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(54) SYNTHESIS GAS PRODUCTION

(54)

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SYNTHESIS GAS PRODUCTION

The present invention relates to an improved process for the production of synthesis gas by a non-catalytic partial oxidation of saturated hydrocarbons, such as methane, ethane or fuel oil, and more particularly to a method for inhibiting undesirable preignition reactions between the process reactant streams. Synthesis gas is widely used in the chemicals manufacturing industry as an intermediate in many chemical production processes and is comprised mainly of a mixture of carbon monoxide and hydrogen. Minor quantities of other gases are also present in most synthesis gases produced.

In a typical non-catalytic partial oxidation process for producing synthesis gas, preheated reactants comprising a methane or similar saturated hydrocarbon stream and an oxidant stream, such as oxygen, are introduced at the top of a mixing section of a reactor and then pass at high velocity into a reaction chamber, which may be separated from the mixing section by a perforated partition. Just below the perforated partition, or immediately inside the reaction chamber, ignition of the reactants occurs and the resultant burning at high temperature produces synthesis gas. The saturated hydrocarbon reactant and the oxidant reactant must be brought into admixture in a synthesis gas-producing proportion. Depending upon the saturated hydrocarbon reactant used, the ratio by volume of saturated hydrocarbon to oxidant may vary from about 0.1 to about 1.4.

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Using methane and oxygen as the reactant streams, a product synthesis gas comprising mainly carbon monoxide and hydrogen is produced. In some cases, where it is desired to control the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas, the desired ratio may be obtained by adding small quantities of carbon dioxide to the saturated hydrocarbon feed stock stream.

10 Immediately below the reaction chamber the products of combustion are cooled by direct contact with water or with water and heat recovery devices. Final temperature is determined according to the end use of the synthesis gas produced and is normally in the range of from about 55°C. to about 400°C.

20 It has been found that to obtain high yields in a non-catalytic synthesis gas production process, it is incumbent that the following conditions prevail: Both the hydrocarbon and oxidant reactants should be preheated prior to mixing to as high a temperature as possible without causing preignition during the mixing operation; intimate mixing of the preheated hydrocarbon reactant and preheated oxidant reactant should be effected in as short a time interval as possible to diminish the occurrences of preignitions at the mixing point before the mixed reactants can be passed to the reaction chamber and also to minimize preheat loss at the mixing point; and the actual partial oxidation of the hydrocarbon to form the product synthesis gas should be effected

at temperatures and residence times as may be necessary to permit essentially complete conversion of the hydrocarbon reactant to the desired synthesis gas product. More specifically, for a given mixture of reactants, the percentage of synthesis gas product has been found to vary according to the temperature to which the reactants are heated, the production being enhanced by high temperature. The extent of preheating is limited by practical considerations. The oxidant stream, for example, should not be heated to or above a temperature at which substantial oxidation would occur in the conduit system containing said oxidant. The hydrocarbon stream should not be heated to or above a temperature at which substantial pyrolysis of said hydrocarbon stream would occur and cause harmful deposit of carbon on the walls of the hydrocarbon conduits, the walls of the reactor apparatus and in the preheater tubes.

The most salient and by far the most serious problem encountered in attempting to attain optimum synthesis gas yields according to the above-described process is the occurrence of excessive preignition reactions between the reactants at the mixing point or at other points through which the admixed reactants pass prior to entering the reaction chamber. Such preignition reactions have a very detrimental effect, since the materials of which sections of the synthesis gas reactor other than the reaction chamber itself are constructed cannot long withstand the high temperatures resulting from them. Known attempts to mitigate the preignition problem have, in the main,

been addressed to automatic stoppage of the reactant oxidant flow upon occurrence of a preignition reaction or a reduction in preheat temperatures of the reactant hydrocarbon and reactant oxidant streams. Reactant oxidant stream stoppages necessarily result in stoppages of reactor operation which are bothersome and expensive. Operating at lower preheat temperatures brings about reduced yield of the product synthesis gas. In addition to the diminution of the product synthesis gas production output caused by stoppages when such preignition reactions occur, there is a further loss of yield due to the loss of reactants occurring in the preignition reaction per se.

10 It is to the elimination of unwanted preignition reactions in synthesis gas production that the present invention is addressed and the invention comprises an improved process for synthesis gas production wherein preignition reactions are minimized without reduction of reactant stream preheat temperatures and consequent reduction of yield. The invention provides a synthesis gas production process which enables the use of higher than normal preheat temperatures for the reactants without increasing the danger of preignition reactions, thus increasing the product yield for a given amount of reactants. Further benefits accruing in the use of the present invention are that less oxidant reactant is needed to produce a desired amount of product synthesis gas, and the combustion reaction stability is improved.

