United States Patent [19]

Aldridge

[11] **3,838,993**

[45] **Oct. 1, 1974**

[54] **TWO STAGE PROCESS FOR THE CONVERSION OF HEAVY HYDROCARBONS TO A METHANE RICH GAS STREAM**

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[22] Filed: **Dec. 20, 1972**

[21] Appl. No.: **316,924**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 125,581, March 18, 1971, abandoned.

[52] **U.S. Cl.** **48/214,** 48/215

[51] **Int. Cl.** **C01b 2/14,** C01b 2/22, C10g 11/28

[58] **Field of Search** 48/214, 215, 197

[56] **References Cited**

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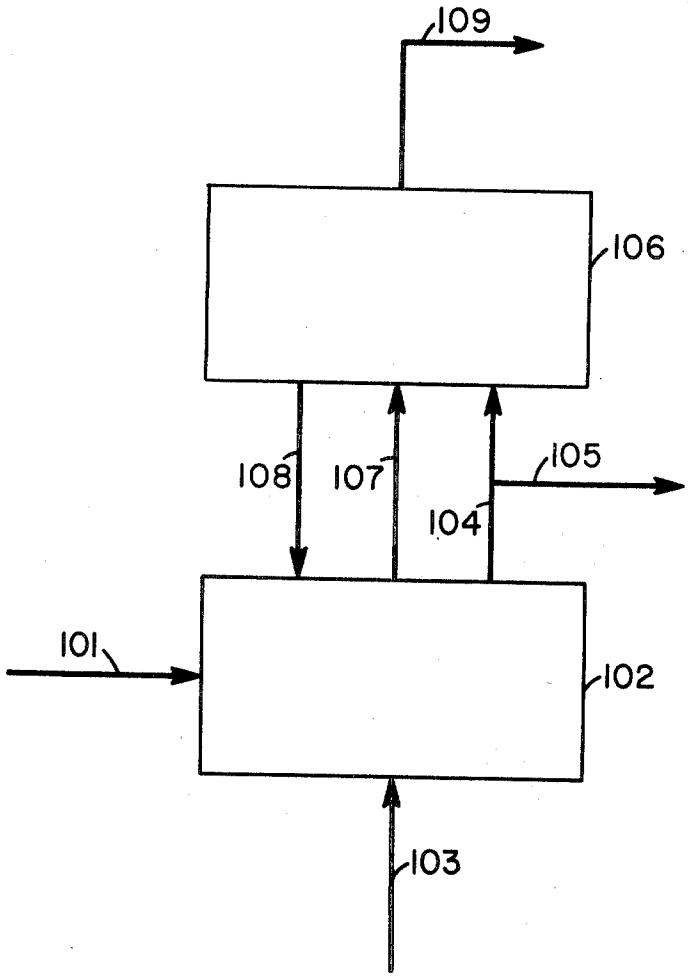
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Primary Examiner—R. E. Serwin

[57] **ABSTRACT**

Heavy hydrocarbons are treated with steam in the presence of a non-molten particulate alkali metal containing catalyst to produce a methane-containing vapourous product. At least a portion of the vaporous product is converted to additional methane in a second stage in the presence of the non-molten alkali metal containing catalyst. Each of the stages is operated at pressures above 200 psig and temperatures between about 1,000° and 1,500°F.

