

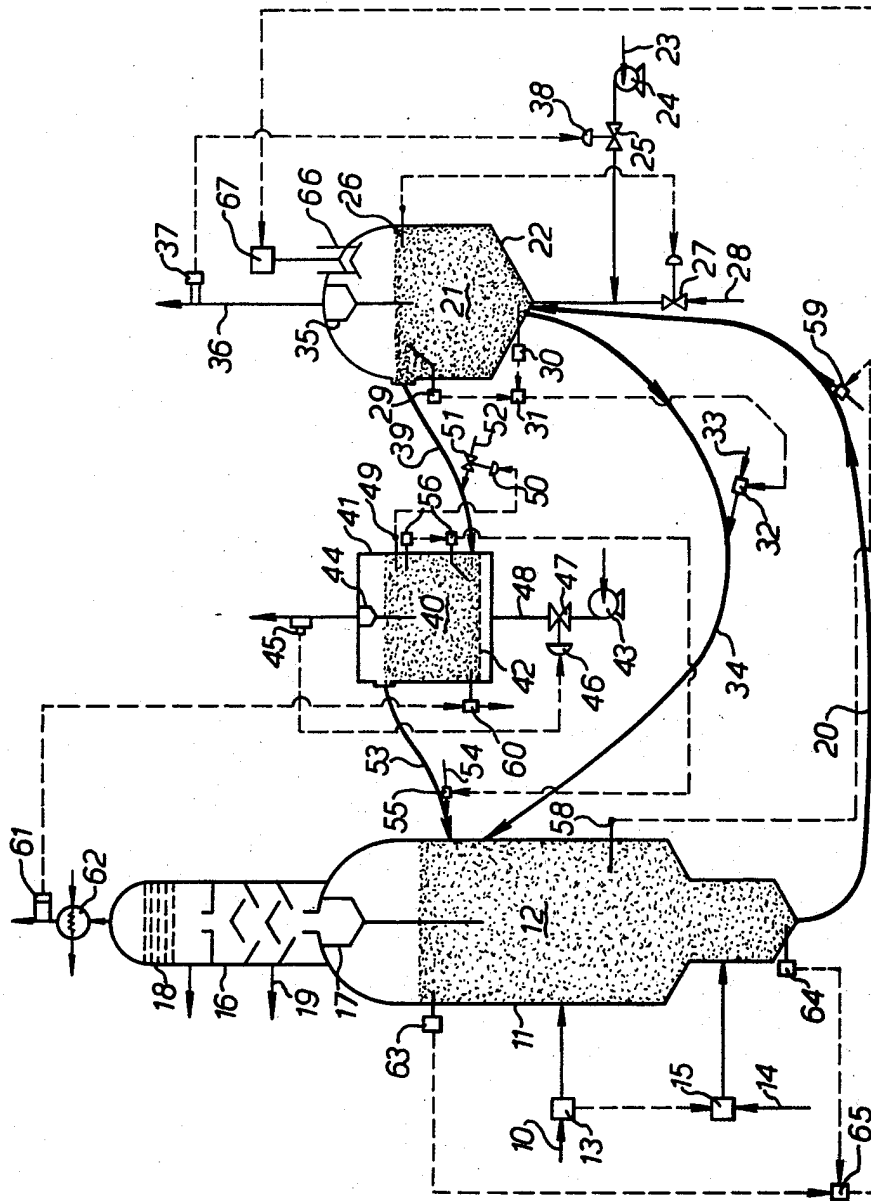
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CONVERSION OF HEAVY PETROLEUM FEEDSTOCKS

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**CONVERSION OF HEAVY PETROLEUM
 FEEDSTOCKS**
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14 Claims

ABSTRACT OF THE DISCLOSURE

A modified fluid coking process in which particles comprising CaO replace the coke in the coker, and the coke deposited on the particles is burned off in the burner. Sulphur from the coke is fixed in the particles mainly as CaS. Some of the particles pass indirectly back to the coker via a regenerator in which they are contacted with oxygen with the release of SO₂ in useful concentrations.

