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(54) Title: LOW TEMPERATURE PROCESS FOR PRODUCING SYNTHESIS GAS		
(57) Abstract <p>A novel injector/reactor apparatus and an efficient process for the partial oxidation of hydrocarbon, such as methane, to convert such hydrocarbon to useful synthesis gas for recovery and/or subsequent hydrocarbon synthesis. Sources of a hydrocarbon, such as methane, and oxygen or an oxygen-containing gas are preheated and pressurized and injected through an injector means at high velocity into admixture with each other in the desired relating proportions, at a plurality of mixing nozzles, to form a gaseous premix having a pressure drop preferably of at least 1 % through the injector. The gaseous premix is injected in a time period which is preferably less than 9 milliseconds, preferably at a velocity between about 25 to 1000 feet/second, into a partial oxidation reaction zone such that the gaseous premix reacts therein in a flame having a temperature less than 3500 °F, to reduce the amounts of CO₂, H₂O and heat produced in the partial oxidation reaction and form and recover a useful syngas.</p>		

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LOW TEMPERATURE PROCESS FOR PRODUCING SYNTHESIS GAS

BACKGROUND OF THE INVENTION

Field of The Invention:

The present invention relates to improvements in processes and apparatus for producing synthesis gas, or syngas, from light hydrocarbon gas such as methane or natural gas by the oxidation thereof. Such syngas, comprising a mixture of carbon monoxide and hydrogen, is useful for the preparation of a variety of other valuable chemical compounds, such as by application of the Fischer-Tropsch process. Another valuable syngas produced by gas phase partial oxidation (GPOX) of light hydrocarbon gases is referred to as multicomponent synthesis gas (MCS) and contains, in addition to carbon monoxide and hydrogen, olefins (C_nH_{2n}), alkynes (C_nH_{2n-2}) such as acetylene, and unsaturated diene compounds, which compounds are useful, per se.

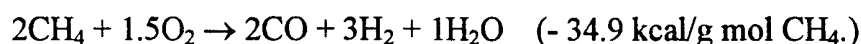
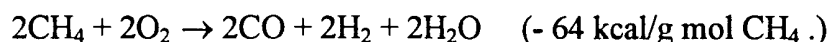
The combustion stoichiometry of methane gas at 1000°F is highly exothermic and produces CO_2 and H_2O according to the following reaction:



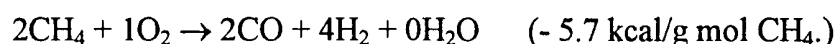
The formed gases are not useful for the production of valuable chemical compounds, and the high temperatures generated present problems with respect to reactors and catalysts which would be required to produce valuable products from the formed gases.

It is known to produce synthesis gases or syngases, by partial oxidation of hydrocarbons, by steam or CO_2 reforming of hydrocarbons, or by some combination of these two chemistries. The partial oxidation reaction of

methane is a less highly exothermic reaction which, depending upon the relative proportions of the methane and oxygen and the reaction conditions, can proceed according to the following stoichiometry:



or



It is most desirable to enable the partial oxidation reaction to proceed according to the latter reaction in order to produce the most valuable syngas and minimize the amount of heat produced, thereby protecting the apparatus and the catalyst bed, and to reduce the formation of steam, thereby increasing the yield of hydrogen and carbon monoxide, and enabling the steam-reforming reaction to convert any steam and hydrogen into useful syngas components.

Conventional syngas-generating processes include the gas phase partial oxidation process (GPOX), the autothermal reforming process (ATR), the fluid bed syngas generation process (FBSG), the catalytic partial oxidation process (CPO) and various processes for steam reforming. Each of these processes has advantages and disadvantages when compared to each other.

The GPOX process, illustrated for example by U.S. Patent 5,292,246; UK Application GB 2,202,321A and EPO Application 0 312,133, involves the oxidation of the feed hydrocarbon gaseous, liquid or solid form, in the gas phase rather than on a catalyst surface. The individual components are introduced at a burner where they meet in a diffusion flame, which produces over-oxidation and excessive heat generation. The gas may be preheated and pressurized, to reduce the reaction time.

The manufacture of multicomponent synthesis gas (MCS), such as olefins and acetylene via gas phase partial oxidation (GPOX) of light hydrocarbons and oxygen is known technology, developed by BASF (see, for example, U.S. 3,542,894), Montecatini (U.K. 932,429), and others. The common feature of the reactor is that the light hydrocarbon and oxygen are initially mixed in a large mixing chamber, and then the mixture flows through many passages in a burner face to the combustion chamber. Residence time is minimized by employing a short reactor with liquid quench systems, and at these short (millisecond) residence times, multicomponent syngas is the resulting product. One disadvantage shared by MCS reactors is the problematic premix zone where the hot hydrocarbon/oxygen mixture does, on occasion, pre-ignite causing significant harm to process equipment. The tendency to pre-ignite is exacerbated by feed pressure and effectively limits MCS reactors to pressures less than 6 atm. Multicomponent synthesis gas (MCS) is defined as gas mixtures containing carbon monoxide and hydrogen, as well as olefins (with a general formula of C_nH_{2n} and with a functional group of $C=C$) having from 2 to 5 carbon atoms, and alkynes (with a general formula of C_nH_{2n-2} and with a functional group of $C\equiv C$) having from 2 to 5 carbon atoms. MCS mixtures can optionally contain other unsaturated hydrocarbons such as cumulated and conjugated dienes (with a general formula of C_nH_{2n-2} and with a functional group of $C=C=C$ and $C=C-C=C$, respectively) having 3 to 5 carbon atoms, enynes (with a general formula of C_nH_{2n-4} and with a functional group of $C=C-C\equiv C$) and diynes (with a general formula of C_nH_{2n-6} and a functional group of $C\equiv C-C\equiv C$) having 4 to 5 carbon atoms.

Syngas generally, and MCS mixtures particularly, also contain inert components, e.g., nitrogen, carbon dioxide, functionally inert hydrocarbons such as alkanes and aromatic hydrocarbons, and water vapor. They may also contain trace amounts of sulfur and nitrogen containing species, for example, HCN, NH_3 , H_2S ,

organic sulfides, and others. Such mixtures, as created in the partial oxidation zone, may also contain some amount of heavier hydrocarbons, including tar and soot.

The ATR process and the FBSG process involve a combination of gas phase partial oxidation and steam reforming chemistry.

In the ATR process, illustrated for example by U.S. Patent 5,492,649 and Canadian Application 2,153,304, the hydrocarbon feed and the oxygen feed, and optionally steam, are heated, and mixed and mixed in a diffusion flame at the outlet of a single large coaxial burner or injector which discharges into a gas phase oxidation zone. The gases are reacted in the gas phase in the partial oxidation combustion zone, and then flow into a large bed of steam reforming catalyst, such as large catalyst pellets, or a monolithic body, to complete steam reforming. The entire hydrocarbon conversion is completed by a single reactor aided by internal combustion. The burner is the key element because it mixes the feedstreams in a turbulent diffusion flame. The reaction products are introduced to the fixed bed catalyst zone, preferably of large catalyst pellets, at high temperatures from the combustion zone, due to the over-oxidation which occurs in the diffusion flame of the burner, where the oxygen and hydrocarbon gas meet. The diffusion flame includes oxygen-rich and hydrocarbon-rich zones. These result in both complete combustion and substantially higher temperatures, in the oxygen-rich zones, and hydrocarbon cracking and soot-formation, in the hydrocarbon-rich zones.

In the ATR process, the gases are intended to react before they reach the catalyst, i.e., the oxidation chemistry occurs in the gas phase, and only the steam reforming chemistry occurs in the catalytic bed. In fact, long residence times are required because diffusion flames are initiated with a large amount of over-oxidation, accompanied by a large amount of heat. Thus, time is required for the relatively slow, endothermic gas phase steam reforming reactions to cool the

gas enough for introduction into the catalyst bed to prevent thermal damage to the catalyst.

In the FBSG process illustrated for example by U.S. Patent 4,877,550; 5,143,647 and 5,160,456, the hydrocarbon gas, such as methane, and oxygen or an oxygen-supplying gas are introduced separately into a catalyst fluid bed for mixing therewithin. While the gases may be introduced at a plurality of sites, to more evenly distribute the gases over the inlet of the fluid bed of the reactor, the fact that the gases mix within the fluid bed results in over-oxidation hot spots and catalyst sintering or agglomeration due to the oxygen concentration being higher and closer to full-combustion stoichiometry in areas closest to the oxygen injection sites.

The gas phase partial oxidation and steam reforming chemistry employed in the FBSG and the Autothermal Reforming (ATR) process have very similar material balance when using similar feed. However, ATR is limited in size by the scalability of its injector design, and the more-scaleable FBSG is economically debited by the cost of fluid solids and dust cleanup and by the expense of replacing agglomerated and/or eroded catalyst. The dust comprises catalyst fines due to catalyst attrition in the bed, and these fines are expensive to clean out of the syngas. While the chemistry is correct, these two processes have significant drawbacks. Both require very large reactors. For FBSG there is a significant expense in fluid solids management. For Autothermal Reforming there is a large and problematic methane/oxygen feed nozzle.

In the autothermal reforming process, the methane and oxygen-containing gases are mixed and reacted in a diffusion flame, and the oxidized effluent is passed into a steam reforming zone for steam reforming of the effluent in the presence of a fixed arrangement of a conventional steam reforming catalyst, such as a fixed catalyst bed or a ceramic foam or monolith carrier impregnated

with a steam reforming catalyst. The high temperature in the catalytic reforming zone places great demands on the reforming catalyst, which must withstand these conditions and be capable of substantially retaining its catalytic activity and stability over many years of use.