27 Claims, 2 Drawing Figures



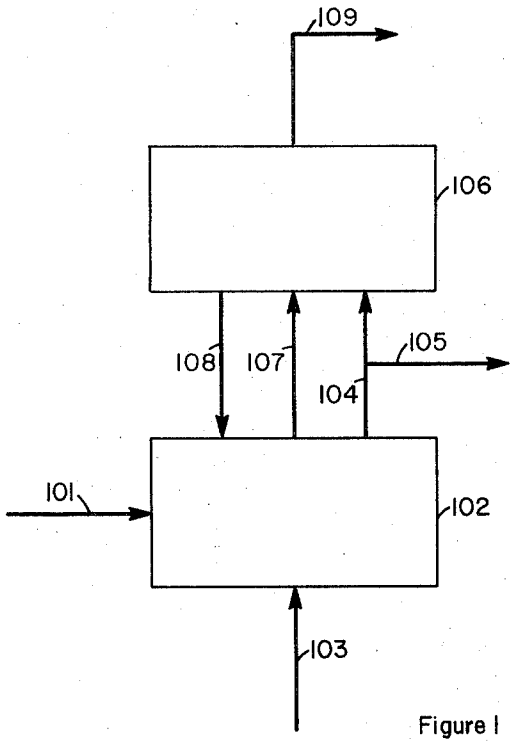


Figure 1

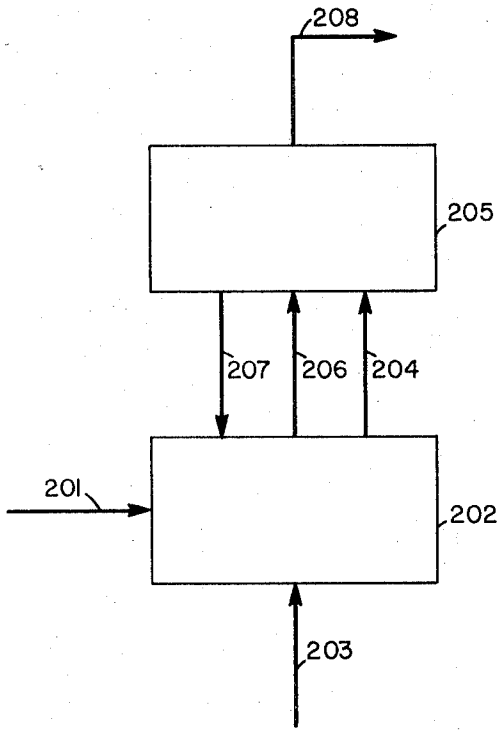


Figure 2

TWO STAGE PROCESS FOR THE CONVERSION OF HEAVY HYDROCARBONS TO A METHANE RICH GAS STREAM

RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 125,581 filed Mar. 18, 1971, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a two-stage process for the conversion of a hydrocarbon feed containing heavy hydrocarbons to a methane rich stream in the presence of a particulate alkali metal containing catalyst.

2. Description of the Prior Art.

The use of alkali metal compounds as catalysts in various hydrocarbon conversion processes is well known. For example, U.S. Pat. No. 2,893,941 discloses the use of a minute quantity (i.e., ppm) of K_2CO_3 in a steam cracking process to inhibit coke formation. It is also known (U.S. Pat. No. 3,112,257) that hydrocarbon oils can be desulfurized by contact with steam in the presence of a Group VI to VIII metal-alkali metal catalyst system at temperatures under 900°F. Alkali metal compounds are also known to increase hydrogen production when steam gasifying solid carbonaceous material (see U.S. Pat. No. 3,252,773) and when coking hydrocarbon oils (see U.S. Pat. No. 3,179,584). As disclosed in U.S. Pat. No. 3,252,774, it is further known that liquid hydrocarbons can be converted to a hydrogen-rich gas stream by contact with steam and a large excess of molten alkali metal catalyst system at low feed rates.

It is also known that methane can be produced by steam reforming naphtha or lighter boiling hydrocarbons in the presence of a steam reforming catalyst and that certain steam reforming nickel containing catalysts may be promoted by small amounts of alkali metal (see U.S. Pat. No. 3,320,182). Attempts to steam reform higher boiling hydrocarbon feedstocks with such processes have led to rapid deactivation of the conventional steam reforming catalysts due to carbon deposition thereon. Furthermore, hydrocarbon feedstocks having large amounts of sulfur contaminants generally required a desulfurization treatment prior to the catalytic steam reforming process since the conventional steam reforming catalysts are sulfur sensitive.

Furthermore, it is known to produce a fuel gas from heavy liquid hydrocarbons in a two-zone process wherein a high temperature combustion zone is operated in conjunction with a hydrocracking zone containing particulate contact material (see U.S. Pat. No. 3,202,603).

It has now been found that a hydrocarbon feedstream containing at least 10 weight percent hydrocarbons boiling above 600°F. at atmospheric pressure, can be converted to a methane rich gas stream in a two-stage process operated under specified conditions and employing a particulate alkali-metal containing catalyst. Methane is produced in the first stage and additional methane is produced in the second stage so that the total methane yield is greater than that obtainable in a one-stage operation. Furthermore, the two-stage process is more thermally efficient than a one-stage process because of the heat exchange which occurs between the two stages. Moreover, the gasification can be carried out at temperatures not greater than 1,500°F. with the process of the present invention.

