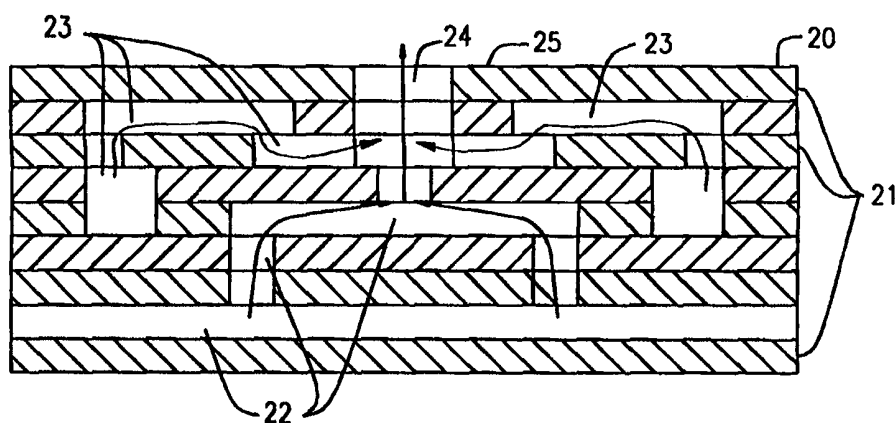




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<b>(21) International Application Number:</b> PCT/US98/08073 <b>(22) International Filing Date:</b> 20 April 1998 (20.04.98)  <b>(30) Priority Data:</b> 08/845,707                      25 April 1997 (25.04.97)                      US  <b>(71) Applicant:</b> EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US).  <b>(72) Inventors:</b> HERSHKOWITZ, Frank; 11 Lyons Road, Liberty Corner, NJ 07938 (US). DECKMAN, Harry, W.; 2 Woods Edge Court, Clinton, NJ 08809 (US). REYNOLDS, Robert, P.; 22 Goosetown Road, Clinton, NJ 08809 (US). GONATAS, Constantine; 3027 Carnegie, Houston, TX 77005 (US). FULTON, John, W.; 14 Powder Horn Terrace, Randolph, NJ 07869 (US). SHOENMAN, Leonard; 5600 Kingswood Drive, Citrus Heights, CA 95610 (US). ITO, Jackson; 2507 Occidental Drive, Sacramento, CA 95826 (US).  <b>(74) Agents:</b> SIMON, Jay et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).		<b>(81) Designated States:</b> AU, BR, CA, CN, JP, KR, MX, NO, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** DISTRIBUTED INJECTION PROCESS AND APPARATUS FOR PRODUCING SYNTHESIS GAS

**(57) Abstract**

A novel injector/reactor apparatus and an efficient process for the partial oxidation of light hydrocarbon gases, such as methane, to convert such gases to useful synthesis gas for recovery and/or subsequent hydrocarbon synthesis. Sources comprising a light hydrocarbon gas, such as methane (23), and oxygen or an oxygen-containing gas (22), preheated and pressurized, are injected through an injector means at high velocity into admixture with each other in the desired relative proportions, at a plurality of mixing nozzles which are open to the partial oxidation zone of a reactor and are uniformly-spaced over the face of the injector means, to form a reactant gaseous premix having a pressure at least 3% lower than the lowest upstream pressure of either of the streams of the individual gases. The gaseous premix is injected in a time period which is less than its autoignition time, preferably less than 9 milliseconds, at a velocity between about 25 to 1000 feet/second, into the partial oxidation zone of the reactor. The gas mixture reacts before or simultaneously with the autoignition time delay of the mixture, to reduce the amounts of CO<sub>2</sub>, H<sub>2</sub>O and heat produced by the partial oxidation reaction to form a useful syngas which is cooled and recovered.

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## DISTRIBUTED INJECTION PROCESS AND APPARATUS 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 ( $C_n H_{2n}$ ) alkynes ( $C_n H_{2n-2}$ ) such as acetylene, and unsaturated diene compounds, which compounds are useful, per se.