Conventional steam-reforming catalysts, or autothermal or combined reforming catalyst, can be described as being selected from the group consisting of uranium, Group VII metals, and Group VIII noble and non-noble metals. Metals may be used in combination with each other and with other metals such as lanthanum and cerium. The metals are generally supported on thermally-stable inorganic refractory oxides. Preferred catalyst metals are the Group VIII metals, particularly nickel. In the case of nickel, any nickel-containing material is useful, e.g. nickel supported on alpha alumina, nickel aluminate materials, nickel oxide, and preferably a supported nickel containing material.

Support materials include α -alumina, aluminosilicates, cement, and magnesia. Alumina materials, particularly fused tabular alumina are particularly useful as catalyst support. Preferred catalyst supports may be Group II metal oxides, rare earth oxides, α -alumina, modified α -aluminas, α -alumina-containing oxides, hexa-aluminates, Ca-aluminate, or magnesium-alumina spinel. In some cases, catalysts are stabilized by addition of a binder, for example calcium aluminum oxide. Silicon Dioxide level in the catalyst is preferred to be maintained at a very low level, e.g. less than 0.3 wt% to avoid volatilization and fouling of downstream equipment.

The shape of the catalyst carrier particles may vary considerably. Raschig rings 16 mm in diameter and height having a single 6-8 mm hole in the middle are well known in the art. Other forms, such as saddles, stars, and spoked wheels are commercially available.

According to the autothermal steam reforming process of US Patent 5,492,649 the production of high amounts of carbon or soot in the diffusion flame oxidation step is avoided by mixing the methane gas with the oxidizer gas while swirling the latter at the injection nozzle to provide a large number of mixing points in the diffusion flame. However, such process still produces the partial oxidation reaction in a diffusion flame, which results in over-oxidation and an excessively high temperature effluent which can damage the steam reforming catalyst and the face of the injector.

According to Canadian Application 2,153,304, the formation of soot is avoided or reduced by increasing the temperature at the exit of the steam reforming zone to a temperature between about 1100° to 1300°C, and/or by introducing the gaseous hydrocarbon feed in increments. Temperatures in this application speak only to zone exit temperatures, and not any peak temperatures that occur within a zone.

CPO (catalytic partial oxidation) attempts to eliminate the gas phase partial oxidation reactions entirely, and instead perform all of the partial oxidation reactions on a highly active catalyst (usually Rh) to convert the hydrocarbon catalytically at such a high rate or low dwell time that the gas phase reactions, or combustion stoichiometry, never have the opportunity to occur. It is crucial that the gases fed to a CPO catalyst be thoroughly premixed in order to avoid gas phase reactions which damage the catalyst, reduce its activity and promote non-complete combustion reactions. Also, while more selective than gas phase POX, CPO catalysts currently known have not exhibited such high levels of steam reforming activity that would permit them to reform over-oxidized feeds at the high space velocities employed in CPO. Thus, it is especially critical in CPO to avoid non-selective gas-phase oxidation.

It is known that successful operation of the catalytic partial oxidation (CPO) process on a commercial scale requires high conversion of the hydrocarbon feedstock at high hourly space velocities, using preheated mixtures of oxygen gas and methane in a preferred ratio of about 0.5, and under elevated pressures. Reference is made to Jacobs et al. U.S. patent 5,510,056 (Shell) for its disclosure of such a process.

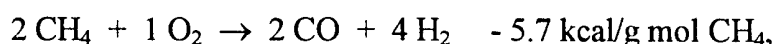
The problems with such known processes are that they are dangerous, since pre-formed preheated mixtures of oxygen and methane, at pressures of interest for syngas production, e.g., 10 atmospheres or more, are co-reactive and explosive, and any gas stage reaction or autoignition prior to introduction to the reaction zone, results in combustion stoichiometry which is highly exothermic and produces catalyst sintering.

Summary of the Invention

The present invention relates to a novel compact apparatus and an efficient process for the partial oxidation of hydrocarbons, particularly for light hydrocarbon gases, to convert such gases, such as methane, to valuable synthesis gas at moderate H_2/CO ratios desired for subsequent hydrocarbon synthesis. The essence of the present process involves providing sources of fluid hydrocarbon, such as a light hydrocarbon gas containing one or more C_1 to C_4 alkanes, and oxygen or an oxygen-containing gas, preheating and pressurizing said fluids, and injecting said individual fluids at high velocity through a plurality of isolated small passages of an injector manifold, into impingement and admixture with each other to form a gaseous premix having a pressure which is more than 1% lower, preferably more than about 3% lower and possibly more than about 5% lower than the lowest upstream pressure (P_u) of either of the gases relative to the gas pressure (P_c) in the entrance of the gas phase partial oxidation zone, and having the desired stoichiometric molar proportions, e.g., oxygen (O_2) to carbon (C) molar ratio of

from 0.3 - 0.8, preferably 0.45 - 0.70, at a plurality of injection nozzles or mixing cups which are open to a partial oxidation reaction zone and are spaced over the face surface of an injector, preferably of the type used in the rocket or aerospace industry. The gaseous premix is injected into the partial oxidation reaction zone within a maximum residence time after impingement at the injector nozzles or cups which is shorter than the autoignition time delay of the gaseous premix and preferably is less than 9 milliseconds, more preferably less than 2 milliseconds and most preferably less than 0.5 millisecond, and at a high velocity such as about 25 and 1000 ft/sec, preferably 50 and 500 ft/sec, and most preferably between 50 and 300 ft/sec, into a combustion or reaction zone comprising a gas phase partial oxidation zone ("POX zone").

The partial oxidation reaction occurs before or simultaneously with the autoignition time delay of the gaseous premix, resulting in a temperature of the gas phase partial oxidation zone that is, in all places, less than 3500°F, preferably less than 3200°F, and most preferably less than 3000°F, and resulting in reduced amounts of CO₂, H₂O and heat produced by the partial oxidation reaction to favor the desired stoichiometry, i.e.,



The present process and apparatus represents an improved gas phase partial oxidation (GPOX) process, autothermal reforming (ATR) process and fluid bed syngas generation (FBGS) process by rapidly premixing the hydrocarbon and the oxidizing gas, substantially reducing the delay time between the mixing of the preheated, pressurized reactant gases in the desired relative amounts or proportions and the introduction of the homogeneous gaseous premix to the gas phase partial oxidation reaction zone, the peak temperature of which POX zone is thereby greatly reduced, and the effluent of which POX zone may be recovered directly (as in GPOX) or fed directly into a catalytic zone (as in ATR or FBSG). The reduced

delay time or duration of existence of the formed stoichiometric mixture, prior to controlled reaction, avoids the problems of over-oxidation (as occurs in the ATR and FBSG processes where the gases are first contacted in a diffusion flame), soot formation (as occurs in the ATR process), and the dangers normally presented by the explosive nature of a preheated mixture of oxygen and methane gas.

The effluent of the POX zone may be passed into a steam reforming zone in which some hydrocarbons remaining in the effluent from the partial oxidation reaction zone are converted with the aid of a steam reforming, autothermal, or combined reforming catalyst, which catalyst may be active for steam reforming, CO₂ reforming, soot gasification, and other reactions that POX zone effluents undergo on such catalytic materials. The steam reforming zone comprises a catalyst retained in a fixed arrangement, such as a bed of conventional reforming catalyst or the catalytic passages of a parallel-pore ceramic or metallic monolith, or a ceramic or metallic foam monolith.

The present process and apparatus represents an improved partial oxidation process by premixing the hydrocarbon and the oxidizing gas to form a premix having a pressure which is at least 1% lower than the lowest upstream pressure of either stream, and preferably, substantially reducing the delay time between the mixing of the preheated, pressurized reactants in the desired stoichiometric amounts and the introduction of the homogeneous premix to the gas phase oxidation zone.

The feeding of the premix feed to the gas phase oxidation zone avoids the problems of over-oxidation and soot formation, as occurs in conventional GPOX, FBSG, or ATR process where feeds are first mixed in a diffusion flame, while the reduced delay time or duration of existence of the formed stoichiometric premix, prior to controlled reaction, avoids the dangers

presented by the explosive nature of a preheated mixture of oxygen and hydrocarbon.

The present process and apparatus enables the partial oxidation reaction to be completed while the bulk of the gaseous premix is in the gas phase POX zone as a homogeneous and stoichiometric mixture, since a uniform gaseous premix can be formed at and ejected from each of the plurality of ejector nozzles or cups which are distributed over the wide diameter injector face corresponding to the width of the diameter of the entry face of the gas phase partial oxidation zone, thereby avoiding the introduction of bulk gaseous streams which are oxygen-lean or oxygen-rich, which can interfere with the desired stoichiometric reaction and can result in hot spots which can burn or sinter the downstream catalyst and/or destroy the solid monolith carrier, and/or damage the face of the injector or the walls of the reactor.

An embodiment of the present invention relates to the improvement of MCS-producing reactor systems by the use of a plurality of mixing nozzles to produce and directly feed the gaseous premix to the partial oxidation zone. In this manner, the separate premixing of the prior art is completely eliminated. The burner face, instead of being used to just hold the flame, is the face of the injector used to mix the feeds. Pilot oxygen injection can continue to be used on the burner face, in the same way it is used in the BASF, Montecatini and other art processes. In this embodiment, one specific improvement is the capability to operate the MCS-generating burner at pressures above 6 atm, preferably above 10 atm, which pressures are unachievable using conventional MCS-producing premix feed injectors.

