

May 21, 1963

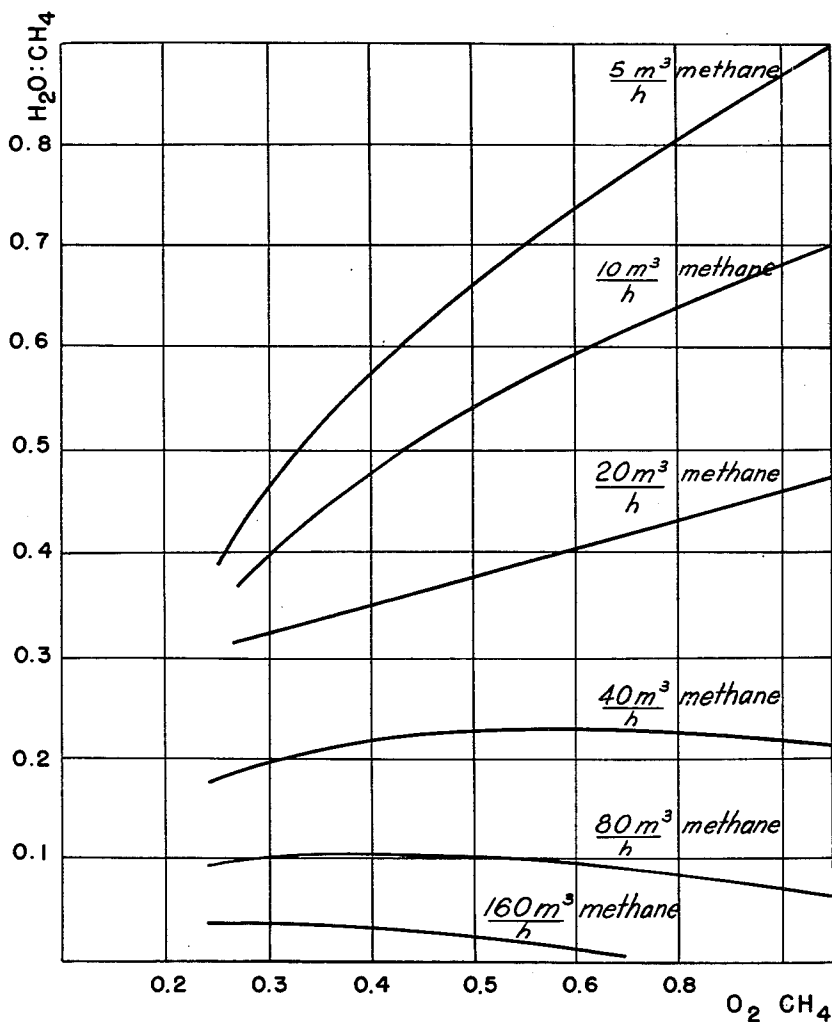
E. BARTHOLOME ETAL
CONVERSION OF GASEOUS HYDROCARBONS INTO
CARBON MONOXIDE AND HYDROGEN

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Filed June 22, 1955

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FIG. 1



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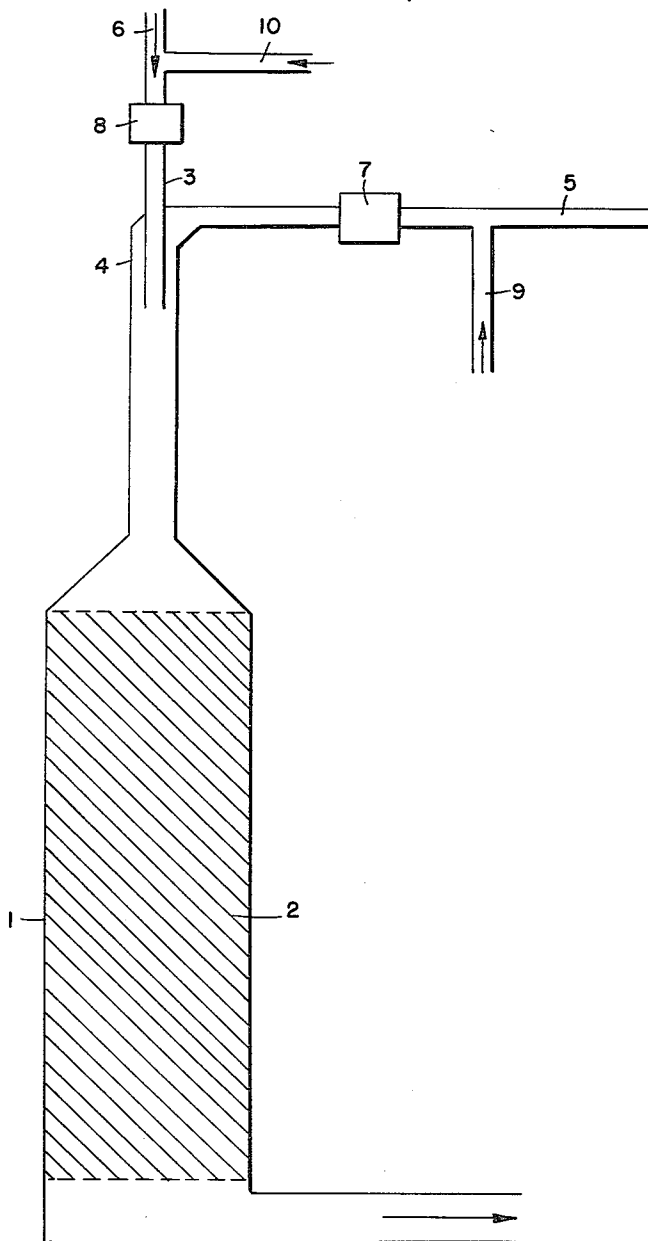
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FIG. 2