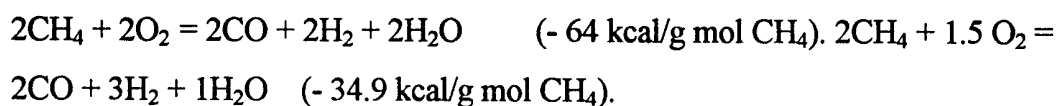
The combustion stoichiometry of methane gas at 1000°F is highly exothermic and produces  $CO_2$  and  $H_2O$  according to the following reaction:



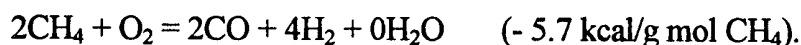
The formed gases are not useful for the production of valuable chemical compounds, and the high temperatures generated present problems with respect to reactors and catalysts which would be required to produce valuable products from the formed gases.

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It is known to produce useful gases, known as synthesis gases or syngases, by partial oxidation of methane and other light hydrocarbon gases, by steam or CO<sub>2</sub> reforming of methane and other light hydrocarbon gases, 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

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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, US Patent 3,542,894), Montecatini (UK 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. 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 in general and MCS mixtures in particular, may also contain inert components, e.g., nitrogen, carbon dioxide, functionally inert hydrocarbons such as alkanes and aromatic hydrocarbons, and water vapor. MCS mixtures may also contain trace amounts of sulfur and nitrogen containing species, for example HCN,  $NH_3$ ,  $H_2S$ , organic sulfides, and others. MCS

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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 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.

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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. Patents 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.

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, and therefore it is especially important to provide premixed feed, which is slower to begin gas phase chemistry. Also it is especially important to provide the premixed feed at high temperature and velocity to enable the catalytic reaction of the premixed gases at short contact times. However, it is dangerous to premix heated methane and oxygen and it is difficult to avoid gas phase reactions between these gases, which proceed at undesirable combustion stoichiometry to produce steam and carbon dioxide.

For catalytic partial oxidation (CPO), while certain metals can catalyze the desired oxidation chemistry at very short contact times, it is necessary to premix the methane and oxygen gases at high temperature, pressure and velocity to enable the catalytic reaction to proceed at short contact times in reduced scale reactors, and so that the chemistry occurs at the correct stoichiometry throughout the catalytic zone. The use of catalyst-impregnated monoliths can catalyze the desired chemistry with residence times below about 0.05 sec. When compared to conventional ATR reactors, FBSG reactors and GPOX reactors, this represents more than a one hundred fold decrease in residence time and, therefore, in residence volume. However, such a reactor is unworkable without a means to premix  $\text{CH}_4$  or other



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hydrocarbon and O<sub>2</sub> at high temperature, pressure, and velocity, safely and while avoiding gas phase reactions that are not within the desired partial oxidation zone and/or in contact with the catalyst. In other words, the catalytic partial oxidation process has the potential to provide extraordinary reactor productivity in view of the extremely high space velocities of the throughput if the aforementioned problems are avoided.

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 1:2, or 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.

It has been proposed to conduct a high efficiency catalytic partial oxidation (CPO) process using pre-formed mixtures of high temperature, high pressure methane and oxygen gases and steam at space velocities up to 500,000 hr<sup>-1</sup>, using a mixing and distributing means having a plurality of mixing tubes within which the gases are mixed prior to discharge through a multi-disc catalyst stack. Reference is made to EPO 303,438, assigned to Davy McKee Corp., which discloses a high temperature, high pressure partial oxidation process, and a mixing and distribution catalyst bed apparatus for producing a gaseous reaction product comprising methane,

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carbon oxides, hydrogen and steam in the absence of a reforming reaction. The preheated methane and oxygen gases are combined in the mixing tubes, through small orifices, and are discharged from the tubes at a distance downstream of the orifices sufficient to produce mixtures of the gases prior to discharge from diverging nozzles which reduce the velocity of the gas mixture at the inlet to the partial oxidation catalyst zone.