When the injector and partial oxidation zone of the present invention is used to produce MCS, the residence time in the POX zone should be kept below .02 seconds, preferably below 0.005 seconds. After reaction in the POX zone, the

products of the POX zone should be cooled to a temperature below 300°C as rapidly as possible (within .002 to .050 seconds), for example, using water injection.

In one embodiment of the present invention, different regions of the gas phase partial oxidation zone are fed with different, homogenous feed mixtures to produce predetermined localized results. Specifically, a minority of the feed injection nozzles, up to about 25% thereof, may be designed with predetermined relative orifice sizes to create a gaseous premix that has slightly higher or lower than average oxygen/methane ratio. For example, one out of every seven injection nozzles, representing the center injection nozzle in a hexagonal pattern, may be designed with larger oxygen orifices to discharge a more oxygen-rich composition that would have higher flame speed, would be more difficult to extinguish, and thus would serve as a "pilot light" to prevent the reaction of the bulk mixture from being extinguished, particularly at the high gas velocity associated with high reactor productivity. In addition, injection nozzles near the perimeter of the wide diameter injector face may be designed with larger methane orifices to discharge a more methane-rich composition that would provide a cooler environment near the walls of the partial oxidation zone, reducing heat loss and cost of reactor construction. A key feature of the present invention is that these stoichiometric variations are designed into the injector assembly in a controlled fashion, for example the "pilot light" discussed above may be designed to provide an oxygen-rich gaseous premix at a precisely controlled oxygen (O₂)/carbon ratio in the range of 0.6 to 1.0 and such oxygen-rich composition mixture is ejected into the partial oxidation zone as a highly mixed composition, minimizing the problems of hot spots and soot generation that occur with the diffusion flames of ATR and GPOX or with the oxygen injection of MCS-producing processes.

The hydrocarbon stream introduced to the mixer/injector may be any gaseous or liquid hydrocarbon stream that will support partial oxidation, including light gases and petroleum streams, as well as carbon-containing waste streams that

are in liquid form. Preferably, the hydrocarbon is a gas stream comprised substantially of C_1 - C_4 hydrocarbons. In addition, the fuel stream introduced to the mixer/injector may contain components other than methane and C_2 - C_4 hydrocarbons. Some components, for example H_2O and CO_2 , may be present in the hydrocarbon gas in relatively large amounts, such as from about 0.0 to 1.0 mol of H_2O or CO_2 per carbon atom of the light hydrocarbon gas. Other components, for example, H_2 , CO , Ar , N_2 , NH_3 , HCN , H_2S , COS , CS_2 , organic sulfur-containing compounds, organic oxygenates, and C_5+ hydrocarbons may be present in lower concentrations, typically less than 0.10 mol of the component per carbon atom of the light hydrocarbon gas although higher levels may be present. The oxygen-containing gas stream introduced to the mixer/injector may likewise contain components other than oxygen. These components are typically N_2 , CO_2 , H_2O , and Ar . Some of these components, especially N_2 , CO_2 , and H_2O , may be present in major amounts, from 0.0 to 4.0 mol per mole of oxygen (O_2). Other components are typically present in lesser amounts, normally less than 0.1 mol of component per mole O_2 . When this invention is applied to the partial oxidation zone of a secondary reforming process, components such as H_2 , CO , CO_2 , and N_2 may be present in larger concentrations, and oxygen to carbon ratios will follow conventions for that technology.

The introduction of gaseous premix into a gas phase partial oxidation zone results in a "flame" within that zone. A flame may loosely be defined as the region of space in which the fuel and oxidant are reacting via gas phase chemistry. Within any small element of the flame, a high temperature occurs because an amount of fuel reacts with an amount of oxidant in an exothermic reaction. The combustion reactions are most exothermic when there is enough oxidant to fully combust the fuel to H_2O and CO_2 products. The Equivalence Ratio, Φ , is defined as the ratio of fuel to oxidant, divided by that ratio which occurs at full combustion stoichiometry. Thus, $\Phi=1$ refers to exactly the correct amount of fuel

and oxidant for full combustion, $\Phi < 1$ refers to excess oxidant, and $\Phi > 1$ refers to excess fuel. Commercially interesting partial oxidation processes generally operate at $\Phi > 3$.

For any given flame, the flame temperature is a key result of the manner in which feeds are injected into the flame zone. There are two broad classes of flames that are determined by nature of feed injection; Diffusion flames and Premix flames.

“Diffusion” flames occur when the fuel and oxidant are injected into the flame as separate streams. The name is given because reaction must occur at the boundary between the fuel and oxidant streams, and fuel and oxidant must “diffuse” to that boundary. A principal property of diffusion flames is that, regardless of the overall stoichiometry of the flame, combustion of fuel at the boundary tends to proceed as if there were an unlimited amount of oxidant. In other words, the combustion that occurs at the fuel/oxidant boundary in a diffusion flame occurs at or near the stoichiometry of full combustion, even if the overall stoichiometry of the flame is set for partial oxidation.

“Premix” flames, as the name suggests, are flames in which all the fuel and oxidant are mixed to uniform composition before being introduced into the flame. In a perfect premix flame, all portions of the flame are fed with a composition that is the same as the overall stoichiometry of the flame, all portions of the flame react to a flame temperature that reflects the overall stoichiometry of the flame.

Flame Temperature is also a critical parameter in the design and operation of any reactor system that must confine such a flame. This is because any components within the reactor that might come into contact with, or be dominated by, the flame must be able to withstand the temperature of the flame.

Thus it is very important to measure and predict the temperatures of flames, as a function of the kind of injector that is employed. In this sense, the flame temperature that is important to a reactor system, is a flame temperature that persists in time and space. Such are the temperatures that may be measured with physical devices (e.g. thermocouples) that are inserted into the flame. We use the term "steady state temperature" to denote such temperatures that persists in space and time. More specifically steady state temperature is a temperature that persists over a volume (a space) greater than 0.1 cubic centimeter, and for a time greater than 0.001 seconds in a given location. In most practical flames, the steady state temperature varies somewhat from one location to another within the flame, thus the flame temperature often refers to the set of temperatures that describe the flame.

There are many ways to predict the temperature that will occur as a result of some local reaction of fuel and oxidant. Flame chemistry is complex, and many intermediates (such as acetylene) have a strong impact on flame temperature. Thus, temperature predictions disclosed herein are prepared using a detailed kinetic model. Because we are interested in steady state temperatures that persist in space and time, we select the reaction temperature predicted by that model after reaction time of 0.001 seconds. Specifically, the predictions disclosed here are made using the model published by Mims, et. al., in the Journal of Physical Chemistry, 1994, volume 98, pages 13357 to 13372. The 0.001 seconds of reaction time are computed as a 1st 0.0005 seconds of time in a perfectly stirred reactor (psr), followed by 0.0005 seconds in a plug flow reactor. All reactions are computed as adiabatic. Such psr/plug sequences are used in the aerospace industry as simplified representations of flame hydrodynamics. Other choices of prediction means will result in somewhat different temperatures. But the differences between such means are small compared to the large differences between diffusion and premix flames that are the subject of this application.

The difference between Premix and Diffusion flame temperatures can be seen in the following example. Consider a Partial Oxidation stoichiometry that might be used in Auto Thermal Reforming; 1.0 moles CH_4 , 0.5 moles H_2O , and 0.5 moles of O_2 , a feed temperature of 500°C (932°F) and a reaction pressure of 25 atm (353 psig). When reacted as a premix, the local reaction in the flame will everywhere proceed at the equivalence ratio of the overall mixture, which is $\Phi=4$. This results in a flame temperature of 1498°C (2728°F). However, when reacted as a diffusion flame, the reaction will occur at the boundary between the fuel and the oxidant, where reaction will proceed at $\Phi=1$. This results in a flame temperature (assuming all the steam was in the CH_4) of 3150°C (5700°F). Of course, even for diffusion flames, at $\Phi=1$, it is theoretically possible to add so much diluent to the feed that the flame temperature drops to a low value, even below 3500°F . However, such levels of diluent are not economically attractive for synthesis gas manufacture. While it is well known that some uses of partial oxidation zones, such as secondary reforming, involve larger levels of diluents, it is preferred in the present invention that diluent levels be kept to the minimum levels required for any such use. Low diluent level can be quantified in terms of oxygen concentration in the combined feed to the process, which is preferred to be greater than 5 mole% in the present invention.

Only in acetylene manufacture is there a process whereby hydrocarbon is converted to syngas-containing stream in a partial oxidation zone that contains a premix flame. This is because, use of conventional premix injectors (as used for acetylene) causes substantial pre-ignition problems previously described. However, with the injectors of the present invention, it is now convenient to operate a POX zone with feed that is extensively mixed. The advantages of a premix flame zone (less soot, lower temperature) can now be extended to partial oxidation products other than acetylene. Thus, one embodiment of the present invention is a process for the conversion of hydrocarbons to synthesis gas that is

substantially free of acetylene, the reaction zone of said process comprising at least a gas phase partial oxidation (POX) zone, operated as a premix flame, and having a flame temperature that is everywhere less than 3500°F, preferably less than 3200°F, and most preferably less than 3000°F. A syngas that is substantially free of acetylene should have less than 5 mole% acetylene, preferably less than 1 mole%.

