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(12) (19) (CA) **Brevet-Patent**

(11) (21) (C) **2,103,939**
(22) 1993/08/12
(43) 1994/02/14
(45) 2000/04/25

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(51) Int.Cl.[5] C01B 3/38, C01B 3/36, B01J 19/26
(30) 1992/08/13 (DK1013/92) DK

(54) **REACTEUR ET METHODE POUR LA PREPARATION D'UN GAZ RICHE EN HYDROGENE OU EN OXYDE DE CARBONE**

(54) **PROCESS AND REACTOR FOR THE PREPARATION OF A GAS WHICH IS RICH IN HYDROGEN AND/OR CARBON MONOXIDE**

(57) A process is provided herein for the preparation of a gas which is rich in hydrogen and/or carbon monoxide. The process includes the partial oxidation of a hydrocarbon feedstock in a reactor with an upper portion, a lower portion, and a refractory lining which is attached to an inner surface of the reactor. The process includes the first step of introducing the feedstock and an oxygen-containing gaseous atmosphere into the upper portion of the reactor. That feedstock is then partially oxidized with oxygen in the upper portion of the reactor. A part of that partially-oxidized feedstock is then contacted with a reforming catalyst which is arranged on the refractory lining in at least the upper portion of the reactor. In this way, the lining is cooled by endothermic reforming reactions proceeding in the partially-oxidized gas on the refractory lining.

ABSTRACT

A process is provided herein for the preparation of a gas which is rich in hydrogen and/or carbon monoxide. The process includes the partial oxidation of a hydrocarbon feedstock in a reactor with an upper portion, a lower portion, and a refractory lining which is attached to an inner surface of the reactor. The process includes the first step of introducing the feedstock and an oxygen-containing gaseous atmosphere into the upper portion of the reactor. That feedstock is then partially oxidized with oxygen in the upper portion of the reactor. A part of that partially-oxidized feedstock is then contacted with a reforming catalyst which is arranged on the refractory lining in at least the upper portion of the reactor. In this way, the lining is cooled by endothermic reforming reactions proceeding in the partially-oxidized gas on the refractory lining.

(a) TITLE OF THE INVENTION

PROCESS AND REACTOR FOR THE PREPARATION OF A GAS WHICH IS RICH IN HYDROGEN AND/OR CARBON MONOXIDE

(b) TECHNICAL FIELD TO WHICH THE INVENTION RELATES

The present invention is directed to the preparation of a gas which is rich is hydrogen and/or carbon monoxide. In particular, the invention relates to a process and reactor for the preparation of such gas either by non-catalytic partial oxidation or by autothermal catalytic reforming of a hydrocarbon feedstock.

(c) BACKGROUND ART

Gases which are rich in hydrogen and/or carbon monoxide are mainly used as synthesis gas in the production of ammonia and methanol or other organic compounds. The gases find further employment during steel production, and as fuel or town gases.

Industrial preparation processes most usually comprise autothermal catalytic reforming and non-catalytic partial oxidation of hydrocarbons.

In non-catalytic, partial-oxidation processes, a hydrocarbon feedstock is combusted together with air, oxygen, or oxygen-enriched air in a burner which is mounted at the top of a reaction vessel. Oxygen is, thereby, supplied in amounts which are less than the amounts which are required for complete combustion, and hydrogen and carbon monoxide are produced in an effluent gas, mainly by the following flame reactions:

$$C_n H_m + n/_2\, O_2 \leftrightarrow n\, CO + m/_2\, H_2 \quad (1)$$

$$C_n H_m + n\, O_2 \leftrightarrow n\, CO_2 + m/_2\, H_20 \quad (2)$$

Both reactions are strongly exothermic for all hydrocarbons.

Partial oxidation is typically employed in the gasification of heavy oils, where the temperature in the gas rises during the combustion to 1000C°-1500°C, which is high enough to give a sufficient low content of unconverted hydrocarbons in the combustion effluent gas.

Lighter feedstocks ranging from natural gas to naphtha fractions with a boiling point up to 200°C are conventionally treated by autothermal, catalytic reforming of the feedstock.