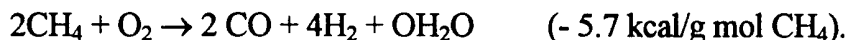
The mixing and distribution means of EPO 303,438 is ineffective in enabling the desired stoichiometry, i.e.,  $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2 + \text{OH}_2\text{O}$ , to produce the most useful syngas to the exclusion of other than very small amounts of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$ . This appears to be due to the fact that such mixing and distributing means is inadequate and allows the heated methane and oxygen to co-exist in the gaseous state, upstream of the partial oxidation catalyst zone, for too long a residence time, such as more than about 9 milliseconds, so that the methane and oxygen initiate non-catalytic reaction in the gaseous state to produce the wrong or undesirable stoichiometry, resulting in the production of steam and  $\text{CO}_2$ , reduced amounts of  $\text{H}_2$  and  $\text{CO}$  and high heat generation which can result in catalyst sintering or agglomeration and waste, and damage to the apparatus.

Furthermore, the control of pressure drop through the mixing and distributing means appears to be inadequate. Specifically, EPO 303,438 and the related WO 90-06282 disclose a fuel stream pressure drop of 0.0% of downstream pressure, while related WO 90-06281 discloses a fuel stream pressure drop of 2.2% of downstream pressure and related WO 90-06297 is silent regarding fuel pressures. Inadequate control of pressure drop through the mixing and distributing means results in reactor instability and in nozzle-to-nozzle variations in gas stoichiometry, which facilitates non-catalytic reaction in the gaseous state to produce the wrong or undesirable stoichiometry, facilitates hot spots and carbon deposition, and can result in catalyst agglomeration and waste, and damage to the apparatus.

### Summary of the Invention

The present invention relates to a novel compact apparatus and an efficient process for the partial oxidation of 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 pressurized and preheated sources of a light hydrocarbon gas containing one or more  $C_1$  to  $C_4$  alkanes, such as methane, and oxygen or an oxygen-containing gas, and injecting said individual gases at high velocity and comparable momentums through a plurality of isolated small passages of an injector manifold, and through individual gas orifices into a plurality of injection nozzles or cups or mixing zones which are open to the reaction zone and are spaced over the face of an injector of the type used in the rocket or aerospace industry, into admixture with each other to form a gaseous premix having a pressure at least 3% lower than the lowest upstream pressure of either of the streams of the individual gases and having the desired stoichiometric molar proportions, e.g., oxygen ( $O_2$ ) to carbon (C) molar ratio of from 0.3 up to 0.8 to 1 mole of (C), preferably 0.45 - 0.70 to 1.0. The formed gaseous premix is introduced to the reaction zone before an autoignition residence time after impingement at the mixing zones or within the injector nozzle cups, and any gap or catalyst-free zone or refractory heat shield, and preferably within less than 9 milliseconds, more preferably less than 2 milliseconds and most preferably less than 0.5 millisecond, at a velocity between about 25 and 1000 ft/sec, preferably 50 and 500 ft/sec, and most preferably between 50 and 300 ft/sec, into a reaction zone comprising a partial oxidation zone, a fluid bed catalyst or a catalyst retained in a fixed arrangement, such as into the catalytic passages of a parallel-pore ceramic or metallic monolith, or a ceramic or metallic foam monolith, or a fixed bed of particulate catalyst, so that the gaseous premix reacts within the reaction zone before or simultaneously with the autoignition time delay of the mixture, to reduce the amounts of  $CO_2$ ,  $H_2O$  and heat produced by the partial oxidation reaction to favor the desired stoichiometry, i.e.,

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The present process and apparatus represents an improved gas phase partial oxidation (GPOX) process, catalytic partial oxidation (CPO) process, autothermal reforming (ATR) process and fluid bed syngas generation (FBGS) process by premixing the light hydrocarbon fuel gas 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 reaction zone such as a flame (GPOX), a gas phase oxidation zone (ATR) or a catalytic zone (CPO 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), gas phase ignition and reaction in advance of the catalytic zone, which is detrimental to the CPO process, and the dangers normally presented by the explosive nature of a preheated mixture of oxygen and methane gas.