It will be recognized by those skilled in the art, that the gaseous premix formed when the hydrocarbon stream and the oxidant stream are ejected into the mixing zone or cup will not be perfectly mixed at the point of initial contact. In any real physical device, some time or distance will be required before perfect mixing is achieved. As used herein, the term "feed stream" means the individual streams, such as hydrocarbon or oxygen containing gas, that are being fed to the mixing zone or feed nozzle cup, and the term "gaseous premix" means the physical combination of these feed streams in a state that is highly mixed. Of greatest importance in the present invention is that the streams achieve a high degree of mixedness in a minimum amount of time, and before gas phase or catalytic reactions begin to occur at any substantial level. In order to quantify this degree of mixedness, the measure "Efficiency of Mixing", abbreviated as E_m , is used.

E_m is calculated from the composition profile of the stream of gaseous premix. Composition profiles can be obtained by sampling the stream at many locations, or by use of other diagnostic tools. For example, imaging the Rayleigh-scattered light of a laser beam can, under properly controlled conditions, provide composition variations across partially mixed streams. The composition data is used to calculate how much of each feed stream is present at each location. For example, if one is mixing air with methane, the oxygen and nitrogen mole fractions would be combined to represent the mole fraction of the air stream.

For the case where hydrocarbon (abbreviated HC) and oxygen-containing (abbreviated OX) feed streams are being mixed, we define E_m using the following equation:

$$E_m = ((X_{HC}/X_{OX})_{MIN}/(X_{HC}/X_{OX})_{MAX})^{0.5}$$

Where X_{HC} and X_{OX} represent mole fractions in the gaseous premix of hydrocarbon gas and oxygen-containing gas, and the subscripts "MIN" and "MAX" designate that these are the minimum and maximum ratios found in the gaseous premix. Thus, $(X_{HC}/X_{OX})_{MIN}$ represents the minimum HC/OX mole fraction ratio found in the composition profile. As so defined, E_m reaches a value of 1.0 when the gases are perfectly mixed, and will have a value of 0.0 if the stream has any locations that are completely unmixed (has a location where the composition is equal to that of either feed stream).

In the practice of the present invention, the gaseous premix achieves a high degree of mixedness, quantified as E_m , in a minimum amount of time. We specify this rate of achieving high mixedness by specifying the distance downstream of the injector at which a given E_m level will be attained. Because injector sizes may vary greatly, and because mixing distances tend to scale linearly with injector size, we define the distance downstream from the point of initial contact between the gases, adjacent the floor of the injector in proportion to a critical nozzle dimension. In particular, we define L as the distance downstream of the mixing nozzle, and we define D as the diameter or similar dimension of the largest orifice through which either feed stream is introduced into admixture in the nozzle. D_{AX} is the diameter of the exit orifice feeding the gas stream that is most axial with the gaseous premix path, or most near the center of the injector or of the stream being introduced in the fewest number of orifices within the nozzle. It is preferred that mixing nozzles be used in the present invention that achieve an $E_m > 75\%$ at a distance downstream of L/D_{AX} up to about 10, and preferably between about 1 to 6. It is more preferred that nozzles

achieve $E_m > 80\%$ at this distance, and most preferred that nozzles achieve $E_m > 90\%$ at this distance downstream.

Alternatively, since some of this downstream distance may occur within the partial oxidation zone, one embodiment of the present invention is defined by the premix achieving an E_m of 50% at the point of entry into the POX zone.

An important parameter defining the effectiveness of mixing is the "momentum ratio" of the streams being mixed. The momentum of a stream is defined as the product of the velocity of the stream as it is injected into the mixing zone multiplied by the stream's mass rate. For efficient mixing the ratio of the momentums of the mixed streams should be comparable. Poor mixing performance can occur if momentums of the streams are disparate. In the case of a mixing nozzle with axial injection of oxygen-containing gas and radial-injection of hydrocarbon gas, the ratio of the momentum of the hydrocarbon gas to the momentum of the oxygen-containing gas is preferably in the range of 0.5 - 4.0, most preferably from 1.0 - 3.0. For the opposite case of axially-injected hydrocarbon gas and radially-or somewhat radially-injected oxygen-containing gas, the ratio of the momentum of the hydrocarbon gas to the momentum of oxygen-containing gas is in the range of 0.25 - 2.0, preferably from 0.33 - 1.0. It is understood that if a gas is injected in more than one stream into a mixing chamber then the sum of the momentums or summed momenta of all of the streams of the particular gas is used in the calculation of the momentum ratio.

The present multi-orifice, large diameter injectors operate at extremely high speeds, up to sonic speeds, and discharge the separate gases, e.g., methane and oxygen, in a predetermined ratio from closely-spaced orifices, i.e., within up to about 0.5 inch of each other, into direct contact with each other within a plurality of small mixing nozzles or cups at the injector surfaces, or at an angle

between about 60° up to about 180° relative to each other for intersecting contact or impingement and admixture immediately above the injector surface, for discharge or injection of the homogeneous preheated pressurized gaseous premix into the gas phase partial oxidation zone at extremely high velocity and at a pressure which is more than 1% or 3% or 5% lower than the lowest upstream pressure of either of the gases. The dwell time of the gaseous premix within or immediately beyond the injector surface prior to injection into the partial oxidation reaction zone preferably is less than about 9 milliseconds, more preferably less than about 2 milliseconds, and most preferably less than 0.5 millisecond, resulting in a gas phase partial oxidation zone whose temperature in all places is less than 3500°F, preferably less than 3200°F, and most preferably less than 3000°F. Also the velocity of the homogeneous gas mixture as it is ejected from the mixing nozzles is from about 25 to 1000 ft/sec, more preferably between about 50 to 500 ft/sec and most preferably between about 50 and 300 ft/sec, whereby efficient syngas production is enabled by compact reactors of higher throughput than heretofore possible.

As used herein, references to the velocity at which the gaseous premix is passed to the partial oxidation zone should be taken to mean the local gas velocity as the gaseous premix leaves the mixing nozzles, and not some reactor-average superficial velocity.

A critical feature of the high speed gas injectors of the present partial oxidation process is that they are designed to produce a drop or reduction of the initial gas pressure through the injector which is greater than 1%, preferably greater than 3% and possibly greater than about 5% of the lowest upstream gas pressure (P_u) of either of the individual gas streams, which upstream pressure is normally between 2 and 200 atmospheres, preferably between about 5 and 100 atmospheres, i.e., the pressure reduction, or ΔP , or $P_u - P_c$ divided by the reaction chamber inlet pressure, or P_c , is $> 1\%$, preferably $> 3\%$ and possibly $> 5\%$ relative to the reaction chamber inlet pressure. This pressure drop causes the oxidation gas and the

hydrocarbon gas to be drawn into more intimate admixture immediately in advance of injection into the partial oxidation (POX) zone to form the desired stoichiometric gaseous premix. The pressure drop also improves the uniformity of flow of the gases through the injector to avoid instabilities. This is particularly important in the case of economically advantageous, very large reactors which employ a plurality of side-by-side mixers/injectors to supply the premix to the large-diameter reactor, most particularly in reactors containing a gas phase partial oxidation zone, which system is deleteriously affected by the soot formation and high temperatures that accompanies non-homogenous feed. The pressure drop as the gases pass through the injector results in a high gas mixing efficiency (E_m) as close as possible to the face of the injector to produce the gaseous premix of the gases having the desired stoichiometry immediately in advance of the passage of the gaseous premix into the partial oxidation zone. The desired ratio of the hydrocarbon gas and the oxygen gas always has an excess of the hydrocarbon to prevent over-oxidation, excessive heat and soot formation. In cases where the mixing nozzles of the injector are tubular cups or wells recessed below the face surface of the injector, the point of 75 to 90% E_m occurs at a location which depends on the diameter (D_{AX}) of the most axial feed gas orifice into the cup or well, i.e., E_m occurs at an L/D_{AX} of 10 or less, such as 3 or 6. As mentioned, this mixing efficiency is enabled by the uniform pressure drop, or ΔP , as the gases pass through the isolated small passages of the injector manifold and through the nozzle orifices to impinge at each of the mixing zones, chambers, or cups, and the uniformity of the pressure drop assures uniform continuous gas supply to each of the mixing nozzles or cups even when a plurality of injectors are assembled side by side and fed from common gas sources to feed very large diameter gas phase POX reaction chambers.

It is an advantage of the present invention that the present apparatus enables a partial oxidation reaction that is fed by a more homogeneous or uniform supply of reactant gas premix composition. Because the feed gas is a mixture of

hydrocarbon and oxygen-containing streams that is very reactive, particularly reactive at the high pressures and temperatures desired for syngas generation, the time available to mix the gases before introducing them into the partial oxidation zone is very limited. Thus, we have discovered that feed injectors that achieve high levels of E_m in very short physical distances - distances on the order of inches, not feet, achieve high E_m in short L/D_{AX} wherein D_{AX} is the diameter of the axial stream orifice, usually the oxygen gas orifice, and L is the distance downstream from the point of initial contact between the gases, such as the lowest level of the radial gas orifices, adjacent the cup floor containing the axial gas orifice. However, for the large scale reactors of commercial interest, use of single injectors would require a large D_{AX} at any reasonable injector velocity, and so achieving high E_m in a short L/D_{AX} is not sufficient. Thus a key feature of this invention is the use of an injector having a plurality of mixing nozzles or chambers or cups, which serves to reduce the injector dimensions (reducing D_{AX}) and reduce the physical distance (and hence time) required to achieve a gaseous premix having a high degree of feed uniformity.