The present invention relates to the conversion of heavy petroleum feedstocks and more particularly to the conversion of such feedstocks containing sulphur.

Heavy petroleum feedstocks such as residual are generally of low value and they may be employed either alone or in blends with lighter feedstocks as fuels, or they may be converted to products of greater value by various known processes.

One of the processes heretofore employed for the conversion of heavy feedstocks is the process known as "fluid coking" wherein the feedstock is sprayed, having been previously heated (if necessary) to facilitate spraying, into a bed of hot fluidized coke particles in a reactor. A brief description of fluid coking processes is given in "Petroleum Refinery Engineering," 4th edition, by Nelson, pp. 689-691. The feedstock is cracked into lighter products in the vapour phase and into coke, the coke being deposited on the coke particles of the fluidized bed. The products in the vapour phase are recovered and comprise normally liquid hydrocarbons which are of relatively higher value than the feedstock and which can be used for automotive and jet engine fuel use and/or manufacture, together with normally gaseous hydrocarbons sometimes in admixture with hydrogen, all of which are useful products or feedstocks for further processing e.g. for the manufacture of olefins.

The particles of coke are circulated from the reactor to a burner wherein they are fluidized in an oxygen-containing gas and thereby partially combusted and raised in temperature, some of the thus heated coke particles being returned to the reactor for further use, the remainder of the coke being withdrawn as a by-product. In a typical fluid coking unit, the feedstock is converted to about 70% of normally liquid products and about 25% of coke, and 8% of the latter is consumed in the burner to provide heat for the process.

When the feedstock contains sulphur and other materials such as vanadium and sodium which are generally regarded as deleterious contaminants, the contaminants tend to be more concentrated in the coke than in the useful vapour phase products recovered from the reactor, and hence, the gases leaving the burner have high concentrations of sulphur, while the coke by-product is high in sulphur and in other contaminants. As a result, the burner off-gases are not very suitable for further use since if the carbon monoxide content is employed to produce heat, the resulting flue gases are polluted with sulphur oxides, while if they are employed to produce synthesis or industrial gases, the sulphur content tend to deactivate

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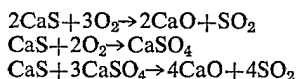
water-gas shift catalysts. Similarly, the uses to which the coke may be put are restricted by the presence of contaminants.

The present invention provides a method of converting a sulphur-containing heavy petroleum feedstock comprising the steps of passing the feedstock into a first bed of fluidized particles comprising calcium oxide or a precursor thereof at a temperature between 500 and 700° C. whereby the feedstock is converted to vapours comprising normally liquid and gaseous products of reduced sulphur content and to carbonaceous material of increased sulphur content which deposits on the said particles, recovering the said vapours from the first bed and transferring particles from the first bed to a second bed wherein the particles are fluidized at a temperature of 800° C. to 1000° C. in a gas containing oxygen in an amount sufficient to convert at least some of the carbonaceous material to gases containing a carbon oxide whereby the carbonaceous deposits on the particles are at least partially removed, and at least some of the sulphur originally present in the carbonaceous deposits reacts with the calcium oxide to form calcium sulphide, recovering the gases containing at least one carbon oxide from the second bed, transferring some of the particles from the second bed to the first bed and transferring particles from the second bed to a lower zone of a third bed in which the particles are fluidized at a temperature of 1000 to 1100° C. in an oxygen containing gas whereby at least some of the calcium sulphide in the particles is converted to calcium oxide with the release of SO₂, and transferring particles from an upper zone of the third bed to the first bed.