SUMMARY OF THE INVENTION

In accordance with the invention, a hydrocarbon feed containing at least 10 weight percent hydrocarbons having a boiling point above 600°F. at atmospheric pressure is contacted with steam in a first reaction zone containing a particulate catalyst bed comprising an alkali metal component, a solid particulate support and an in-situ formed carbonaceous deposit on said support, wherein said alkali metal component (calculated as the metal) comprises at least 1.0 weight percent of the total solids inventory of said bed, said first reaction zone being maintained at a pressure above 200 psig and at an average temperature varying between about 1,000° and 1,500°F. to produce a vaporous product comprising H_2, CO, CO_2 and CH_4, and solid carbonaceous material, at least a portion of which deposits on said support. Thereafter, at least a portion of said particulate catalyst and at least a portion of said vaporous product are passed to a second reaction zone maintained at a pressure above 200 psig and at an average temperature varying between about 1,000°F. and 1,500°F. to produce a methane rich gaseous product which is then recovered from the second reaction zone.

In one embodiment of the invention, the second reaction zone is maintained at a higher temperature than the first reaction zone and unreacted steam and CO_2 are removed from the vaporous product of the first reaction zone prior to passing at least a portion of the remaining vaporous product to the second reaction zone. The higher temperature second zone supplies a portion of the heat required in the first zone by circulation of the particulate catalyst between the two zones. When the vaporous product of the first reaction zone also comprises other light hydrocarbon products (besides CH_4), including normally liquid hydrocarbons, these liquid hydrocarbons may also be removed from the vaporous stream prior to passing at least a portion of the steam-removed and CO_2-removed vaporous stream to the second reaction zone.

In another embodiment of the invention, the total vaporous product of the first reaction zone is passed to the second reaction zone and the second reaction zone is maintained at a lower temperature than the first reaction zone.

Furthermore, a portion or all of the liquid hydrocarbon products separated from the vaporous product of the first reaction zone or from the gaseous product of the second reaction zone may, if desired, be recycled to the first reaction zone.

In another embodiment, an oxygen-containing gas, such as, oxygen or air may also be introduced into the first reaction zone,

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 in the accompanying drawing is a diagrammatic flow plan of one embodiment of the invention.

FIG. 2 is a diagrammatic flow plan of another embodiment of the invention.

PREFERRED EMBODIMENTS OF THE INVENTION

The preferred embodiments of the invention will be described with reference to FIGS. 1 and 2.

The process of this invention is suitable for the conversion of a great variety of hydrocarbon feedstreams containing heavy hydrocarbons and which may further contain contaminants such as sulfur compounds, metals and/or nitrogen compounds. It is suited for the treatment of hydrocarbon feeds containing at least 10 wt. percent hydrocarbons boiling above 600°F. at atmospheric pressure and it is especially suited for hydrocarbon feeds containing at least 10 wt. percent hydrocarbons having a boiling point greater than 900°F. at atmospheric pressure. By way of example, suitable hydrocarbon feeds include whole petroleum crude; petroleum atmospheric residuum; petroleum vacuum residuum; heavy hydrocarbon oils and other heavy hydrocarbon residua; deasphalted residua; the asphaltene fraction from deasphalting operations; bottoms from catalytic cracking process fractionators; coker produced oils; cycle oils, such as catalytically cracked cycle oils; pitch, asphalt and bitumen from coal, tar sands or shale; naturally occurring tars, as well as tars resulting from petroleum refining processes; shale oil; tar sand oil which may contain sand; hydrocarbon feedstreams containing heavy or viscous materials including petroleum wax fractions. Furthermore, to any of these suitable hydrocarbon feeds may be added a solid carbonaceous material such as coke or coal.

Referring to FIG. **1,** a hydrocarbon feed is introduced by line **101** into a first reaction zone **102** to contact steam in the presence of a particulate alkali metal containing catalyst maintained as a fluid bed therein. Steam is introduced into reaction zone **102** by line **103.** This steam also serves as fluidizing gas. If desired, an oxygen-containing gas may also be introduced into the first reaction zone to provide a portion of the heat required in that zone by combustion of at least a portion of the feed and/or carbonaceous material and/or gaseous products present therein or the heat may be provided by other methods to be described later.