Finally, the use of a plurality of injector nozzles presents the problem that multiple nozzles can interact and become unstable, and also presents the problem that multiple injector nozzles must all be fed at the same stoichiometry. Thus, a key feature of this invention is the use of elevated pressure drop for the feed streams in the nozzles to provide uniform, stable, and non-interacting flows of admixed streams into the partial oxidation zone.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatic illustration of a compact injector/syngas apparatus as used for autothermal reforming according to one embodiment of the present invention;

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the partial oxidation section 19 to assure the uniform passage of a homogenous gaseous premix of the hydrocarbon and oxygen gases, in the desired predetermined oxygen (O_2)/carbon (C_1) ratio of about 0.3-0.8 preferably 0.45-0.7, into the partial oxidation section 19 and then into the catalytic zone 12.

Separate methane supply conduit 17 and oxygen supply conduit 18 feed continuous streams of preheated, pressurized methane and oxygen into and through the manifold methane passages 23 and oxygen passages 22, respectively, for intermixing within the plurality of jet nozzles or cups 14 at the face surface 13 of the injector means 11, or for angular impingement immediately beyond the face surface 13 of the injector means 11. The methane passages 23 and oxygen passages 22 have exit orifices sized so that the pressure drop of each gas as it passes through these passages and orifices is maintained at a value that is more than 1% lower, preferably more than 3% lower, and possibly more than 5% lower than the lower of the upstream pressures (P_u) in the methane conduit 17 or the oxygen conduit 18 relative to the inlet pressure (P_c) to the POX section 19. This ensures even distribution of the hydrocarbon and oxygen gases to the plurality of jet nozzles or cups 14, ensuring that each jet nozzle or cup has the same oxygen/carbon ratio, which uniformity eliminates local hot spots, local soot formation, and reactor instabilities.

Thereafter the effluent from the partial oxidation section 19 flows into and through the fixed catalyst bed 16 within the catalytic steam reforming section 12. Bed 16 preferably comprises a thermally-stable inorganic refractory oxide support which is impregnated with steam reforming catalyst such as one or more metals from Group VIII of the Periodic Table, preferably one or more noble metals or nickel. The steam reforming reaction is endothermic and draws heat from the POX effluent to cool the gases while it reacts steam and residual methane to form gases which are useful for the synthesis of other chemical compounds.

The reaction of the gaseous premix within the partial oxidation zone 12 requires means to cause the initiation of the reactions. Suitable means to initiate reaction in a gaseous partial oxidation zone include heating of the zone, as well as the introduction of a spark, plasma, or hot glow plug into the zone.

It is preferred that the jet nozzles or cups 14 are sized so that the gas residence time of the mixture in the injector means 11 is substantially less than the autoignition delay time of the mixture, and preferably less than 9 milliseconds, more preferably less than 2 milliseconds, and most preferably less than about 0.5 millisecond. This prevents reaction of the gaseous premix in the gas phase within the injector means 11, and/or before becoming highly mixed, which reaction would proceed with excessive heat generation that is damaging to the catalyst and the syngas reactor.

Suitable feed injectors that meet the aforementioned requirements have been developed, for use in the aerospace industry. One such device is known as a microinjector or platelet burner. The principal of this injector is that many small mixing nozzles ("microjets") are uniformly-spaced over one large diameter face. Any mixing approach can be used in the nozzles, but some will be more amendable to fabrication and to rapid mixing. A preferred approach is the use of nozzles called "triplets", in which there is a central or axial flow of one reactant, such as an oxygen gas, through the oxygen passages of a manifold, and the second reactant, such as a hydrocarbon gas, is introduced in two opposed, or somewhat radial jets up to about 1 inch below the burner face through isolated methane passages of the manifold. An advantage of this triplet design as applied to the present process is that it has very good anti-flashback properties, which are highly desired for hot, high pressure CH_4/O_2 mixing. Figures 2 and 3 illustrate such an injector, manifold, isolated gas passages, injector face, and suitable triplet mixing nozzles or cups.

Injector face sections 30 of the type shown in Fig. 3 can be built in large diameters, with spacing of the mixing elements or cups 24 smaller than 1 inch up to several inches. Thus, to achieve homogeneous reaction premixes, mixing lengths and residence times are kept low. In a preferred embodiment, a minority of the feed injection nozzles 24 may be designed to be a different nozzle 28 that creates a gaseous premix having a slightly higher than average oxygen/methane ratio. One such pattern, wherein one out of six injection nozzles is a high-O₂ nozzle 28 (marked with a "*") is shown in Fig. 3. The presence of such nozzles 28, ejecting gaseous premix with a higher oxygen/carbon ratio can serve to prevent the reaction of the bulk mixture from being extinguished, particularly at the high gas velocity associated with higher reactor productivity.

A preferred high velocity interior-mixing or recessed cup injector 20, developed for use in the aerospace industry, is illustrated by Fig. 2 of the present drawings and is illustrated by Figs. 3-6 of U.S. Patent 3,881,701, the disclosure of which is hereby incorporated herein by reference thereto. However, the exterior-mixing injectors illustrated by Figs. 1, 2 and 2a of Patent 3,881,701 are also suitable for use according to the present invention, whereby the reactant gases impinge and mix immediately above or beyond the injector surface. The platelet-type injectors of this Patent are produced by forming fine fluid-flow methane and oxygen passages on the surfaces of or within a plurality of thin metal plates 21 containing interconnecting bores in predetermined areas, and diffusion bonding the metal plates together to form injectors comprising manifolds containing fine isolated gas passages for oxygen and methane, which passages communicate at a plurality of microjet nozzles or cups 24 at a face surface 25 of the injector, or impinge immediately beyond the injector surface 25, to mix the gases and eject the gaseous premix at high velocity. The present injector means 11 are gas delivery manifolds which are engineered to provide equal specified flow of both gases to all microjet nozzles or cups 24.

Referring to Fig. 2, of the Drawings, the injector means 20 thereof comprises a plurality of thin metal plates 21 which are provided in predetermined areas thereof with segregated oxygen passages 22 and methane passages 23, respectively, which communicate with sources of oxygen and methane, respectively, under high temperatures and pressures (P_u). The passages 22 and 23 divide the total flow of the individual gases into a very large number of precisely-metered, very small streams of the individual gases, which streams communicate within each of a plurality of mixing nozzles or cups 24 which are open to the face surface 25 of the injector 20 means. Cups 24 are tubular, such as oval or cylindrical.

The injector means 20 isolates the heated, pressurized streams of the methane and oxygen until they mix within the plurality of cups 24 and are injected as a gaseous premix at high velocity of 25 to 1000 ft/sec, more preferably 50 to 500 ft/sec., most preferably 50 to 300 ft/sec., at a reduced pressure or a pressure drop of more than 1%, preferably more than 3% however, and possibly more than 5% lower than the lowest upstream pressure (P_u), relative to the pressure (P_c) of the gas phase partial oxidation zone (19 on Figure 1), where the partial oxidation reaction occurs.

A further advantage of the gas mixers/injectors of Fig. 2 is that one or both gases can be used to cool the face surface 25 of the injector means 20 by heat exchange therewith to mitigate chemical damage and prevent heat damage thereto due to the proximity to the high temperature partial oxidation section 19, which has a temperature between about 700°-1925°C (1300-3500°F), preferably between about 870°-1650°C (1600-3000°F). This cooling is accomplished by the circulation of the gas or gases, preheated to feed temperatures of approximately 100°-700°C (200-1300°F), through circulation passages, such as 23, immediately below and parallel to the uppermost plate 21 forming the face surface 25 of the injector means 20 to cool the face surface 25 well below the temperature, such as

1400°C (or such as 2600°F), within the POX reaction zone 19, as the gas or gases pass through the manifold to the mixing cups 24.

Fig. 2 illustrates a cup 24 which may have a diameter of about 0.10" and a depth of about 0.10" which may be doubled to an extended depth of about 0.20", for example. The methane gas inlets 23 are split inlets each having an exit orifice width W of about 0.05" which inject hot pressurized methane gas flows horizontally from opposed sides of the cup 24 radially against the vertical flow of hot pressurized oxygen gas introduced through the central inlet 22 and exit orifice having a diameter of about 0.060", for example, to form the homogeneous reactant gaseous premix which is ejected from the cup 24 in less than 9 milliseconds, preferably less than 2 ms, most preferably less than 0.5 ms.

Figs. 4 and 5 illustrate an individual triplet mixing nozzle or cup 50 as an alternative design for each cup 14 of Fig. 1 or for each cup 24 of Figs. 2 or 3. Referring to the triplets of Figs. 4 and 5, the somewhat radial horizontal methane supply conduits 51 and 52, each having a width W of about 0.30", are slightly offset relative to each other so that the methane gas flows therefrom horizontally and tangentially against the vertical or axial oxygen gas flow from central vertical oxygen conduit 53 each have an exit orifice diameter D_{AX} of about 0.30", to cause the gas mixture to swirl within the mixing cup 50 as it is formed and ejected in less than 9 ms. The mixing cups 50 of Figs. 4 and 5 have a design preferred for use feeding gas phase partial oxidation zones 19. The larger injector of Figs. 4 and 5 is more resistant to fouling, and thus may be preferred provided that residence time limits within the injector are not exceeded. The gaseous premix ejected from the mixing cup 50 can be characterized for mixedness E_m at a plane 55 located a distance L downstream of the injector means, extending from the point of initial contact between the gases, e.g., the lower level of the radial gas orifices, adjacent

the floor of the mixing cup, as shown in Fig. 5. Preferred injectors achieve $E_m > 75\%$, more preferably $> 80\%$ at downstream distances $L < 10 D_{AX}$.