Thus, it will be appreciated that a heavy petroleum feedstock, contaminated as aforesaid, can be converted to relatively uncontaminated lighter products in the first bed, with the production in the second bed of substantially sulphur-free off-gases suitable for conversion by the water-shift reaction to substantially pure hydrogen, blue water gas, synthesis gases for ammonia manufacture or for Fischer-Tropsch reactions, the type of off-gas depending on the nature of the oxygen-containing gas supplied to the second bed. The off-gases from the third bed contain SO₂ in proportions which, with suitable conditions of operation of the process, are sufficiently high for the SO₂ to be useful rather than a pollutant.

The temperature in the third bed is maintained in the range 1000 to 1100° C., preferably 1050-1070° C., by sensing the temperature in the third bed and increasing the rate of transfer of particles from the cooler second bed when the temperature in third bed increases, and decreasing the rate of transfer when the temperature decreases.

The reaction which take place in the third bed leading to the evolution of SO₂ can be represented as follows:



The overall reaction is exothermic and at temperatures of 1000 to 1100° C., almost all of the sulphide which reacts is converted to oxide, the remainder being converted to sulphate which may be reduced to the oxide on a subsequent pass through the third reactor.

In order to ensure that the SO₂ content of the off-gases from the third reactor is at a usefully high level and not diluted by unreacted oxygen-containing gas, the off-gases may be monitored for SO₂ or oxygen, and if the concentration of SO₂ falls or the oxygen concentration increases, the rate of supply of the oxygen containing-gas to the third reactor is reduced accordingly. Theoretically, the SO₂ concentration can be 15% when the oxygen-containing gas is

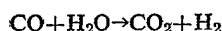
air, but 10–12% is usually achieved in operation, and the SO₂ at this level of concentration is useful for the manufacture of pure SO₂, sulphuric acid and for reduction to sulphur.

The activity of the particles to fix sulphur as calcium sulphide for subsequent release as SO₂ from the third reactor tends to diminish as the particles are recycled, and it is preferred to bleed off some particles either continuously or intermittently to maintain activity. Preferably, the particles are bled off and dumped from the bottom zone of the third reactor in response to a signal indicating that the sulphur-trapping activity has diminished or is insufficient. A suitable indication of sufficient activity is obtained by monitoring the sulphur content of at least some of the vapour(s) recovered from the third bed: for convenience, it is preferred to monitor the H₂S content of the vapours, either before or after normally liquid products have been condensed therefrom since the H₂S content of the vapours will be related to the sulphur content of the feedstock and of the various products recovered from the first reactor. A substantially constant inventory of active particles circulating in the three reactor beds must be maintained, and this may be achieved by sensing the amount of particles in the first bed and adding fresh particles to the second (and/or third) bed(s) in accordance with any deficiency of particles sensed in the first bed.

The temperature and oxidising potential in the second bed must be so maintained that the carbonaceous deposit is substantially removed from the particles therein without causing sulphur to be lost from the particles. A suitable method of maintaining the oxidizing potential below the level for converting calcium sulphide to sulphate or to calcium oxide (which reactions occur to any extent only when the oxidizable deposit has been removed) is to monitor the carbon dioxide concentration in the off-gases from the second bed, and varying the rate of supply of oxygen to the bed in accordance with the variation in CO₂ content of the off-gases. The CO₂ concentration is preferably maintained at less than 75% of the maximum concentration which can be achieved by stoichiometric combustion of the carbonaceous deposit. Thus, if the oxygen containing gas supplied to the second bed is air, the CO₂ concentration is preferably less than 11% and more preferably less than 8%, the remainder of the off-gas being carbon monoxide and non-combustible components of the oxygen. When the CO₂ concentration exceeds a predetermined maximum concentration (according to the composition of the oxygen-containing gas), the rate of supply of oxygen containing gas is reduced until the CO₂ concentration in the off-gas is returned to or tending towards a satisfactorily low concentration.

Generally speaking, the amount of carbonaceous deposit on the particles will be related to the Conradson carbon number of the feedstock to the first bed, and accordingly, the rate of supply of oxygen to the second bed may be made generally proportional to the rate of supply of feedstock to the first bed, the proportionality factor taking into account the Conradson carbon number of the feedstock.