The catalyst may be maintained in a fixed, moving or fluid bed. Moving or fluid bed catalyst systems are preferred for conversion of feed materials containing the heaviest hydrocarbons. Because of the ease of maintaining uniform temperature distribution and preventing the formation of coke agglomerates, a fluidized catalyst system is particulatly preferred for the conversion of feedstocks containing large amounts of hydrocarbons having a 900°F. plus boiling point at atmospheric pressure. The catalyst bed in the first reaction zone is a bed of particulate solids which contains the catalyst, coke by-product, and ash constituents including metal contaminants of the hydrocarbon feed. The catalyst comprises an alkali metal component, a solid particulate material as carrier or support and a solid carbonaceous coating or deposit which is formed in situ on the support when the process is in operation. The active catalytic component is believed to be the alkali metal. The alkali metal component is preferably provided in the catalyst system by either depositing or mixing initially an alkali metal compound with a suitable solid particulate support. This depositing or mixing can be performed within the reaction vessel or outside the reaction vessel with subsequent introduction of the composite into the reaction vessel. Under process conditions, it is believed that the alkali metal compound is at least partially reduced to the free metallic state.

Suitable alkali metal catalyst components include the carbonates, acetates, formates, sulfides, hydrosulfides, sulfites, vanadates, oxides and hydroxides of sodium, lithium, cesium and potassium. In general, any alkali metal compound which is at least partially reducible to the free metallic state under process conditions may be used.

The solid particulate support may be chosen from a wide variety of solids. The support may be a gasifiable (at process conditions) solid or a substantially non-gasifiable (at process conditions) solid. Although a gasifiable solid such as coke or activated carbon is suitable as support, a non-gasifiable solid support is preferred because changes of temperature or steam-to-carbon ratios in the reaction zone could result in degradation of the gasifiable support, including partial or total loss of the support from the bed and the possible consequent entrainment of alkali metal containing fines out of the reaction zone. The preferred non-gasifiable particulate solid supports include zeolites, refractory inorganic oxides, such as, silica-alumina, magnesia, calcium oxide, zirconia, gamma alumina, crude or partially purified bauxite, alpha-alumina, alundum, mullite, silica; synthetically prepared or naturally occurring material such as pumice, clay, diatomaceous earth (kieselguhr); porcelain, glass or marble spheres or other inert spherical materials.

The carbonaceous deposit is formed when the process is in operation. Part of the feed is converted to a solid carbonaceous material, a portion of which deposits on the alkali metal containing support particles present in the reaction zone. While applicant does not wish to be bound by theory, it is believed that at least a portion of the alkali metal migrates to the carbonaceous deposit on the support to form the desired catalyst system.

A preferred catalyst comprises K_2CO_3 or Cs_2CO_3 mixed with or deposited on a refractory inorganic oxide such as alumina, silica, silica-alumina, magnesia, crude or partially purified bauxite or mixtures thereof. A sufficient amount of alkali metal compound is added to the catalyst bed to maintain at least 1.0 weight percent alkali metal (calculated as the metal) based on the total bed solids inventory (support plus alkali metal compound, solid carbonaceous products, ash, residual metals, etc.) present in the catalyst bed under processing conditions. Preferably, the weight of alkali metal in the bed will range broadly between 1.0 and 35 weight percent (calculated as the metal), more preferably between 3 and 30 weight percent and most preferably between 4 and 25 weight percent. An example of an equilibrium composition of the total solids inventory of the catalyst bed would be about 25 weight percent K_2CO_3 (calculated as K_2CO_3), 35 weight percent solid support, 20 weight percent coke, 20 weight percent ash derived from impurities of the feed. A portion of the catalyst bed solids may be withdrawn from the system periodically or continuously to prevent excessive accumulation of ash in the bed. Fresh or regenerated catalyst would then be introduced into the system to maintain the desired catalyst inventory. The catalyst system exhibits an unusually high cracking activity as well as methane formation activity.

The first reaction zone is maintained at a pressure above 200 psig, preferably a pressure between about 250 and 1,500 psig, more preferably at pressures between about 400 and 1,000 psig and at numerically integrated average temperatures between about 1,000° and 1,500°F., preferably between about 1,200° and

1,400°F., more preferably between about 1,250° and 1,425°F. By numerically integrated average temperature is meant the procedure wherein a temperature-distance plot (curve) is averaged by taking the sum of n equally spaced ordinate values of temperature and dividing this sum by *n*.