20 In accordance with the present invention, an improvement is provided in the process for production of synthesis gas

by non-catalytic partial oxidation of a hydrocarbon feed stock reactant consisting substantially of a saturated hydrocarbon, wherein a preheated stream of the hydrocarbon feed stock reactant and a preheated stream of oxidant reactant are admixed in a mixing zone in a synthesis gas-producing proportion and the combined streams passed into a reaction zone wherein the partial oxidation is effected. This improvement comprises introducing into the reactant hydrocarbon feed stock, prior to mixing the reactant hydrocarbon feed stock and the reactant oxidant, a preignition inhibitor in concentration of  
10 from about 0.1 per cent to about 6 per cent by volume of the hydrocarbon feed stock, said preignition inhibitor comprising at least one member selected from the group consisting of air, oxygen and oxygen-enriched air, whereby preignition of the mixture, prior to partial oxidation in the reaction zone is diminished.

According to the process of the present invention, air, commercially pure oxygen and oxygen-enriched air are useful preignition inhibitors. The quantity of inhibitor added  
20 to the reactant hydrocarbon stream should be sufficient to convert reaction-inducing materials present in the stream to an inactive state. Employing a reactant hydrocarbon stream consisting of substantially pure methane, it has been found that a preignition inhibitor concentration of from about 0.1 per cent to about 1.25 per cent by volume of the reactant hydrocarbon feed stock yields excellent results, but that additional preignition inhibitor in concentrations up to about 6 per cent by

volume of the reactant hydrocarbon feed stock may be added without harmful effects or diminution of the synthesis gas yield.

Although it has been found that preignition inhibitors according to the present invention may be introduced into the reactant hydrocarbon stream at any convenient point upstream of the mixing zone wherein the reactant hydrocarbon and reactant oxidant are mixed, it is preferred to introduce the inhibitor just prior to the preheating of the reactant hydro-  
10 carbon stream. This assures sufficient time for the inhibitor to convert the reaction-inducing materials in the reactant hydrocarbon stream to an inactive state. In a particular set of circumstances, however, the most effective preignition inhibitor introduction point will be readily ascertainable by those familiar with the art.

Prior to the use of preignition inhibitors in accordance with the present invention, and illustrative of a typical synthesis gas process, a substantially pure methane stream, having a flow rate of 65 MCFH, to which was added,  
20 prior to major reactant admixing, 5.5 MCFH of carbon dioxide, said carbon dioxide being added as a reactant and for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas, was preheated to 550°C. Simultaneously, an oxidant stream consisting of substantially pure oxygen, having a flow rate of 47.0 MCFH was preheated to 150°C. When the preheated methane and preheated oxygen were admixed, preignition reactions in the mixing zone

occurred on an average of about every 4 hours. The average product gas composition by percentage of total volume, on a dry basis was found to be: carbon monoxide 37.4 per cent; hydrogen 56.8 per cent; carbon dioxide 4.8 per cent; methane, nitrogen and trace quantities of other gases 1.0 per cent.

In another illustration of a typical synthesis gas production process, a substantially pure methane stream having a flow rate of 60 MCFH, was preheated to 450°C. 8.5 MCFH of carbon dioxide was added to this methane stream prior to major reactant admixing, as a reactant, for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, an oxidant stream consisting of substantially pure oxygen, having a flow rate of 44.0 MCFH was preheated to 160°C. When the preheated methane and preheated oxygen were admixed, preignition reactions in the mixing zone occurred on an average of about every 6 hours. The average product gas composition by percentage of total volume, on a dry basis, was found to be: carbon monoxide 37.8 per cent; hydrogen 55.9 per cent; carbon dioxide 4.6 per cent; methane, nitrogen and trace quantities of other gases 1.7 per cent.

Subsequently, preignition inhibitors were added, in accordance with the present invention, to the hydrocarbon stream prior to admixing the methane and oxidant streams, and the following data was obtained.