The present process and apparatus enables the partial oxidation reaction to be completed while the gaseous premix is in the gas phase POX zone and/or in contact with the catalyst as a homogeneous mixture, since uniform gaseous premixes are formed at and ejected from the plurality of mixing nozzles which are distributed over a wide diameter injector face, which greatly aids in the distribution of the reactants across the inlet of the reactor, thereby avoiding the introduction of oxygen-lean or oxygen-rich gas mixtures, which can interfere with the desired stoichiometric reaction and can result in hot spots which can burn or sinter the catalyst and/or destroy the solid monolith carrier.

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The hydrocarbon gas stream introduced to the mixer/injector may contain components other than methane and C<sub>2</sub>-C<sub>4</sub> hydrocarbons. Other components, for example H<sub>2</sub>O and CO<sub>2</sub>, may be present in the hydrocarbon gas in relatively large amounts, such as from about 0.0 to 1.0 mol of H<sub>2</sub>O or CO<sub>2</sub> per carbon atom of the light hydrocarbon gas. Other components, for example, H<sub>2</sub>, CO, Ar, N<sub>2</sub>, NH<sub>3</sub>, HCN, H<sub>2</sub>S, COS, CS<sub>2</sub>, organic sulfur-containing compounds, organic oxygenates, and C<sub>5</sub>+ 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<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and Ar. Some of these components, especially N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, may be present in major amounts, from 0.0 to 4.0 mol per mole of oxygen (O<sub>2</sub>). Other components are typically present in lesser amounts, normally less than 0.1 mol of component per mole O<sub>2</sub>.

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 chamber of the prior art is completely eliminated. The burner face, instead of being used just to 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 processes.

One embodiment of the present invention is particularly applicable to injection into a gas phase partial oxidation zone, such as for GPOX, ATR, and MCS-producing processes, in which the initial chemistry takes the form of a flame that is stabilized near the face of the injector. In this embodiment, different predetermined regions of the partial oxidation zone may be fed with different, homogenous feed mixtures to produce localized effects. Specifically, a minority of the feed injection nozzles, up to

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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 ( $O_2$ ) / carbon ratio in the range of 0.75 - 1.5 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.

It will be recognized by those skilled in the art, that the uniform gaseous premix that are formed when the hydrocarbon stream and the oxidant stream are ejected into the mixing area of nozzle 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 streams, such as hydrocarbon or oxygen containing gas, that are being fed to the mixing area or feed nozzle, 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

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amount of time, and most preferably 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 a stream of the 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 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 stream. 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, and most

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preferably before gas phase or catalytic reactions begin to occur at any substantial level. 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 of the injector in proportion to some critical nozzle dimension. In particular, we define  $L$  as the distance downstream from the point of initial contact between the gases, adjacent the floor 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  $L/D_{AX}$  equal to up to about 10, 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.

An important parameter defining the effectiveness of mixing is the "momentum ratio" of the stream 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 radially-or somewhat radially-injected 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



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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 recesses or cups at the injector surfaces, or at an angle of from 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 mixture into the reactor or combustion chamber at extremely high speeds. The dwell time of the gas mixture within or immediately above the injector surface prior to passage into the reaction zone is less than about 9 milliseconds, preferably less than about 2 milliseconds, and most preferably less than 0.5 millisecond, to substantially avoid undesirable gas phase reactions upstream of the combustion zone. 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 present high speed gas mixers/injectors is that they are designed to operate with a drop or reduction of the initial gas pressure into the mixer/injector which is more than 3%, preferably more than 5% and possibly more