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CONVERSION OF GASEOUS HYDROCARBONS INTO CARBON MONOXIDE AND HYDROGEN

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Filed June 22, 1955, Ser. No. 517,346

Claims priority, application Germany June 26, 1954

4 Claims. (Cl. 48—196)

This invention relates to an improved process for the conversion of gaseous hydrocarbons into carbon monoxide and hydrogen.

It is already known that gaseous hydrocarbons can be converted into carbon monoxide and hydrogen with an amount of oxygen insufficient for complete combustion in the presence of catalysts. It has already been proposed to saturate the hydrocarbon to be reacted and the oxygen-containing gas before they meet with steam at a temperature which is equal and lies between about 60° and 70° C. Attempts have also been made to reduce the peak temperature occurring in the first part of the catalyst layer by adding steam to the gaseous hydrocarbons to be reacted.

In all these methods it has been found that, especially in the reaction of hydrocarbon-containing mixtures which contain large amounts of hydrogen, as for example coke oven gas, it is only possible to avoid a flame formation at the meeting point with difficulty and only within narrow limits of the gas impact of the catalyst. With smaller gas speeds, which have the advantage that the pressure drop across the reaction room is not so high, a stationary flame producing a gas containing a large amount of soot readily forms in the mixing zone.

We have now found that the reaction of gaseous hydrocarbons with an amount of oxygen insufficient for complete combustion to form carbon monoxide and hydrogen using a fixed-bed catalyst can be carried out in wide limits of gas feed rate while safely avoiding a stationary flame at the meeting point of the gases by supplying to the oxygen-containing gas, before the gases are mixed, steam in such an amount that local flame reaction which is initiated at the mixing point is carried away from the mixing apparatus. The hydrocarbon-containing gas may also contain steam but in this case it is necessary that the volume relation of steam to the oxygen containing gas in this gas is greater than the volume relation of steam to the hydrocarbon-containing gas in this hydrocarbon-containing gas.

The amount of steam to be added to the oxygen-containing gas may be determined in a simple way by preliminary test in dependence on the gas feed rate chosen. For this purpose the hydrocarbon-containing gas and the oxygen-containing gas are brought together in the mixing apparatus concerned at first without steam. When ignited, a stable flame forms. By gradually adding steam to the oxygen-containing gas it is then possible to determine the amount of steam which is necessary to carry away the flame. Contrary to expectation it has been found that even with simple mixing apparatus in which the gases to be mixed do not have any substantial pressure drop, the formation of a stable flame can be avoided with certainty within wide limits of gas feed rates with relatively small amounts of steam.

In FIG. 1 the results in determining the amount of steam needed to carry away the flame in a certain mixer has been represented graphically, methane being used as the hydrocarbon containing gas while practically pure oxygen is used as the oxygen containing gas. The two gases are preheated to 150° C. The mixing ratio of oxygen and methane is plotted on the abscissa, whereas the

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ordinate reflects the minimum amount of steam which has to be admixed to the oxygen in order to safely prevent the formation of a stationary flame at the point of mixing with a given feed rate of methane indicated as parameter for the different curves. From the curves it results that it is possible, within a very large range of feed rates, to prevent a flame with an economical amount of steam. It has been found that by adding steam to the methane as well, the amount of steam to be added to the current of oxygen, which has been indicated in FIG. 1, can be diminished only to a negligible extent. It is therefore necessary to add the steam wholly or mainly to the oxygen in order to do with economical amounts of steam.

The known conditions for the reaction of hydrocarbons with oxygen to form carbon monoxide and hydrogen are used, for example temperatures of 700° to 1300° C. at atmospheric or increased pressure, as for example at 1 to 30 atmospheres. Suitable catalysts are for example refractory porous substances, such as magnesite, chamotte or other siliceous substances, which are provided with one or more elements of the 8th group of the periodic system, in particular nickel.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

Example 1

Referring to FIG. 2 of the accompanying drawing a coke oven gas containing about 30% of methane is reacted with oxygen at atmospheric pressure in a reaction chamber 1 having an internal width of 2.5 metres and a height of about 3 metres which is filled with a granular catalyst 2 of magnesite with a content of about 3% by weight of nickel. The mixing of the gases is carried out in apparatus consisting of two concentric tubes 3 and 4, the inner shorter tube 3 serving for the supply of oxygen while the coke oven gas flows through the annular space formed by the two tubes.