EXAMPLE I

In one example illustrative of the present invention, a substantially pure methane stream, having a flow rate of 60 MCFH, was preheated to 450°C. 9.2 MCFH of carbon dioxide was added to this methane stream, prior to admixture of the major reactants, as a reactant, for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, a reactant oxidant stream consisting of substantially pure oxygen, having a flow rate of 45.0 MCFH, was preheated to 150°C. Air for preignition inhibition and reaction stabilization was introduced into the methane stream, prior to preheating, at a flow rate of 0.750 MCFH. When the preheated methane containing the air inhibitor and preheated oxygen were admixed, no preignition reactions in the mixing zone or elsewhere occurred during operating periods extending up to several days. The average product gas composition by percentage of total volume, on a dry basis, was found to be: carbon monoxide, 37.0 per cent; hydrogen, 56.0 per cent; carbon dioxide, 5.6 per cent; methane, nitrogen and trace quantities of other gases, 1.4 per cent. Improved stability in the combustion process was also noted.

EXAMPLE II

In another example illustrative of the present invention, a substantially pure methane stream, having a flow rate of 50 MCFH was preheated to 500°C. 8.5 MCFH of carbon dioxide was added to this methane stream, prior to admixture of

the major reactants, as a reactant, for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, a reactant oxidant stream consisting of substantially pure oxygen, having a flow rate of 37.6 MCFH, was preheated to 150°C. Air for preignition inhibition and reaction stabilization was introduced into the methane stream, prior to preheating, at a flow rate of 0.625 MCFH. When the preheated methane containing the air inhibitor and preheated oxygen were admixed, no preignition reactions in the mixing zone or elsewhere occurred during operating periods extending up to several days. The average product gas composition by percentage of total volume, on a dry basis, was found to be: carbon monoxide, 37.4 per cent; hydrogen, 56.0 per cent; carbon dioxide, 5.0 per cent; methane, nitrogen and trace quantities of other gases, 1.6 per cent. Combustion stability also showed marked improvement.

#### EXAMPLE III

In a third example illustrative of the present invention, a substantially pure methane stream, having a flow rate of 90 MCFH, was preheated to 600°C. 12.75 MCFH of carbon dioxide was added to this methane stream, prior to admixture of the major reactants, as a reactant, for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, a reactant oxidant stream consisting of substantially pure

oxygen, having a flow rate of 68.3 MCFH, was preheated to 150°C. Air for preignition inhibition and reaction stabilization was introduced into the methane stream, prior to preheating, at a flow rate of 1.125 MCFH. When the preheated methane containing the air inhibitor and preheated oxygen were admixed, no preignition reactions in the mixing zone or elsewhere occurred during operating periods extending up to several days. The average product gas composition by percentage of total volume, on a dry basis, was found to be:

10 carbon monoxide, 37.4 per cent; hydrogen, 56.8 per cent; carbon dioxide, 4.4 per cent; methane, nitrogen and trace quantities of other gases, 1.4 per cent. An improvement in the combustion process was also observed.

#### EXAMPLE IV

In a fourth example illustrative of the present invention, a substantially pure methane stream, having a flow rate of 60 MCFH, was preheated to 450°C. 10.4 MCFH of carbon dioxide was added to this methane stream, prior to admixture of the major reactants, as a reactant, for the

20 sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, a reactant oxidant stream, consisting of substantially pure oxygen, having a flow rate of 45.8 MCFH was preheated to 150°C. Air for preignition inhibition and reaction stabilization was introduced into the methane stream, prior to preheating, at a flow rate of 0.383 MCFH. When the

preheated methane containing the air inhibitor and preheated reactant oxygen were admixed, no preignition reactions in the mixing zone or elsewhere occurred during an operating period of 24 hours, at the end of which period the process was intentionally stopped. The average product gas composition by percentage of total volume, on a dry basis, was found to be: carbon monoxide, 37.4 per cent; hydrogen, 57.2 per cent; carbon dioxide, 4.2 per cent; methane, nitrogen and trace quantities of other gases, 1.2 per cent. Improved stability  
10 in the combustion reaction was also noted.

#### EXAMPLE V

In a fifth example illustrative of the present invention, a substantially pure methane stream, having a flow rate of 60 MCFH, was preheated to 450°C. 10.1 MCFH of carbon dioxide was added to this methane stream, prior to admixture of the major reactants, as a reactant, for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, a reactant oxidant stream, consisting of substantially  
20 pure oxygen, having a flow rate of 46.1 MCFH was preheated to 150°C. Air for preignition inhibition and reaction stabilization was introduced into the methane stream, prior to preheating, at a flow rate of 3.343 MCFH. When the preheated methane containing the air inhibitor and preheated reactant oxygen were admixed, no preignition reactions in the mixing zone or elsewhere occurred during an operating

period of 24 hours, at the end of which period the process was intentionally stopped. The average product gas composition by percentage of total volume, on a dry basis, was found to be: carbon monoxide, 37.8 per cent; hydrogen, 56.6 per cent; carbon dioxide, 4.6 per cent; methane, nitrogen and trace quantities of other gases, 1.0 per cent. Improved stability in the combustion reaction was also noted.