In the embodiment illustrated in FIG. **1**, it is preferred to maintain the second reaction zone at a temperature at least as high as the actual temperature maintained in the first reaction zone. Preferably the temperature in the second reaction zone is maintained at a higher temperature than the actual temperature of the first reaction zone. More preferably, the second reaction zone is maintained at a temperature at least 50°F. higher than the actual temperature of the first reaction zone.

The rate at which the hydrocarbon feed is introduced into the first reaction zone will depend in part upon the operating conditions within that zone. Under the above given operating conditions, suitable feed rates would be at least 0.02 weight part of feed per weight part of bed solids total inventory per hour, preferably feed rates between 0.02 and 2 weights part of feed per weight part of bed solids total inventory per hour, more preferably between 0.05 and 1.5 weight part of feed per weight part of bed solids total inventory per hour, most preferably between 0.1 and 1.0 weight part of feed per weight part of bed solids total inventory per hour.

The steam rate in the first reaction zone is set such as to get practical steam conversion.

Desirably, steam is introduced into the reaction zone in amounts such that R, the ratio of molecules of steam to atoms of carbon in the hydrocarbon feed as expressed by the equation:

$$\text{moles of steam introduced/atoms of carbon in feed} = R$$

R varies between 0.7 and 15, preferably between 1.7 and 5.

It may be necessary to put additional heat into the first reaction zone. This may be done in several ways. The hydrocarbon feed may be preheated to temperatures of about 400°–950°F. before introduction into the first reaction zone. A preferred method is to inject small quantities of an oxygen-containing gas such as air or oxygen into the first reaction zone either separately or with the fluidizing steam to produce the highly exothermic reaction:

$$C + O_2 \rightarrow CO_2 + 169200 \text{ Btu}$$

A still further method would include circulating a portion of the catalyst between the first reaction zone and a separate heating zone, such as, an air burner, and recycling the heated portion to the first reaction zone. A further method would include electrical heating of the catalyst bed or other indirect methods of heating the bed. Furthermore, any combination of each of these methods could also be employed.

Treatment of the hydrocarbon feedstream with steam under the given operating conditions produces a vaporous product and a solid carbonaceous material, a portion of which deposits on the particulate alkali metal containing support particles. The vaporous product comprises H_2, CO, CO_2, unreacted steam and CH_4. Depending on the hydrocarbon feedstock used, the vaporous product may also contain light hydrocarbon products other than CH_4. These other light hydrocarbon products may include C_2 to C_4 hydrocarbon products, and aromatics such as benzene and toluene. The vaporous product is removed from the first reaction zone by line **104** and treated (by condensation) to remove unreacted steam and further treated to remove CO_2 by conventional means indicated at line **105.** At least a portion of the remaining vaporous product is passed to a second reaction zone **106.** At least a portion of the particulate catalyst is passed via line **107** to the second reaction zone.

The second reaction zone is operated at a pressure above 200 psig, preferably between about 250 and **1,500** psig, more preferably between about 400–1,000 psig, and at numerically integrated average temperatures between about 1,000° and **1,500**°F., preferably between about 1,200° and 1450°F., more preferably between about 1,250° and 1,425°F.

As has already been indicated above, the temperature in the second reaction zone may be higher than the actual temperature in the first reaction zone, although, both reaction zones are operated within the same broad temperature range.

In the second reaction zone, at the start of the process, is maintained a bed of the same catalyst as that initially employed in the first reaction zone. When the process is in operation, there is interchange of catalyst particles between the first and second reaction zones via line **107** and between the second reaction zone and the first reaction zone via line **108.**

The catalyst in the second reaction zone may be maintained as a fixed, moving or fluid bed, the latter two being preferred. The bed in the second reaction zone may be in a different state from that of the first reaction zone, that is, if the first reaction zone has a fluidized bed, the second reaction zone need not have a fluidized bed, although a fluidized bed would be preferred.

In the second reaction zone, the H_2 and CO of the vaporous product formed in the first reaction zone react in the presence of the particulate alkali metal containing catalyst to form additional methane and H_2O.

The gaseous product of the second reaction zone, which is a methane rich gaseous stream, is removed from the second reaction zone via line **109.**

The embodiment shown in FIG. **2** differs from that shown in FIG. **1** in that the total vaporous product of the first reaction zone is passed to the second reaction zone. In such an embodiment, the second reaction zone is preferably operated at a lower temperature than the first reaction zone to obtain better methanation in the presence of the unreacted steam of the vaporous product.