It will be apparent to those skilled in the art that the specific number, spacing and dimensions of the present nozzles can be varied depending upon the particular process being conducted and the dimensions of the reactor and the partial oxidation section 19 being used in association with the injector means 11, and the size of the latter.

For example the cup 50 of Fig. 4, preferably cylindrical, can have a diameter of several inches, preferably up to about one inch, and a maximum depth, down to the methane inlets similarly dimensioned. At these dimensions, the diameter or width of the exit orifices of the oxygen inlet conduits 53 and of the methane inlet conduits 51 & 52 will be larger in order to provide sufficient gas volumes and pressures to maintain a methane-to-oxygen ratio which is greater than 1, at least at the majority of the nozzles 50, to avoid over oxidation, especially CO_2 formation, in all areas of the reactor before combustion begins.

Also, it is important to maintain the gas pressure drop (ΔP) through the injector at a value which is more than 1% lower, preferably more than about 3% lower, and possibly more than 5% lower than the lowest upstream pressure (P_u) of either of the gases, relative to the inlet pressure (P_c) existing within the POX section 19, i.e., $(P_u - P_c)/P_c$ is greater than 1%, preferably greater than about 3%, and possibly greater than 5%, where P_u is the lowest upstream gas pressure, $\Delta P = (P_u - P_c)$ is the pressure drop within the injector and P_c is the inlet pressure of the partial oxidation section 19. The upper limit of this value can become impractically high as the flow velocity through the injector means 11 approaches sonic. Generally the flow velocity is maintained within practical limits for economic reasons and to avoid flame blow-out or catalyst bed attrition. Also lower flow velocity permits

cooling of the POX gases by the endothermic steam reforming reaction, to protect the catalyst bed 12.

According to a further embodiment of the present invention, the formed useful syngas is cooled, recovered and treated for use in further synthesis processing. Such treatment may include purification to remove the low amounts of ammonia and hydrogen cyanide produced in the partial oxidation process. Suitable processes for removing ammonia and hydrogen cyanide from gaseous streams are well known in the art. The removal of ammonia and hydrogen cyanide may be effected in a single stage or in a plurality of stages. The cooling step may be effected before or after the purification treatment steps, as appropriate to accommodate preferred temperatures of the treatment process. Small amounts of hydrogen may be separated out of the syngas for use in a hydrocarbon upgrading stage.

The treated syngas may be used in processes that produce methanol and methanol based products, hydrocarbon synthesis (HCS) products such as liquid hydrocarbons, olefins, alcohols and aldehydes, oxo-synthesis products, ammonia and ammonia based fertilizers and chemicals, town gas or reduction gas used for the production of sponge iron, etc.

In a conventional hydrocarbon synthesis (HCS) process, liquid and gaseous hydrocarbon products are formed by contacting the present syngas comprising a mixture of H_2 and CO with a suitable Fischer-Tropsch type HCS catalyst, under shifting or non-shifting conditions. Suitable Fischer-Tropsch catalysts comprise one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru, and Re. In one embodiment, the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg, La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. Preferred supports for cobalt-containing catalysts comprise titania,

particularly when employing a slurry HCS process in which higher molecular weight, e.g., C₁₀₊ products, primarily paraffinic liquid hydrocarbon products are desired.

The hydrocarbon products produced by an HCS process according to an embodiment of the present invention are typically upgraded to form suitable products such as, synthetic crude oil, liquid fuels (e.g., jet and diesel), or lubricating, industrial or medicinal oil, waxy hydrocarbons, olefins (by, e.g., catalytic cracking or steam cracking). These processes are well known to those skilled in the art and need not be described here. All or a portion of the HCS products can be fractionated and then converted in one or more steps with or without a suitable catalyst or in the presence of hydrogen or both.

Hydroconversion is usually preferred and includes mild hydrotreating (minimal branching) to make pumpable liquids, hydroisomerization (somewhat more branching, e.g., 25-65%, and preferably mono-methyl branching) for making distillates such as jet fuels and diesel fuels, and more severe hydroisomerization (wherein virtually all, e.g., less than 10wt% and preferably less than 5wt% of the feed remains unconverted) to make lube oils. These processes are also well known and reported in the literature in so far as catalysts and reaction conditions are concerned.

The foregoing description is only illustrative of the invention. Accordingly, the present invention is intended to embrace all alternatives, modifications and variances which fall within the scope of the appended claims.

EXAMPLE 1 (COMPARATIVE)

Current commercial reactors that include gas phase partial oxidation zones use a single feed injector (sometimes called a "burner nozzle") that is coaxial in design. One recent advanced design is the Haldor Topsoe "CTS" burner nozzle,

which is described in US 5,492,649, and 5,496,170. The results of this burner are further described in a presentation by Christenson et. al. at the AIChE Ammonia Safety Symposium in Vancouver, BC, Canada, 10-3-6/94 (paper 3g). The computational fluid dynamic (CFD) analysis shown in Christenson et. al. (their figure 7 & 8) clearly show the flame's hot spot begins in between the cooler fuel and oxidant streams and extends into the oxygen-rich core, as is typical of diffusion flames.

US 5,492,649 lists example feed compositions for ATR, oxygen-blown Secondary Reforming, and air-blown secondary reforming. Using the compositions and conditions in these tables, we have made a temperature prediction for the peak flame temperature that would occur if these flames were operating as a diffusion flame, and the flame temperature that would be achieved if the flames were operating as premix. This is shown in the table below:

	Air-Blown Secondary Reformer	O ₂ -Blown Secondary reformer	Auto- Thermal reformer
Computed Peak Flame Temperature, °F			
As Diffusion Flame	3890	4733	5267
As Premix Flame	1940	2235	2865
Peak Flame Temperature, Disclosed in Christenson, °F			
	~3600	~4500	4500-6300

It is seen in the Table that in every case the peak flame temperature disclosed by Christenson (the 10/94 AIChE Ammonia Safety Symposium) are

temperatures that are typical of Diffusion Flames operating at the stoichiometry of the relevant POX process. Thus, even the most advanced injectors of today's art, injectors purported to have good mixing, are functioning in the diffusion flame mode.

EXAMPLE 2

One embodiment of the invention disclosed herein is an injector system that can be used in a commercial partial oxidation system to produce synthesis gas. A key feature of this injector system is the use of a plurality of injector nozzles that create and inject a gaseous premix into the partial oxidation zone. It was previously described herein that the mixing efficiency of these injector nozzles can be characterized using Rayleigh Scattered light and an algebraic relationship that relates the composition distribution measured via Rayleigh Scattering to an overall E_m value of the Efficiency of Mixing.

Another characteristic of the composition characterization using Rayleigh Scattered light, is that it defines the manifold of flame temperatures that are to be expected from the injector. Figure 6 shows the oxidant/fuel mole ratio as a function of radial position across the injector, as measured at a downstream distance 6.3 times the radial (oxygen) port diameter for an injector of the type described in Figure 4. It is seen that the mole ratio varies to some degree, from a maximum of 0.49 to a minimum of 0.37. Such a distribution corresponds to an E_m value of 0.869.

The average mole ratio, 0.418, is representative of an ATR feed mixing case where the overall equivalence ratio (Φ) is 3.64, the fuel stream comprises 27.3% H_2O in methane and the oxidant stream comprises 4.3% H_2O in O_2 . If this stream is completely premixed before combustion, it will result in a flame temperature (by the previously given method) of 2820°F. If this was a

diffusion flame, the peak temperature in the flame would be the temperature for the $\Phi=1$ mixture of fuel and oxidant, which in this case would result in a peak flame temperature of 5720°F.

The present injector system results in a premix flame, not a diffusion flame. In the case of the present injector, the flame temperature will everywhere be representative of the oxidant/fuel ratio of the combustible mixture at the location the mixture ignites. This oxidant/fuel ratio is measured by Rayleigh Scattering, and reproduced in Figure 6. A flame temperature can be calculated for each mole ratio in Figure 6, using the method previously described. For the purposes of this example, feed temperatures is set at 932°F and the flame pressure at 25atm. The predicted flame temperature for this injector is plotted in Fig. 7.

For these feed conditions, and for the mixing efficiency achieved with this injector, flame temperatures are everywhere less than 3000°F. Temperature is slightly higher where the mixture has more oxygen and lower where the mixture has less oxygen. The Peak temperature of this flame is 2990°F.

Thus, injectors of the present invention, by providing a premix stream with high E_m (in this example 0.869), provide for a flame that has uniformly low temperature, substantially lower than the 5720°F temperatures that would occur in the diffusion flames created by injectors of the prior art.

CLAIMS:

1. A gas-phase partial oxidation (POX) zone for the conversion of hydrocarbons characterized in that the steady state temperature in the POX zone is less than 3500°F and the pressure is greater than 6 atm.
2. A process for the conversion of hydrocarbons in a reaction zone comprising at least a gas-phase partial oxidation (POX) zone characterized in that the steady state temperature in the POX zone is less than 3500°F, the product of the reaction zone being substantially free of acetylene.
3. The process of claim 1 or 2 wherein the partial oxidation zone is fed by hydrocarbon- and oxygen-containing streams thereby producing a flame.
4. The process of claim 1 or 2 wherein the steady state temperature in the POX zone is less than 3200°F.
5. The process of claim 1 or 2 wherein the steady state temperature in the POX zone is less than 3000°F.
6. The process of claim 1 or 2 wherein the POX zone is fed by a gaseous premix of hydrocarbon- and oxygen-containing streams which premix is characterized as having an efficiency of mixing (Em) greater than 50%.