The oxygen containing gas supplied to the second bed may be arranged to have a composition such that the off-gases are useful by-products or intermediates. Thus, the gas may be air enriched with oxygen such that the off-gases will contain CO, CO₂ and N₂ in proportions suitable for the application of the water gas shift reaction:



to provide, after washing out the CO₂ by methods known in the art, the remaining gases containing nitrogen and hydrogen in suitable proportions for ammonia synthesis. Another suitable oxygen containing gas comprises a mixture of oxygen and steam so that the off-gases from the second bed consist largely of hydrogen, CO and CO₂; this type of off-gas can be scrubbed to remove CO₂ leaving a

gas suitable for Fischer-Tropsch synthesis reactions, or it may be mixed with steam and passed over a water-gas shift catalyst to provide, after scrubbing out the resulting CO₂, substantially pure hydrogen. In the instances so far mentioned, the amount of oxygen in the oxygen-containing gas can be varied in accordance with known thermodynamic principles and in accordance with the amount of combustible deposit on the particles to give the desired type of off-gas. The off-gases may be used for heat production by combustion instead of intermediates for further processing.

It is important that the temperature in the second bed is maintained in the range 800–1000° C. to ensure that sulphur or sulphur compounds are not evolved: the presence of sulphur or its compounds would gradually inactivate any water gas shift catalyst. Accordingly, it is preferred to sense the temperature in the second bed, and when the temperature rises above a selected temperature, to inject a diluent into the second bed. Suitable diluents are water, steam and nitrogen, and the amount of diluent injected is preferably varied as the bed temperature varies.

It is also important that the temperature in the first bed is maintained between 500 and 700° C., below 500° C., the rate of conversion of feedstock is relatively uneconomical while above 700° C., the amount of cracking of feedstock to light hydrocarbons and hydrogen and the amount of carbon deposit on the particles become excessive. Accordingly, if the rate of supply of feedstock to the first bed is substantially constant, the temperature in the first bed may be sensed, and the rate of transfer of particles from the first bed to the second bed decreased when the temperature in the first bed rises and decreased when the temperature in the first bed decreases: thus the amount of carbonaceous material transferred from the first bed to the second bed for combustion leading to heat generation is accordingly restricted, and the heat return to the first bed is decreased. Alternatively, the feedstock supply rate may be increased with an increase in temperature and decreased with a decrease in temperature, but this is less convenient for most refinery operations.

The amount of particles in the second bed is preferably maintained within a chosen range sufficient for a particle having an average size and an average deposit of carbonaceous material thereon to have an adequate residence time for removal of at least a major portion, or preferably substantially all, of the carbonaceous deposit. The residence time will, of course, depend on the design of the vessel containing the second bed, and the amount of particles in the second bed is maintained in the chosen range by sensing the amount in the bed (e.g., by static pressure determinations) and transferring particles to the first bed at a rate which increases with any increase in the amount in the second bed, and decreases with any decrease in the amount in the second bed.

The particles in the first bed may be fluidized not only by the vaporous conversion product, but also by a suitable fluidizing gas or vapour. For this purpose, steam is preferred since it is relatively cheap and can be removed as water from the products. The steam also acts to strip any volatile materials trapped in the deposit on the particles.

The invention also includes the various products made by the foregoing method. It will be appreciated that the invention enables potential pollutants and waste materials to be converted to commercially useful products and intermediates.

An embodiment of a plant for performing the invention is illustrated by way of non-limitative example in the accompanying drawing, the plant being shown semi-schematically.