#### EXAMPLE VI

In a sixth example illustrative of the present invention, a substantially pure methane stream, having a flow rate of 60 MCFH, was preheated to 450°C. 9.4 MCFH of carbon dioxide was added to this methane stream, prior to admixture of the major reactants, as a reactant, for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, a reactant oxidant stream, consisting of substantially pure oxygen, having a flow rate of 46.1 MCFH was preheated to 150°C. Oxygen for preignition inhibition and reaction stabilization was introduced into the methane stream, prior to preheating, at a flow rate of 0.0786 MCFH. When the preheated methane containing the oxygen inhibitor and preheated reactant oxygen were admixed, no preignition reactions in the mixing zone or elsewhere occurred during an operating period of 24 hours, at the end of which period the process was intentionally stopped. The average product gas composition by percentage of total volume, on a dry basis, was found to be: carbon monoxide, 38.2

per cent; hydrogen, 56.4 per cent; carbon dioxide, 4.4 per cent; methane, nitrogen and trace quantities of other gases, 1.0 per cent. Improved stability in the combustion reaction was also noted.

EXAMPLE VII

In a seventh example illustrative of the present invention, a substantially pure methane stream, having a flow rate of 60 MCFH, was preheated to 450°C. 9.5 MCFH of carbon dioxide was added to this methane stream, prior to admixture of the major reactants, as a reactant, for the sole purpose of controlling the volumetric ratio of hydrogen to carbon monoxide in the product synthesis gas. Simultaneously, a reactant oxidant stream, consisting of substantially pure oxygen, having a flow rate of 46.1 MCFH was preheated to 150°C. Oxygen for preignition inhibition and reaction stabilization was introduced into the methane stream, prior to preheating, at a flow rate of 0.700 MCFH. When the preheated methane containing the oxygen inhibitor and preheated reactant oxygen were admixed, no preignition reactions in the mixing zone or elsewhere occurred during an operating period of 24 hours, at the end of which period the process was intentionally stopped. The average product gas composition by percentage of total volume, on a dry basis, was found to be: carbon monoxide, 38.2 per cent; hydrogen, 56.8 per cent; carbon dioxide, 4.2 per cent; methane, nitrogen and trace quantities of other gases, 0.8 per cent. Improved stability in the combustion reaction was also noted.

From the first three of the foregoing examples, it can be readily seen that preignition inhibition according to the present invention can be nicely effected by introduction of 1.25% by volume of the hydrocarbon reactant of the inhibitor gas, air in these foregoing instances. Oxygen and oxygen-enriched air will also serve as inhibitors and reaction stabilizers. The other tests indicate that the minimum inhibitor per cent by volume concentration of the hydrocarbon feed stock to produce the inhibiting effect is about 0.1 per cent, and that an inhibitor concentration, in terms of per cent by volume of the hydrocarbon feed stock, of at least 6 per cent, can be added to the feed stock stream without producing yield diminution or adversely affecting reaction stability.

In the foregoing discussion and in the examples, the designation of flow rates by the term MCFH means flow rates in thousands of cubic feet per hour. Volumes in cubic feet per hour are the actual metered flows referred to a gaseous basis at 14.7 pounds per square inch pressure absolute and 70°F. temperature. By a substantially pure methane stream is meant one wherein there is at least about 98 per cent pure methane and by a substantially pure oxygen stream is meant one wherein there is at least about 98 per cent pure oxygen.

While the examples presented all relate to the use of a hydrocarbon feed stock consisting of substantially pure methane, preignition inhibitors according to the present invention can be successfully employed with saturated hydrocarbon feed stocks otherwise constituted such as for example natural gas, ethane and fuel oil.

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From the above disclosure, it can be appreciated that applicants' invention furnishes a new and useful process technique in synthesis gas production which provides for increased time periods of preignition-free operation, increased stability in the combustion reaction, increased yield and efficiency by making possible the use of higher than usual reactant preheat temperatures and which permits of decreased oxidant reactant consumption in the process.