Referring to FIG. **2,** the hydrocarbon feedstream is introduced via line **201** into the first reaction zone **202** operated at an average temperature between about 1,300°F. and 1,500°F. Steam is introduced into the reaction zone **202** via line **203** to contact the hydrocarbon feedstream in the presence of the particulate alkali metal containing catalyst.

An oxygen-containing gas may be introduced into reaction zone **202** to provide a portion of the heat requirement therein. The total vaporous product of the first reaction zone comprising H_2, CO, CO_2, CH_4 and unreacted steam is passed via line **204** to a second reaction zone **205.** The second reaction zone is maintained at an average temperature between about 1,300° and 1,000°F. At least a portion of the particulate catalyst is passed to the second reaction zone **205** via line **206.**

During operation of the process, there is interchange of a portion of the catalyst between the two zones. A portion of the catalyst passes from the second reaction zone to the first reaction zone via line **207.** In the second reaction zone, the H_2 and CO react to form additional methane and H_2O.

The gaseous product, which is a stream rich in methane content, is removed from the second reaction zone via line **208.** The methane rich gaseous stream may be treated (e.g., by condensation) to remove unreacted steam and, if desired, further treated to remove CO_2 by conventional means. If the methane rich gaseous stream contains normally liquid hydrocarbon products, the gaseous stream may be put through separating means (not shown) to separate the methane-containing gas from the normally liquid product. Part or all of the liquid hydrocarbon product may be recycled to the first reaction zone.

It is to be understood that the two-stage process of this invention may be carried out in a single vessel or in two separate vessels.

What is claimed is:

1. A process for producing a methane rich gas from a hydrocarbon feed containing at least 10 weight percent hydrocarbons having a boiling point above 900°F. at atmospheric pressure, which comprises:

a. contacting said hydrocarbon feed with steam in a first reaction zone containing a particulate catalyst bed comprising an alkali metal component, a solid particulate support and an in-situ formed carbonaceous deposit on said support, wherein said alkali metal component (calculated as the metal) comprises at least 1.0 weight percent of the total solids inventory of said bed, said first reaction zone being maintained at a pressure above 200 psig and at an average temperature between about 1,000° and 1,500°F. to produce a vaporous product comprising H_2, CO, CO_2 and CH_4, and solid carbonaceous material, at least a portion of which deposits on said support;

b. passing at least a portion of said particulate catalyst and at least a portion of said vaporous product to a second reaction zone maintained at a pressure above 200 psig and at a average temperature between about 1,000° and 1,500°F. to produce a methane rich gaseous product;

c. recovering said gaseous product from said second reaction zone, and

d. passing at least a portion of said particulate catalyst from said second reaction zone to said first reaction zone.

2. The process of claim **1,** wherein the second reaction zone is maintained at a higher average temperature than the actual average temperature maintained in the first reaction zone and wherein the vaporous product of step (a) is treated to remove unreacted steam and CO_2 prior to passing at least a portion of the remaining vaporous product to said second reaction zone.

3. The process of claim **2,** wherein the second reaction zone is maintained at an average temperature at least 50°F. higher than the actual average temperature maintained in the first reaction zone.

4. The process of claim **2** wherein said vaporous product of step (a) also comprises other light hydrocarbon products including normally liquid hydrocarbon products and wherein said normally liquid hydrocarbon products are also removed from said vaporous product of step (a) prior to passing at least a portion of the remaining vaporous product to said second reaction zone.

5. The process of claim **4** wherein at least a portion of the removed normally liquid hydrocarbons is recycled to said first reaction zone.

6. The process of claim **1,** wherein said second reaction zone is maintained at a lower temperature than the first reaction zone and wherein the total vaporous product of the first reaction zone is passed to the second reaction zone.

7. The process of claim **6,** wherein the second reaction zone is maintained at an average temperature between 1,000°F. and 1,300°F. and the first reaction zone is maintained at an average temperature between 1,300°F. and 1,500°F.

8. The process of claim **6,** wherein the vaporous product of step (a) also comprises other light hydrocarbon products including normally liquid hydrocarbon products, and wherein the gaseous product recovered from the second reaction zone is further treated to separate the normally liquid products from the normally gaseous products.

9. The process of claim **8,** wherein at least a portion of separated normally liquid product is recycled to the first reaction zone.