During this process, only a part of the hydrocarbon feedstock is oxidized with an oxygen-containing gaseous atmosphere by the above flame reactions (1,2). Residual hydrocarbons in the gas stream from the combustion are then catalytically steam-reformed by the following endothermic reaction (3):

$$C_n H_m + n H_2O \rightarrow n CO + (m/_2 + n) H_2 \quad (3)$$

Necessary heat for the endothermic steam reforming reaction is, thereby, provided by the exothermic flame reactions (1,2).

Somewhat lower combustion temperatures are used during autothermal catalytic reforming, which is operated at a typical temperature of 900°C-1400°C. Steam is added to the feed in order to moderate the flame temperature and to increase hydrocarbon conversion in the burner effluent gas.

Similar to the partial oxidation process, hydrocarbon feed mixed with steam is burned with an oxygen-containing gaseous atmosphere at the top of a reactor. Residual hydrocarbons in the combusted gas are then steam-reformed in the presence of a catalyst which is arranged as fixed bed in a lower portion of the reactor. Heat for the endothermic, steam-reforming reactions is supplied by the hot effluent gas from the combustion zone in the upper reactor portion and above the catalyst bed. As the combustion gas contacts the catalyst, the temperature in the gas cools to 900°C-1100°C by the steam-reforming reactions in the catalyst bed.

In operating the above processes, suitable hydrocarbon feed, if necessary after preheating, is introduced into a burner mounted at the top of a reactor and is burned with an oxygen-containing gaseous atmosphere. In order to protect the reactor sheet against the high temperatures arising during the exothermic oxidation reactions, industrial reactors are provided with a temperature-resistant and heat-insulating refractory lining on the inner wall of the reactor shell.

The lining materials must be able to withstand high temperature exposure and be suited to resistant erosion by hot gases. Presently, refractory materials most commonly used in industrial reactors of the above types contain more than 90% alumina. Although these materials are high-strength castables or bricks with good heat and wear-resistant properties, deterioration by contact with hot combustion gases containing carbon oxides, steam and hydrogen occurs most severely in the upper reactor portion surrounding the combustion zone. Due to the reducing nature of the gases, alumina in the refractory material is reduced to suboxides of aluminum, which are volatile in the high temperature environment in the reactor upper portion.

Surface evaporation of aluminum suboxides causes degradation of the lining and precipitation of aluminum oxide on the catalyst in the cooler portion of the reactor or on cooler surfaces in downstream equipment of the reaction system. As a result, gas passage through the reaction system is clogged by solids and the system must eventually be shut down.

(d) DESCRIPTION OF THE INVENTION

It has now been found that the above problems during partial oxidation and autothermal catalytic reforming processes in refractory lined reactors are substantially avoided when cooling the surface of the reactor lining below the evaporation temperature of disintegration products from the refractory material by carrying out endothermic steam reforming reactions on the surface of the lining. Those reactions proceed in the combustion effluent gas when a suitable catalyst is arranged on the surface at least in the portion of the reactor, which surrounds the hot combustion zone.

By a first broad aspect of the present invention, a process is provided for the preparation of a gas which is rich in hydrogen and/or carbon monoxide by the steps of partial oxidation of a hydrocarbon feedstock in a reactor with an upper and lower portion and a refractory lining attached to an inner surface of the reactor, the process comprising the steps of introducing the feedstock and an oxygen-containing gaseous atmosphere into the upper portion of the reactor to provide a partially-oxidized feedstock, and contacting a part of the partially-oxidized feedstock with a reforming catalyst which is arranged on the refractory lining in at least the upper portion of the reactor, so as to cool the lining by endothermic reforming reactions proceeding in the partially-oxidized gas on the refractory lining.

By one variant of this first broad aspect of this invention, the process takes place at autothermal catalytic reforming conditions, and the partially-oxidized feedstock from the upper portion of the reactor is further contacted with a steam reforming catalyst which is arranged in the lower portion of the reactor. By one variation thereof, the steam reforming catalyst comprises a fixed bed of a nickel and/or cobalt reforming catalyst.