The feedstock, such as a residuum containing sulphur and other undesirable materials, such as sodium, vanadium and iron, is supplied via line 10 to a fluid coker vessel 11 in which there is contained a bed 12 of fluidized

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particles comprising lime (e.g. calcined limestone or calcined dolomite). The rate of supply of the feedstock is measured by a meter 13, and steam is injected into the base of the coker 11 from line 14 at a rate which is correlated with the fuel supply rate by means of a suitable meter 15. The temperature in the bed 12 is maintained in the range 500–700° C. and in this range, the feedstock is converted to vapour-phase products, and carbonaceous materials such as coke and heavy tars. The coke and tarry materials are deposited on the fluidized particles while the vapour-phase products are carried upwards out of the coker 11 via a cyclone 17 and a slurry trap 16 to a fractionator 18. The sulphur content of the original feedstock tends to be more concentrated in the coke and tarry materials than in the vapour phase products, as do other contaminants such as vanadium and sodium.

In the slurry trap 16, heavy hydrocarbon materials admixed with fines from the bed 12 are trapped, and are recycled via line 19 to the bed 12, possibly, but not necessarily, in admixture with the feedstock in line 10.

The coked and tarry particles move towards the bottom of the coker 11, and any volatile materials trapped thereon are stripped off by the steam from line 14. The coked particles are withdrawn via line 20 and passed to a second bed 21 in a burner vessel 22. The bed 21 contains particles fluidized in an oxygen containing gas which is supplied from line 23 by means of fan 24 at a rate controlled by a valve 25. The oxygen containing gas may be air, oxygen-enriched air, air and steam or steam admixed with substantially pure oxygen.

In the burner bed 21, the carbonaceous deposit on the particles is removed either wholly or to a major extent with the generation of heat. The sulphur content of the deposit is trapped by reaction with the calcium oxide of the particles as calcium sulphide, and the sodium and vanadium also are retained by the particles: the sodium and vanadium retention of the particles is sometimes improved if iron is present, either as an impurity picked up from the original feedstock or as an "impurity" in the particles.

The temperature in the bed 21 must be maintained between 800 and 1000° C. to ensure an adequate minimum temperature for satisfactory combustion and a suitable maximum temperature to prevent the decomposition of the calcium sulphide with the evolution of sulphur or sulphur compounds. To maintain the temperature within these limits, the maximum rate of supply of oxygenated gas from the fan 24 is slightly greater than would be necessary for the highest rates of carbon and coke lay-down on the particles from the feedstock, the actual supply rate to the bed 21 being regulated by the valve 25. A temperature probe 26 senses the temperature in the bed 21, and as the temperature tends towards 1000° C., signals from the probe 26 cause a valve 27 to open progressively thereby allowing a regulated amount of diluent from line 28 into the bed 21. The diluent is preferably steam, but nitrogen may be used in addition or alternatively.

The amount of particles in the bed 21 is determined by pressure transducers 29, 30 from which a differential pressure signal is derived by a differential pressure manometer 31. As the differential pressure approaches a maximum desired value, a signal from the manometer 31 causes a control valve 32 to open progressively, thereby allowing an increase flow-rate of a propelling fluid from a line 33 to the main transfer line 34. The propelling fluid is preferably steam, and it entrains, fluidizes and propels particles along the smoothly curving transfer line 34 from near the base of the burner vessel 22 to the coking vessel 11, the particles entering near the top of the bed 12.

The gases leaving the burner 22 pass through a cyclone 35 to a take-off line 36 and are monitored for CO₂ by an infra-red monitor 37. If the CO₂ content of the off-gases is excessive indicating excessive oxidizing conditions with-

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in the bed 21, a signal to the controller 38 on valve 25 causes the valve 25 to be progressively closed until the CO₂ concentration is acceptably low. The maintenance of a low CO₂ concentration in the off-gases ensures that minimal quantities of calcium sulphide in the burner bed 21 are converted to other compounds, possibly with the loss of sulphur in the off-gases from the burner.