If the coke oven gas 5 and the oxygen 6 heated in the preheaters 7 and 8 are saturated with steam supplied through the tubes 9 and 10 at 70° C. before mixing, so that the two gases contain the same amount of steam measured in percent by volume, occasional pre-ignitions, which in technical operation are unavoidable even at very high gas feed rates up to 2500 cubic metres per hour of moist final gas per square metre of surface of the reaction chamber, lead to a stable flame adhering to the oxygen nozzle.

If the amount of steam contained in the coke oven gas is reduced to half, for example by saturating the coke oven gas with steam at a lower temperature, and the corresponding amount of steam is added additionally to the oxygen, no stable flame forms in the mixing zone even at small feed rates. It is only when the feed rate is below 1300 cubic metres per hour of moist final gas per square metre of surface of the reaction chamber that there is any risk of flame formation in the mixing zone.

Finally if dry coke oven gas is used and there is added to the oxygen saturated with steam at 70° C. as much steam as was contained in the coke oven gas saturated at 70° C., a flame does not form until the gas admission is reduced below 700 cubic metres per hour of moist final gas per square metre of surface of the reaction chamber. By further addition of steam, the gas throughput can be still further reduced without flame formation taking place.

Example 2

250 cubic metres of coke oven gas containing about 30% by volume of methane to which 96 cubic metres of steam have been added, and 46 cubic metres of oxygen to which 29 cubic metres of steam have been added

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are hourly heated to 600° C. in separate preheaters, mixed in a mixer and then converted into synthesis gas in a catalyst filled reaction chamber being 50 centimetres in internal width and about one and a half metre in height at ordinary pressure with the chamber having a temperature of 950° C. at the end of the catalyst bed. The yield per hour is 400 cubic metres of synthesis gas having the following composition:

	Percent by volume
CO ₂ -----	4.4
CO -----	20.9
H ₂ -----	68.2
CH ₄ -----	0.2
N ₂ -----	6.3

In the mixer the mixture of coke oven gas and steam suffers a loss of pressure of less than half a metre water column, while the oxygen/steam mixture suffers a loss of pressure of less than one metre. No permanent flame occurs in the mixer.

If the amount of steam combined with the oxygen is reduced from 29 cubic metres to 19 cubic metres and, in order to maintain the total amount of steam supplied, the amount of steam combined with the coke oven gas is increased from 96 cubic metres to 106 cubic metres, occasional pre-ignition in the mixer will result in the formation of a permanent soot flame.

What we claim is:

1. A process for production of carbon monoxide and hydrogen by a flameless reaction between a hydrocarbon gas and oxygen which comprises mixing in a mixing zone a preheated hydrocarbon-containing gas with a preheated O₂-containing gas in an amount insufficient for complete combustion of the hydrocarbon in said hydrocarbon-containing gas, said mixing being done at a gas velocity sufficiently low and with a volume ratio of O₂ in said O₂-containing gas to said hydrocarbon-containing gas sufficiently high to support, in the absence of the addition of steam to said gases, a stable flame in said mixing zone at said gas velocity and said volume ratio, passing the mixed gases from said mixing zone into an enlarged zone void of solids, preventing pre-ignition of said gases in said mixing zone at said velocity and at said volume ratio and also in said enlarged zone by adding to said O₂-containing gas prior to mixing thereof with said hydrocarbon-containing gas an amount of steam sufficient to prevent formation of a stable flame in said mixing zone if the gases are ignited, and then contacting said mixed gases with a catalyst promoting the incomplete combustion of

said hydrocarbon gas into primarily carbon monoxide and hydrogen, with the further proviso that the hydrocarbon-containing gas prior to mixing with said O₂-containing gas has a volume ratio of steam to said hydrocarbon-containing gas ranging from zero to a ratio substantially less than the volume ratio of steam to O₂-containing gas resulting from said adding of steam to said O₂-containing gas.

2. A process for production of carbon monoxide and hydrogen by a flameless reaction between a hydrocarbon gas and oxygen which comprises mixing in a mixing zone a preheated hydrocarbon-containing gas with a preheated O₂-containing gas in an amount insufficient for complete combustion of the hydrocarbon in said hydrocarbon-containing gas, said mixing being done at a gas velocity sufficiently low and with a volume ratio of O₂ in said O₂-containing gas to said hydrocarbon-containing gas sufficiently high to support, in the absence of the addition of steam to said gases, a stable flame in said mixing zone at said gas velocity and said volume ratio, passing the mixed gases from said mixing zone into an enlarged zone void of solids, preventing pre-ignition of said gases in said mixing zone at said velocity and at said volume ratio and also in said enlarged zone by adding to said O₂-containing gas prior to mixing thereof with said hydrocarbon-containing gas an amount of steam sufficient to prevent formation of a stable flame in said mixing zone if the gases are ignited, and then contacting said mixed gases with a catalyst promoting the incomplete combustion of said hydrocarbon gas into primarily carbon monoxide and hydrogen, with the further proviso that substantially all of the steam supplied to said mixing zone is added to the O₂-containing gas.

3. The process of claim 1 wherein the catalyst comprises a porous refractory material containing at least one element of the eighth group of the periodic system.

4. The process of claim 1 wherein the hydrocarbon in said hydrocarbon-containing gas consists essentially of methane.

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