By a second variant of this first broad aspect of this invention, the process is carried out at non-catalytic, partial oxidation conditions, and an effluent gas, which is rich in hydrogen and carbon monoxide, is directly withdrawn from the lower portion of the reactor.

By a second variant of this first broad aspect of this invention, and/or the above variants thereof, the hydrocarbon feedstock and the oxygen-containing gaseous atmosphere are mixed in a burner before introduction into the upper portion of the reactor.

By a third variant of this first broad aspect of this invention, and/or the above variants thereof, the reforming catalyst is arranged in an amount of between 0.01 g/m^2 and 0.15 g/m^2 on the refractory lining. By a first variation thereof, the catalyst is a reforming catalyst of Group VIII of the Periodic Table. By a second variation thereof, the catalyst is loaded in the lining surface by wash coating techniques. By a variation of this third variation, a binding layer of magnesium aluminum spinel is applied to the lining surface prior to the coating with the catalytic material.

By a second broad aspect of the present invention, a reactor is provided comprising a pressure shell having an upper portion and a lower portion, a refractory lining on an inner wall of the shell, the upper portion of the shell being adapted to receive a hydrocarbon feedstock and an oxygen-containing gaseous atmosphere, and being adapted partially to oxidize the feedstock with oxygen, and a reforming catalyst which is arranged on the refractory lining in at least the upper portion of the reactor.

By one variant of this second broad aspect of this invention, the lower portion of the reactor is provided with a reforming catalyst which is adapted to receive and steam-reform the partially-oxidized gas from the upper portion of the reactor.

By a second variant of this second broad aspect of this invention, and/or the above variants thereof, the reactor is further provided with a burner on top of the reactor, the burner being adapted to mix and burn the hydrocarbon feedstock with the oxygen-containing gaseous atmosphere.

(d) AT LEAST ONE MODE FOR CARRYING OUT THE INVENTION

In operating a specific embodiment of an aspect of the inventive process and reactor, a hydrocarbon feedstock, which is preheated to 400C° to 700°C, is introduced into a burner which is mounted at the top of a refractory lined reactor. In the burner, the feedstock is mixed with steam and an oxygen-containing gaseous atmosphere in an amount providing a process gas with an oxygen/carbon mole ratio of, preferably, between 0.5 and 0.7, and a steam/carbon mole ratio of, preferably, between 0.5 and 1.5. Typical hydrocarbon feedstocks which are suited for the process will range from methane to naphtha fractions with a boiling point up to 200°C, including natural gas, LPG and primary reformed gas, when operating the process of one aspect of this invention under autothermal catalytic reforming conditions. For higher hydrocarbon feedstocks, e.g., heavy oil fractions, the process of another aspect of this invention will be carried out at non-catalytic partial conditions. At both process conditions, the process gas is discharged from the burner into a combustion zone in the upper reactor portion, where part of the hydrocarbons in the gas are reacted with oxygen to carbon oxides and hydrogen by flame reactions (1) and (2) as mentioned hereinbefore.

Depending on the desired composition of the final product gas, oxygen may be supplied from air, e.g., for the preparation of ammonia synthesis gas, or from oxygen or oxygen-enriched air, for the production of oxosynthesis gas and reducing gas, where nitrogen is not wanted in the product gas. During hydrocarbon oxidation, the temperature in the combustion zone raises to 900°C-1500°C.

Cooling of the refractory lining around the combustion zone is performed by passing a part of the combusted effluent gas containing unconverted hydrocarbons across the refractory surface in contact with a steam-reforming catalyst which is arranged thereon. By the endothermic, steam-reforming reaction (3) proceeding in the gas on the refractory surface, the temperature in the effluent gas passing across the catalyzed refractory lining is lowered by 100°C and 300°C, which cools the lining sufficiently below the evaporation point of disintegration products. The actual temperature decrease on the refractory surface depends, thereby, on the amount of hydrocarbons and steam in the gas from the combustion zone, and the activity and amount of steam-reforming catalyst on the refractory material.