10. The process of claim **1,** wherein an oxygen-containing gas is introduced into said first reaction zone.

11. The process of claim **1,** wherein the weight of the alkali metal component (calculated as the metal) in said first reaction zone bed is between 1.0 and 35 weight percent of the total solids inventory of said bed.

12. The process of claim **1,** wherein the weight of the alkali metal component (calculated as the metal) in said first reaction zone bed is between 3 and 30 weight percent of the total solids inventory of said bed.

13. The process of claim **1,** wherein the weight of the alkali metal component (calculated as the metal) in said first reaction zone bed is between 4 and 25 weight percent of the total solids inventory of said bed.

14. The process of claim **1** wherein said alkali metal component is an alkali metal compound which is at least partially reducible to the free metal.

15. The process of claim **1** wherein said solid support is a non-gasifiable material.

16. The process of claim **1** wherein said solid support is a refractory inorganic oxide.

17. The process of claim **1** wherein said solid support is an inorganic oxide selected from the group consisting of silica, alumina, silica-alumina, magnesia, crude or partially purified bauxite or mixtures thereof.

18. The process of claim **1,** wherein said solid support is activated carbon.

19. The process of claim **1,** wherein said solid support is petroleum coke.

20. The process of claim **1,** wherein said catalyst comprises K_2CO_3 or Cs_2CO_3 mixed with said solid support.

21. The process of claim **1,** wherein said catalyst comprises K_2CO_3 or Cs_2CO_3 deposited on said solid support.

22. The process of claim **1,** wherein said steam is introduced into said first reaction zone at a ratio varying between 0.7 and 15 moles of steam to carbon atoms in said hydrocarbon feed.

23. The process of claim 1, wherein said first and said second reaction zones are each maintained at pressures between 250 and 1,500 psig.

24. The process of claim 1, wherein said first and said second reaction zones are each maintained at pressures between 400 and 1,000 psig.

25. A process for producing a methane rich gas from a hydrocarbon feed containing at least 10 weight percent hydrocarbons having a boiling point above 900°F. at atmospheric pressure, which comprises:

a. contacting said hydrocarbon feed with steam and an oxygen-containing gas in a first reaction zone containing a particulate catalyst bed comprising an alkali metal component, a non-gasifiable solid particulate support and an in-situ formed carbonaceous deposit on said support, wherein the alkali metal component (calculated as the metal) comprises at least 1.0 weight percent of the total solids inventory of said bed, said first reaction zone being maintained at a pressure between 250 and 1,500 psig and at an average temperature varying between 1,000° and 1,500°F. to produce a vaporous product comprising H_2, CO, CO_2, and CH_4, and solid carbonaceous material, at least a portion of which deposits on said support;

b. treating said vaporous product to remove unreacted steam and CO_2;

c. passing at least a portion of the steam and CO_2-removed vaporous product and a portion of said particulate catalyst to a second reaction zone maintained at a pressure between 250 and 1,500 psig and at a higher average temperature than the actual temperature maintained in the first reaction zone to produce a methane rich gaseous product;

d. recovering said gaseous product from said second reaction zone, and

e. passing at least a portion of said particulate catalyst from the second reaction zone to the first reaction zone.

26. A process for producing a methane rich gas from a hydrocarbon feed containing at least 10 weight percent hydrocarbons having a boiling point above 600°F. at atmospheric pressure, which comprises:

a. contacting said hydrocarbon feed with steam in a first reaction zone containing a bed of solids comprising a particulate catalyst consisting essentially of an alkali metal component, a solid particulate support and an in-situ formed carbonaceous deposit on said support, wherein said alkali metal component (calculated as the metal) comprises at least 1.0 weight percent of the total solids inventory of said bed, said first reaction zone being maintained at a pressure above 200 psig and at an average temperature between about 1,000° and 1,500°F. to produce a vaporous product comprising H_2, CO, CO_2 and CH_4, and a solid carbonaceous material, at least a portion of which deposits on said support;

b. passing at least a portion of said particulate catalyst and at least a portion of said vaporous product to a second reaction zone maintained at a pressure above 200 psig and at an average temperature between about 1,000° and 1,500°F. to produce a methane rich gaseous product;

c. recovering said gaseous product from said second reaction zone, and

d. passing at least a portion of said particulate catalyst from said second reaction zone to said first reaction zone.

27. The process of claim 26, wherein said particulate catalyst is maintained in a fluidized bed.

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