7. The process of claim 3 wherein the combined composition of the feed has an oxygen concentration greater than 5 mole percent.

8. The process of claim 1 which comprises the step of rapidly cooling the product of the POX zone after a short residence time in the POX zone, to produce a multicomponent syngas.

9. The process of claim 1 or 2 which comprises the step of passing the product of the POX zone to a steam reforming zone comprising catalyst in fixed arrangement and recovering synthesis gas therefrom.

10. The process of claim 1 or 2 comprising providing individual hydrocarbon- and oxygen-containing streams of desired proportions, each stream being at independent elevated pressure and temperature, injecting said individual streams into admixture with each other through an injector means having one or more mixing nozzles to form a gaseous premix, and introducing said gaseous premix from the mixing nozzles into the POX zone.

11. The process of claim 10 wherein said gaseous premix from the mixing nozzles is introduced into the POX zone in a time period less than about 9 milliseconds after it is formed.

12. The process of claim 10 wherein the gaseous premix has a pressure at least 1% lower than the lowest upstream pressure of either of the

individual streams.

13. The process of claim 10 wherein each of the mixing nozzles comprises a cylindrical cup recessed in the face surface of an injector, injecting one of the gases into the cup as an axial stream through an axial orifice in the bottom of the cup, and injecting the other gas into the cup as at least two opposed somewhat radial streams through opposed somewhat radial orifices in the side wall of the cups to form a gaseous premix having an $E_m > 75\%$ at a downstream distance (L) which is less than 10 times the diameter (D_{AX}) of the axial gas orifice.

14. The process according to claim 1 or 2 which comprises the steps of recovering synthesis gas from the partial oxidation zone and further processing the recovered syngas via the Fischer-Tropsch reaction to produce liquid hydrocarbons.

15. The process according to claim 14 which comprises the further step of reacting said liquid hydrocarbons by hydroconversion and recovering an isomerized product.

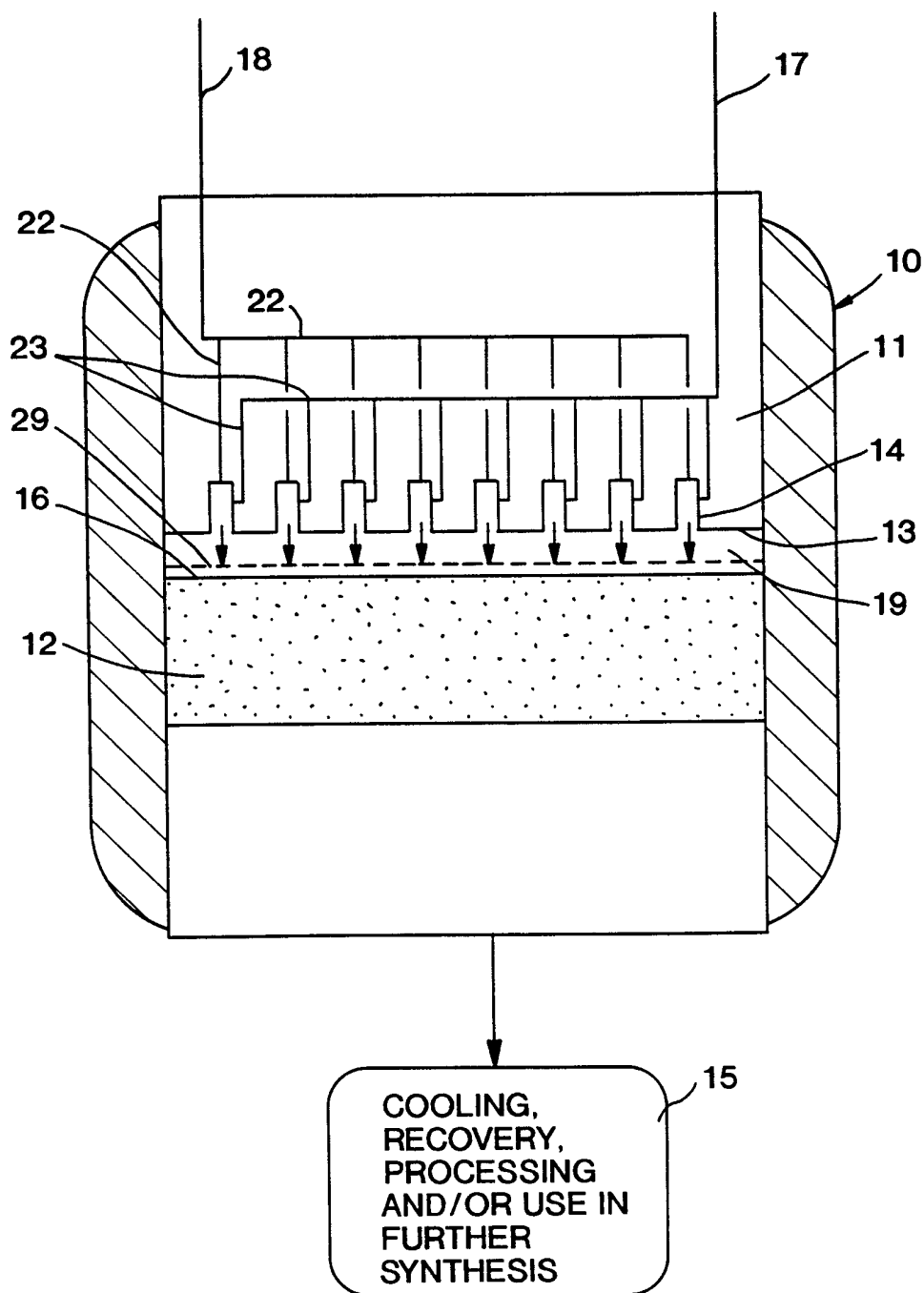


FIG. 1

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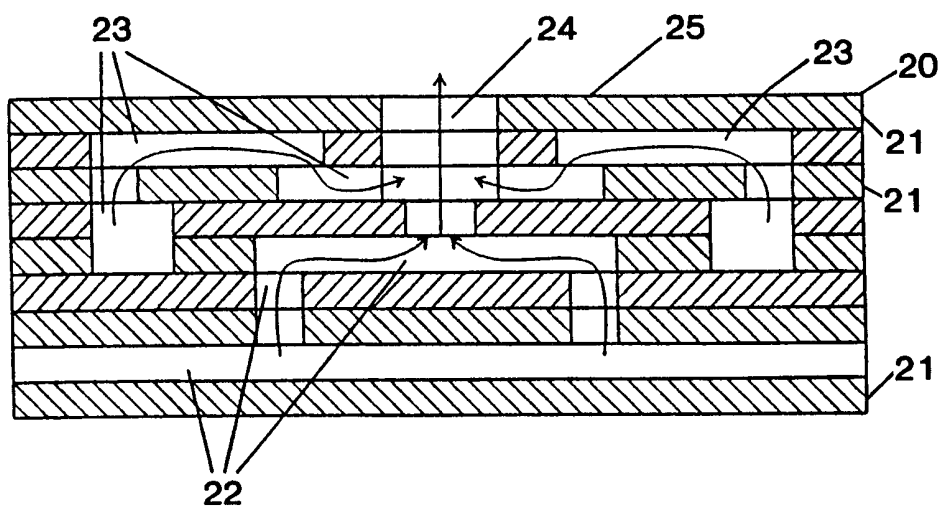