Some particles are transferred from the burner bed 21 via a smoothly curving line 39 to the lower region of a third bed 40 of a regenerator vessel 41 wherein the particles are fluidized above a distributor 42 in an oxygen-containing gas, such as air, supplied by a fan 43. The particles in the bed 40 should be substantially free of carbon, and at the temperatures of 1000 to 1100° C., the calcium sulphide is converted to calcium oxide with the evolution of SO₂ and the production of heat. The SO₂-containing off-gases leave the bed 40 via a cyclone 44 and are monitored either for oxygen or SO₂ by a detector 45. If the SO₂ content of the gases is too low, the signal received from the detector 45 by a valve controller 46 will cause a valve 47 in the air supply line 48 to close until the designed SO₂ concentration is attained. An SO₂ concentration in the range 9% to 11% should be attainable. The detector 45 can be equally used to monitor oxygen: provided the free oxygen content of the off-gases does not exceed 1%, the SO₂ content will be satisfactory, and probably in the range 9% to 11%.

Control of temperature in the regenerator bed 40 is achieved by means of a temperature transducer 49 which acts on the controller 50 of a valve 51 in a steam propellant line 52. As the temperature in the bed 40 increases, the valve 51 is progressively opened, thereby increasing the rate of supply of particles from the relatively cooler bed 21 to the relatively hotter regenerator bed 40, thus reducing the temperature therein.

In order to prevent an excessive accumulation of particles in the bed 40, particles are transferred from a top region of the bed 40 to the coker bed 12 along the smoothly curving line 53 by steam propellant supplied via line 54. The rate of steam supply along line 54 is regulated by control 55 which opens progressively as the static pressure in the bed 40 increases: the static pressure is measured by transducers 56.

It will be appreciated that the particles returned to the coker bed 12 will be considerably hotter than the temperature desired in the bed 12. Most of the heat thus supplied to the coker bed 12 is employed for the actual conversion process which is endothermic. Temperature control in the coker bed 12 is achieved by sensing the temperature using transducer 58, and employing the resulting temperature signal to control the supply of propellant stream from line 59 to the smoothly curving transfer line 20, so that particles are transferred at a decreased rate as the temperature in the coker bed 12 increases and less particles are thereby transferred to the burned bed 21 and regenerator bed 40, less heat thus being generated. If the temperature in the coker bed 12 decreases, the rate of transfer of particles to the burner and regenerator beds is increased. This method of temperature control is applicable when the feedstock supply rate is substantially constant and since for most refinery operations, the coker would be run at about its designed load conditions, this would be the most economical method of temperature control. However, if it is economically possible to vary the feedstock supply rate, an increase in the coker bed temperature can be sensed and employed to cause an increase in the feedstock supply rate, whereby due to the endothermic nature of the conversion reaction, the coking bed temperature will fall. Similarly, a decrease in coker bed temperature can be employed to cause a decrease in the feedstock supply rate. In this type of temperature control method, it is not necessary to vary the rate of supply of particles to the burner bed, although some variation may be made if desired.

The sulphur-fixing activity of the particles is maintained by bleeding off particles through a dump valve 60 from a bottom (oxidizing) region of the bed 40. The regulation of the dump valve 60 is in accordance with a signal from an H₂S monitor 61 which monitors the gases (gaseous hydrocarbons and hydrogen) leaving a condenser 62.

A substantially constant inventory of active particles is maintained in the system as a whole by monitoring the head of particles in the bed 12 by means of transducers 63, 64 and using the differential transducer 65 to control the opening of a bell-mouth lock hopper 66 via a relay 67. Fresh lime, limestone or dolomite particles are introduced when the lock hopper 66 is opened.

It will be apparent to those skilled in the art that the exemplary plant described and illustrated can be modified for performing the invention without departing from the ambit of the appended claims.