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than about 10% lower than the lowest upstream pressure ( $P_u$ ) of either of the streams of the individual gases. The pressure at the inlet to the reactor pressure ( $P_c$ ) is normally between 10 and 100 atmospheres, preferably between about 20 and 50 atmospheres, so that the pressure reduction ( $P_u - P_c$ ), or  $\Delta P$ , divided by the reaction chamber inlet pressure, or  $P_c$ , is  $> 3\%$ , preferably  $> 5\%$  and possibly  $> 10\%$ . This pressure drop causes the oxidation gas and the hydrocarbon gas to be drawn into more intimate admixture immediately in advance of passage into the reaction chamber, to form the desired stoichiometric premix containing between 0.3 and 0.7 mols of oxygen ( $O_2$ ) per mol of methane, which has a single carbon atom, or per mole of (C) if the light hydrocarbon gas is one having more than one carbon atom. The pressure drop also improves the uniformity of flow of the gases through the mixer/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, particularly for FBSG, ATR and CPO processes which employ catalytic reactors, most particularly ceramic or metallic catalyst monoliths and ceramic or metallic foams which require the homogeneous or uniform supply of the reactant gas premix. The pressure drop as the gases pass through the injector results in a high gas mixing efficiency ( $E_m$ ) a short distance beyond 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 mixture 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 cups or wells recessed below the face surface of the injector, the point of 80% to 90%  $E_m$  occurs at a location (L) which depends upon the diameter (D) of the largest gas orifice to the cup or well, i.e.,  $E_m$  occurs at a  $L/D$  of 10 or less, preferably from about 1 to 6, such as 1 or 2. As mentioned, this mixing efficiency is enabled by the uniform pressure drop, or  $\Delta P$ , as the gases pass through the isolated small passages of the manifold of the injector means and through the nozzle orifices to impinge at each

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of the mixing zones, nozzles 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 injector means are assembled side by side and fed through from common gas conduits to feed very large diameter reactors.

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 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 critical 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 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 critical feature of this invention is the use of elevated pressure drop or  $\Delta P/P_c$  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 according to one embodiment of the present invention;

Fig. 2 is a cross-sectional side view of a single nozzle section of a multi-jet face-mix injector useful in association with a syngas reactor according to the present invention;

Fig. 3 is a plan view of the face and certain channels beneath the face surface of a multi nozzle injector as illustrated in Fig. 1;

Fig. 4 is a perspective view of an individual injector mixing nozzle as present in the multi-nozzle injector of Fig. 2, according to one embodiment of the present invention; and

Fig. 5 is a cross-sectional view taken along the line 5-5 of Fig. 4.

### Detailed Description of the Drawings

Referring to Fig. 1, the gas injector/syngas-reactor apparatus 10 thereof comprises an assembly of an upper multi-jet, face-mix gas injector means 11, a lower reactor comprising a partial oxidation reaction zone 12 in closely-spaced alignment with the face surface 13 of the injector means, and a downstream syngas recovery and/or processing unit 15. The plurality of jet nozzles or cups 14 at the face surface 13 of the injector means 11 discharge directly into the partial oxidation zone 12 to assure the uniform injection of homogeneous mixtures of a hydrocarbon gas, such as methane, and oxygen, in the desired predetermined oxygen ( $O_2$ )/carbon ( $C_1$ ) mole

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ratio of from about 0.3 - 0.8, preferably 0.45 - 0.7, into the partial oxidation reaction zone 12. Separate methane supply conduits 17 and oxygen supply conduits 18 feed continuous streams of preheated, pressurized methane and oxygen into and through the methane passages 23 and the oxygen passages 22 and out of exit orifices for intermixing within the plurality of jet nozzles or cups 14. The exit orifices of the methane passages 23 and of the oxygen passages 22 are sized so that the pressure drop of the gas as it passes through these passages is maintained at a value that is more than 3% lower, preferably more than 5% lower, and possibly more than 10% lower than the lowest upstream pressure of either of said gases relative to the reactor pressure. This ensures even distribution of methane and oxygen 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.