Catalysts which are suited for this purpose comprise the well-known reforming catalysts of Group VIII of the Periodic Table, including nickel and/or cobalt, which, for sufficient cooling, are loaded in an amount of between 0.01 g/m^2 and 0.15 g/cm^2 on the lining surface by conventional impregnation or wash coating techniques. When wash coating techniques are used for the loading of the catalyst, it is preferred to apply a binding layer of magnesium aluminum spinel on the surface prior to coating with the catalytic material or precursors thereof.

When the process of an aspect of the invention takes place at autothermal catalytic reforming conditions, the effluent gas from the combustion zone is further passed through a fixed bed of conventional nickel and/or cobalt reforming catalyst which is arranged in the lower portion of the reactor. By passage through the catalyst bed, residual hydrocarbons in the gas are further steam reformed to hydrogen and carbon monoxide.

At non-catalytic partial oxidation conditions of the process of an aspect of this invention, the effluent gas from the combustion zone, which is rich in carbon monoxide and hydrogen, is directly withdrawn from the lower portion of the reactor.

By decreasing the temperature in the refractory lining, as described above, substantially no evaporation of disintegration products from the refractory lining into the effluent gas occurs in the upper hot portion of the reactors. Precipitation of such products which otherwise would cause troubles in the lower cooler portion of the reactor or downstream equipment is, thereby, appreciatively avoided.

CLAIMS

1. Process for the preparation of a gas which is rich in hydrogen and/or carbon monoxide by the steps of partial oxidation of a hydrocarbon feedstock in a reactor with an upper portion and a lower portion and a refractory lining attached to an inner surface of the reactor, said process comprising the steps of:

introducing said feedstock and an oxygen-containing gaseous atmosphere into said upper portion of the reactor to provide a partially-oxidized feedstock; and

contacting a part of said partially-oxidized feedstock with a reforming catalyst which is arranged on the refractory lining in at least said upper portion of the reactor, so as to cool said lining by endothermic reforming reactions proceeding in said partially-oxidized gas on the refractory lining.

2. The process as claimed in claim 1, wherein said process takes place at autothermal catalytic reforming conditions, and wherein said partially-oxidized feedstock from said upper portion of said reactor is further contacted with a steam-reforming catalyst which is arranged in the lower portion of said reactor.

3. The process as claimed in claim 2, wherein said steam-reforming catalyst comprises a fixed bed of a nickel and/or cobalt steam-reforming catalyst.

4. The process as claimed in claim 1, wherein said process is carried out at non-catalytic, partial oxidation conditions, and wherein an effluent gas, which is rich in hydrogen and carbon monoxide, is directly withdrawn from said lower portion of said reactor.

5. The process as claimed in claims 1 to 4, wherein said hydrocarbon feedstock and said oxygen-containing gaseous atmosphere are mixed in a burner before introduction into said upper portion of said reactor.

6. The process as claimed in claims 1 to 5, wherein said steam-reforming catalyst is arranged in an amount of between 0.01 g/m^2 and 0.15 g/m^2 on said refractory lining.

7. The process as claimed in claim 6, wherein said catalyst is a steam-reforming catalyst of Group VIII of the Periodic Table.

8. The process as claimed in claim 6 or claim 7, wherein said steam-reforming catalyst is loaded in the lining surface by wash coating techniques.

9. The process as claimed in claim 8, wherein a binding layer of magnesium aluminum spinel is applied to said lining surface prior to the coating with said steam-reforming catalyst.

10. A reactor comprising:

a pressure shell including an upper portion and a lower portion;

a refractory lining on an inner wall of said shell;

said upper portion of said shell is being adapted to receive a hydrocarbon feedstock and an oxygen-containing gaseous atmosphere, and being adapted partially to oxidize said feedstock with oxygen; and

a reforming catalyst which is arranged on said refractory lining in at least said upper portion of the reactor.

11. The reactor as claimed in claim 10, wherein said lower portion of said reactor is provided with a steam-reforming catalyst which is adapted to receive and steam-reform partially-oxidized gas from said upper portion of said reactor.

12. The reactor as claimed in claim 10 or claim 11, which is further provided with a burner on top of said reactor, said burner being adapted to mix and burn said hydrocarbon feedstock with said oxygen-containing gaseous atmosphere.