## WHAT IS CLAIMED IS:

1. In a process for the production of synthesis gas by non-catalytic partial oxidation of a saturated hydrocarbon feed stock wherein a preheated stream of said feed stock heated to a temperature below the temperature at which substantial pyrolysis of said feed stock occurs and a preheated conduit-contained stream of oxidant heated to a temperature below the temperature at which substantial oxidation of the conduit occurs are admixed in a mixing zone in a synthesis gas-producing proportion and the combined streams passed into a reaction zone wherein  
10 said partial oxidation is effected, the improvement which comprises introducing into said saturated hydrocarbon feed stock, prior to mixing said saturated hydrocarbon feed stock and said oxidant, a preignition inhibitor in concentration of from about 0.1 per cent to about 6 per cent by volume of the hydrocarbon feed stock, said preignition inhibitor comprising at least one member selected from the group consisting of air, oxygen and oxygen-enriched air.

2. The process in accordance with claim 1, wherein  
20 said saturated hydrocarbon feed stock is substantially pure methane.

3. The process in accordance with claim 1, wherein said preignition inhibitor is introduced into said hydrocarbon feed stock prior to preheating said hydrocarbon feed stock.

4. In a process for the production of synthesis gas by non-catalytic partial oxidation of methane, wherein a preheated stream of methane heated to a temperature below the temperature at which substantial pyrolysis of methane occurs and a preheated conduit-contained stream of oxygen heated to a temperature below the temperature at which substantial oxidation of the conduit occurs are admixed in a mixing zone in a ratio by volume of said methane to said oxygen of from about 1.25 to about 1.4 and the combined streams passed into a  
10 reaction zone wherein said partial oxidation is effected, the improvement which comprises introducing into said methane, prior to mixing said methane and said oxygen, a preignition inhibitor in concentration of from about 0.1 per cent to about 6 per cent by volume of the methane, said preignition inhibitor comprising at least one member selected from the group consisting of air, oxygen and oxygen-enriched air.

5. The process in accordance with claim 4, wherein said preignition inhibitor is air.

6. The process in accordance with claim 4, wherein  
20 said preignition inhibitor is oxygen.

7. In a non-catalytic partial oxidation process for the production of synthesis gas having a ratio by volume of hydrogen to carbon monoxide of about 1.5, wherein a preheated stream of methane heated to a temperature below the temperature at which substantial pyrolysis of methane occurs and a pre-

heated conduit-contained stream of oxygen heated to a temperature below the temperature at which substantial oxidation of the conduit occurs are admixed in a mixing zone in a ratio by volume of said methane to said oxygen of from about 1.25 to about 1.4 and the combined streams passed into a partial oxidation reaction zone and wherein carbon dioxide in percent by volume of the methane of from about 8 per cent to about 17 per cent is introduced into said methane prior to the admixture of said methane and said oxygen, the improvement  
10 which comprises introducing into said methane, prior to mixing said methane and said oxygen, a preignition inhibitor in concentration of from about 0.1 per cent to about 6 per cent by volume of the methane, said preignition inhibitor comprising at least one member selected from the group consisting of air, oxygen and oxygen-enriched air.

8. In a non-catalytic partial oxidation process for the production of synthesis gas having a ratio by volume of hydrogen to carbon monoxide of about 1.5, wherein a preheated stream of ethane heated to a temperature below the temperature  
20 at which substantial pyrolysis of ethane occurs and a preheated conduit-contained stream of oxygen heated to a temperature below the temperature at which substantial oxidation of the conduit occurs are admixed in a mixing zone in a ratio by volume of said ethane to said oxygen of about 1, and the combined streams passed into a reaction zone wherein said partial oxidation is effected, the improvement which comprises introduc-

ing into said ethane prior to mixing said ethane and said oxygen, a preignition inhibitor in concentration of from about 0.1 per cent cent to about 6 per cent by volume of the ethane, said preignition inhibitor comprising at least one member selected from the group consisting of air, oxygen and oxygen-enriched air.

9. In a non-catalytic partial oxidation process for the production of synthesis gas having a ratio by volume of hydrogen to carbon monoxide of about 1, wherein a preheated stream of fuel oil heated to a temperature below the tem-  
10 perature at which substantial pyrolysis of fuel oil occurs and a preheated conduit-contained stream of oxygen heated to a temperature below the temperature at which substantial oxidation of the conduit occurs are admixed in a mixing zone in a ratio by volume of said fuel oil to said oxygen of about 0.1, and the combined streams passed into a reaction zone wherein said partial oxidation is effected, the improvement which comprises introducing into said fuel oil, prior to mixing said fuel oil and said oxygen, a preignition inhibitor in concentration of from about 0.1 per cent to about 6 per cent by  
20 volume of the fuel oil, said preignition inhibitor comprising at least one member selected from the group consisting of air, oxygen and oxygen-enriched air.

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