The gas injector means 11 of Fig. 1 illustrates a separate methane ( $\text{CH}_4$ ) supply conduit 17 and oxygen ( $\text{O}_2$ ) supply conduit 18 which feed continuous streams of preheated, pressurized methane and oxygen gases through the injector means 11 for intermixing within the plurality of nozzle jet openings or cups 14 at the face surface 13 of the injector means 11 or for angular impingement downstream of the face surface 13 of the injector means 11. 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 specifically less than 9 milliseconds, preferably less than 2 milliseconds, and most preferably less than about 0.5 milliseconds. This prevents reaction of the gas mixture in the gas phase within the injector means, out of the reaction zone and/or out of contact with the catalyst, which reaction can proceed with excessive heat generation that is damaging to the syngas apparatus.

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It is an essential feature of the present invention to maintain the gas pressure drop ( $\Delta P$ ) through the injector at a value which is more than 3% less, preferably more than about 5% less, and possibly more than 10% less than the lowest upstream pressure ( $P_u$ ) of either of the gases, relative to the pressure at the inlet of the reactor ( $P_c$ ), i.e.,  $\Delta P/P_c = (P_u - P_c)/P_c$ , is greater than 3%, preferably greater than about 5%, possibly greater than 10%, where  $P_u$  is the lowest upstream pressure of either gas,  $\Delta P$  is the pressure drop through the injector and  $P_c$  is the reaction chamber inlet pressure. The upper limit of this value can become impractically high as the flow velocity through the injector approaches sonic. Generally the flow velocity is maintained within practical limits for economic reasons and to avoid or reduce particle attrition in fluidized catalyst beds, and erosion.

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The injection of the present pre-heated and pressurized light hydrocarbon and oxygen gases into admixture in the desired proportions to form a premix having the aforementioned pressure drop, and then into the reaction zone preferably within a time period of less than 9 or 2 or 0.5 milliseconds is an important feature of the present syngas-forming process, whether the process is an autothermal reforming (ATR) process, a fluid bed syngas generation (FBSG) process or a partial oxidation (GPOX) process, or a (CPO) process. In the CPO process there may be a narrow non-reaction gap or a gas permeable refractory heat-shield monolith between the injector surface and the catalytic reaction zone, so that the dwell time of the mixture may be at or near the high end of the aforementioned time periods but will still be less than the autoignition delay time of the mixture. In all of these processes, it is highly advantageous for safety and efficiency reasons, and to reduce the overall length of the apparatus, to form the premix of the pressure-reduced stoichiometric mixture of the pre-heated pressurized gases, using a wide diameter multi nozzle injector, and to inject or blow the homogeneous mixture immediately into a wide diameter reaction zone, i.e., partial oxidation zone, fluidized catalyst bed or fixed catalyst bed, for immediate reaction since the mixture is pre-heated, pressurized, homogeneous and has the desired stoichiometry for the most desirable syngas formation.

Suitable feed injectors that meet these criteria have been developed for use in the aerospace industry. One such device is called a microinjector (or platelet) burner face. 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 microjets, but some are more amendable to fabrication and to rapid mixing. A preferred approach is the use of mixers or nozzles called "triplets", in which there is a central flow of one reactant, such as oxygen, through the oxygen passages of a manifold, and the second reactant, such as methane is introduced in at least two opposed or intersecting jets up to about 1 inch below the burner face through

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somewhat radial offset 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  $\text{CH}_4/\text{O}_2$  mixing. Figures 2 and 3 illustrate such an injector, manifold, isolated gas passages, injector face, and suitable triplet mixing nozzles or cups.

Injector faces 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". Thus, to achieve homogenous reaction mixtures, mixing lengths and residence times are kept very low. A preferred embodiment for CPO employing a ceramic or metallic honeycomb monolith is a design in which the injector face has a one-to-one correspondence and alignment between the microjet cups 14 or 24 and the channels of the monolith. In this special case, no radial mixing width or gap is required outside the monolith itself, and all monolith channels are assured of receiving homogeneous reactant mixtures. Moreover, as discussed hereinbefore, the relative gas stoichiometry may be varied over the face of the injector, by varying the relative sizes of the oxygen and methane orifices of certain predetermined nozzles, in order to produce hotter oxygen-rich flames and/or cooler methane-rich flames where desired.