FIG. 2

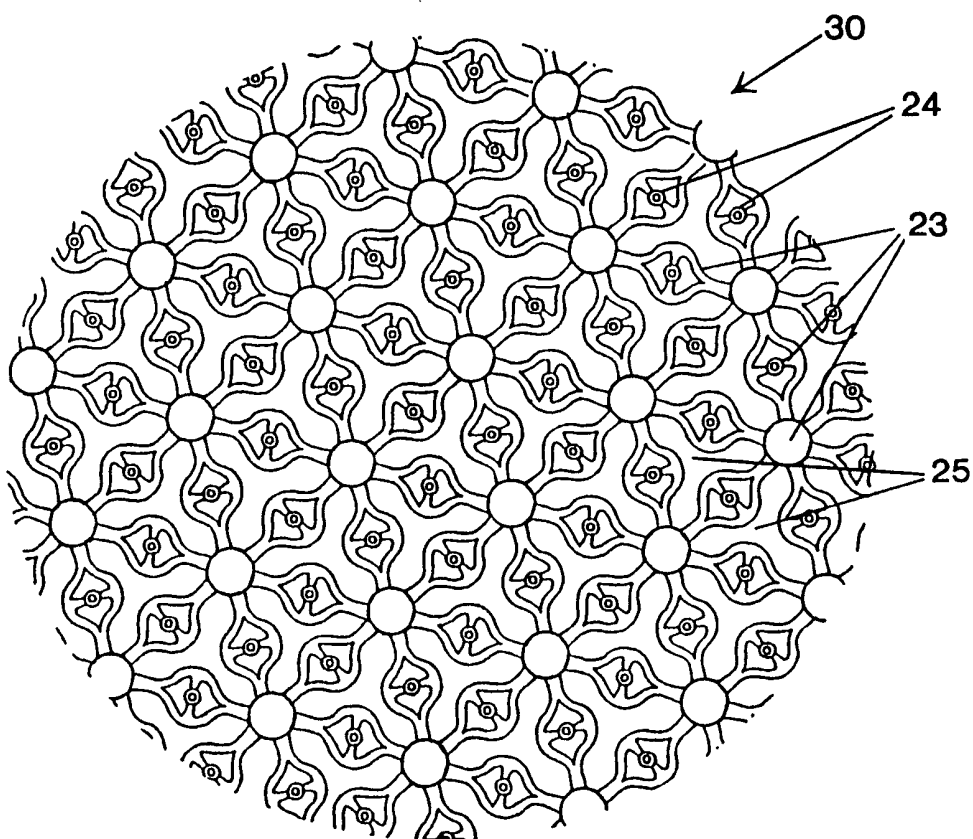


FIG. 3

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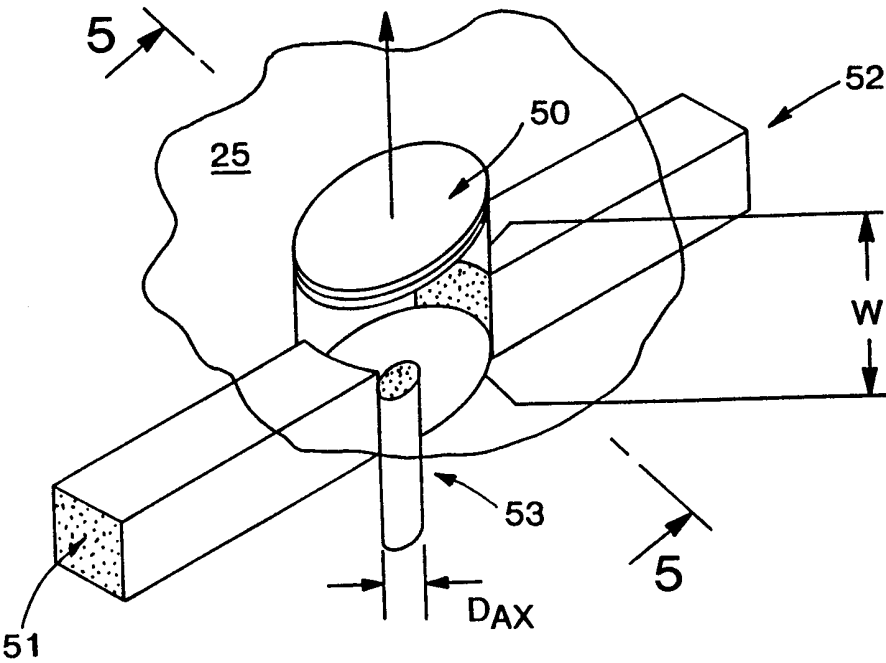


FIG. 4

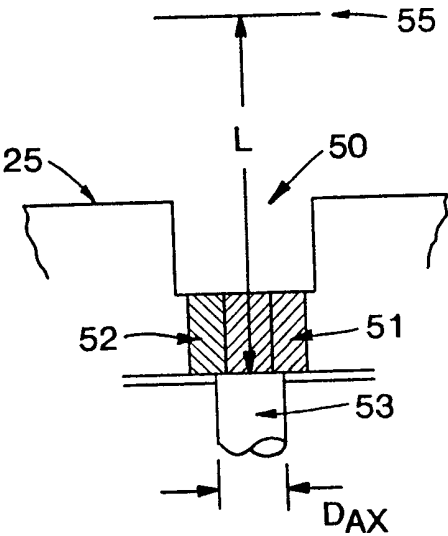


FIG. 5

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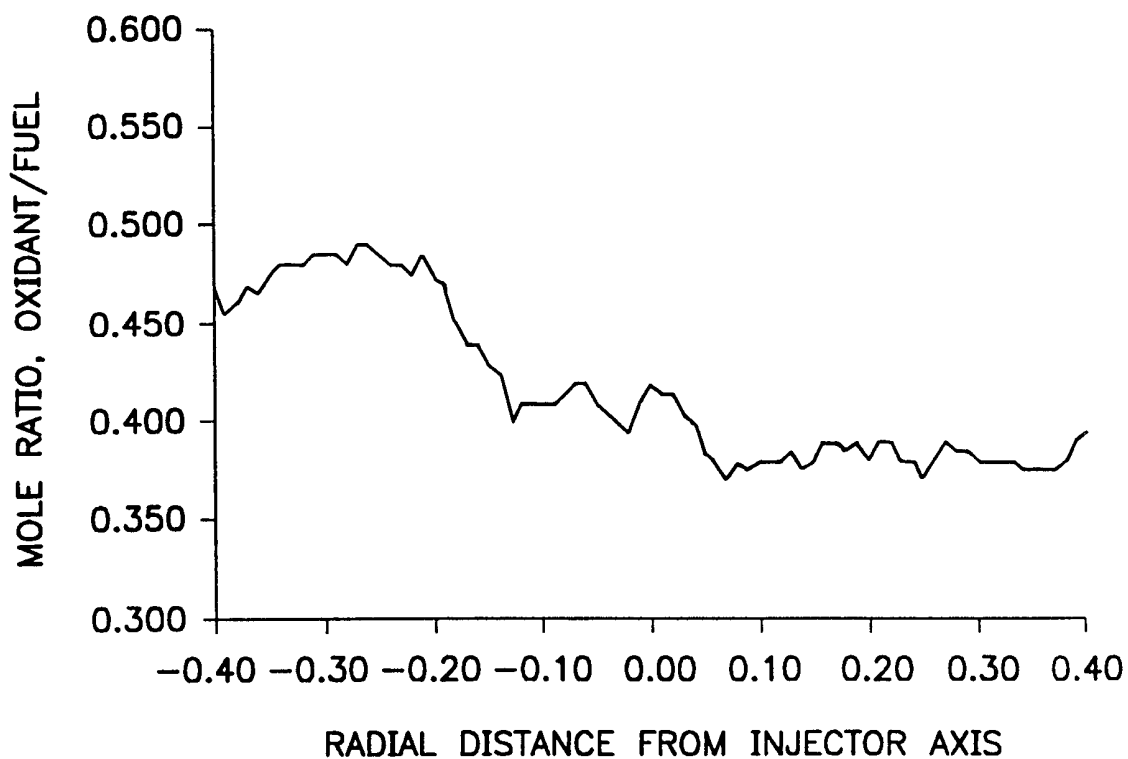


FIG. 6

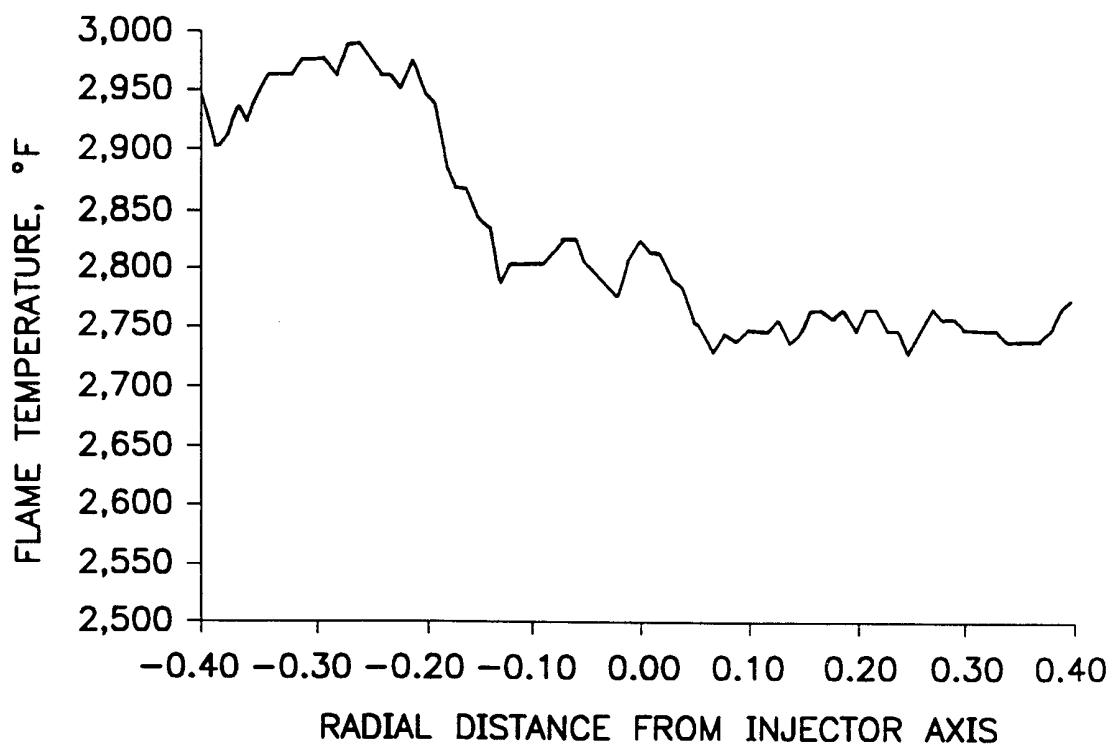


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/07941

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B3/38 B01J8/02 B01J4/00 C01B3/36 F23D14/22
B01F5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B B01J F23D B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 836 831 A (MARTENS FRANCISCUS J A) 6 June 1989 see the whole document ---	1-7, 10-12
X	US 5 492 649 A (CHRISTENSEN THOMAS S) 20 February 1996 cited in the application see the whole document ---	1-7, 9-12
A	US 4 722 181 A (YU TAI I) 2 February 1988 see column 1, line 46 - line 68 see column 2, line 34 - column 3, line 7 see figure ---	1, 2, 10, 13
A	EP 0 303 439 A (DAVY MCKEE CORP) 15 February 1989 see the whole document ---	1, 9, 10
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 July 1998

Date of mailing of the international search report

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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