I claim:

1. A method of converting a sulphur-containing heavy petroleum feedstock comprising the steps of passing the feedstock into a first bed of fluidized particles comprising calcium oxide or a precursor thereof at a temperature between 500 and 700° C. whereby the feedstock is converted to vapours comprising normally liquid and gaseous products of reduced sulphur content and to carbonaceous material of increased sulphur content which deposits on the said particles, recovering the said vapours from the first bed and transferring particles from the first bed to a second bed wherein the particles are fluidized at a temperature of 800° C. to 1000° C. in a gas containing oxygen in an amount sufficient to convert at least some of the carbonaceous material to gases containing a carbon oxide whereby the carbonaceous deposits on the particles are at least partially removed, and at least some of the sulphur originally present in the carbonaceous deposits reacts with the calcium oxide to form calcium sulphide, recovering the gases containing at least one carbon oxide from the second bed, transferring some of the particles from the second bed to the first bed and transferring particles from the second bed to a lower zone of a third bed in which the particles are fluidized at a temperature of 1000 to 1100° C. in an oxygen containing gas whereby at least some of the calcium sulphide in the particles is converted to calcium oxide with the release of SO₂, and transferring particles from an upper zone of the third bed to the first bed.

2. A method according to claim 1 in which the temperature in the third bed is sensed and the rate of transfer of particles from the second bed to the third bed is increased and decreased with respective increases and decreases in the temperature in the third bed.

3. A method according to claim 1 in which the oxygen content of the off-gases leaving the third bed is sensed, and the rate of supply of the oxygen containing gas to the third bed is increased and decreased with respective decreases and increases of the oxygen content of said off-gases.

4. A method according to claim 1 in which the SO₂ content of the off-gases leaving the third bed is sensed, and the rate of supply of the oxygen containing gas to the third bed is increased and decreased with respective increases and decreases of the SO₂ content of said off-gases.

5. A method according to claim 1 in which the sulphur content of at least some of the vapours recovered from the first bed is determined and wherein a portion of particles are dumped from the third bed, said portion being increased with respective increases in said sulphur content.

6. A method according to claim 1 in which the static head of particles in the first bed is sensed, and whenever the static head falls below a selected static head, fresh particles are added to the second bed in an amount sufficient to maintain the static head in the first bed at the selected static head.

7. A method according to claim 1 in which the off-gases leaving the second bed are analyzed for CO₂, and the rate of supply of oxygen to the second bed is increased and decreased with respective decreases and increases of the CO₂ content of said off-gases.

8. A method according to claim 1 in which the rate of supply of oxygen containing gases to the second bed is increased and decreased with respective increases and decreases of the rate of supply of feedstock to the first bed.

9. A method according to claim 1 in which the oxygen containing gas supplied to the second bed comprises air enriched with additional oxygen in such proportions that the gases leaving the second bed have a content of CO, CO₂ and N₂ suitable for subjecting to a water gas shift reaction.

10. A method according to claim 9 in which the gases leaving the second bed are mixed with steam and subjected to a water gas shift reaction to produce a feedstock for the production of ammonia.

11. A method according to claim 1 in which the oxygen containing gas supplied to the second bed comprises oxygen and steam in such proportions that the gases leaving the second bed have a content of carbon monoxide and hydrogen suitable for reactions selected from water gas shift reactions for the production of hydrogen, and Fischer-Tropsch syntheses.

12. A method according to claim 1 in which the temperature in the second bed is sensed and diluent selected from nitrogen, water and steam is supplied to the second bed when the temperature in the second bed is in excess of a required temperature, the amount of diluent varying in accordance with the excess of the temperature relative to the required temperature.

13. A method according to claim 1 in which the temperature in the first bed is sensed and the rate of transfer of particles from the first bed into the second bed decreased when the temperature in the first bed increases and increased when the temperature therein decreases.

14. A method according to claim 13 in which the amount of particles in the second bed is determined to maintain a predetermined amount therein, and the rate of transfer of particles from the second bed to the first bed increased and decreased with respective increases and decreases in the amount of particles in the second bed relative to the predetermined amount.

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