate that the regenerated catalyst particles are in contact with the hot, hydrogen-containing process gas for at most about 5 seconds before being discharged into the dense, fluidized bed in the reaction zone, the catalyst residence time in said reaction zone being at least about 20 times that in the regeneration zone.

12. A fluid hydroforming process carried out at a temperature of from 850–925° F. and at a pressure of 100–500 lbs. per sq. inch at catalytic-to-oil weight ratios of from 0.5 to 3.0 wherein a large reactor and a small regenerator containing dense fluidized beds of finely divided catalyst are used, the naphtha feed being heated to higher than reactor temperature for only a short time before it contacts the catalyst, the regenerated catalyst substantially at regeneration temperature of from 1050–1200° F. after stripping being suspended in hydrogen-containing gas heated to a temperature of 1050–1200° F. with the suspension being rapidly passed to the reactor so that the regenerated catalyst particles are in contact with the hot, hydrogen-containing gas for at most about 5 seconds before being discharged into the dense, fluidized bed in the reaction zone and heat is supplied to the reactor by the hot regenerated catalyst, the hydrogen-containing gas and the naphtha feed.

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