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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. Suitable means to initiate reaction in a catalyst-containing partial oxidation zone may include the above methods, but will more preferably be accomplished by preheating the catalyst to at least the low end of the catalytic partial oxidation temperature range, which temperature range begins at about 700°C. Such preheating can be accomplished, for example, by directing a flow of hot combustion gases through the catalyst, as is known in the art.

A preferred high velocity interior-mixing injector means 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 U.S. Patent 3,881,701 are also suitable for use according to the present invention, whereby the reactant gases impinge and mix immediately above 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 plates together to form injectors comprising manifolds containing fine isolated gas passages 22 for oxygen and 23 for methane, which passages communicate at a plurality of microjet nozzles or cups 24 at a face surface 25 of the injector, or impinge immediately above the injector surface, to mix the gases and eject the gaseous premix at high velocity. The present injectors are gas delivery manifolds which are engineered to provide equal specified flow to all nozzles or cups 24.

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Referring to Figs. 1 and 2, of the drawings, the injector means 20 of Fig. 2 thereof comprises a plurality of thin metal plates 21 which are diffusion bonded to each other after being provided in predetermined areas thereof with segregated oxygen passages 22 and methane passages 23, respectively, which communicate through supply conduits 18 and 17, respectively, with sources of oxygen and methane, under high temperatures and pressures. 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 14 or 24 which are open to the surface 13 or 25 of the injector 11 or 20.

The injector 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., with a pressure drop from the lowest upstream pressure ( $P_u$ ) of either of the gases, which is greater than 3%, preferably greater than 5%, and most preferably greater than 10% of the pressure within the reaction zone ( $P_c$ ). The premix is injected directly into the reactor 12 containing a gas phase partial oxidation zone, or for reaction in the presence of a catalyst.

A further advantage of the gas mixer/injector means 20 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 prevent heat damage thereto due to the proximity to the reaction zone which has a temperature between about 700°-1900°C, preferably between about 870°-1650°C. This cooling is accomplished by the circulation of the gas or gases preheated to feed temperatures of 100°-700°C, preferably between 300° and 600°C, through circulation passages, such as 23, immediately below and parallel

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to the uppermost plate 21 forming the surface 25 of the injector 20 to cool the face surface 25 well below the reaction temperature, such as 1000°C, within the reaction zone of the reactor, as the gas or gases pass through the injector manifold to the mixing cups 24.

It is preferred for use with a fluidized bed reactor that the depth of the cup 24 of Fig. 2 be increased in order to deter entry of loose or fluidized catalyst particles into the cup 24 and stop erosion of the cup by such particles. 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 having an exit orifice diameter of about 0.05", for example, to form the homogeneous reactant gaseous premix which is ejected from the cup 24 in less than 9 milliseconds, preferably less than 2.0 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. The essential difference between the triplets of Figs. 4 and 5 resides in the horizontal methane supply conduits 51 and 52, each having a width  $W$  of about 0.30", which 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 having 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 gas mixture ejected from the mixing cup 50 can be characterized for mixedness  $E_m$  in a plane 55 located a distance  $L$  downstream of the injector means,

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shown in Fig. 5. Preferred injectors achieve  $E_m > 75\%$ , more preferably  $> 80\%$  at downstream distances  $L < 6 D_{AX}$ .

The mixing cups 50 of Figs. 4 and 5 have a design preferred for use in gas phase partial oxidation zones (GPOX or ATR) since the cup depth is only about 0.5 inch for a cup diameter of about .5 inch. Extending (e.g. doubling) the cup depth results in a more preferred injector design for FBSG application, but extended cup depths are not required for use with fixed catalyst bed or gas phase partial oxidation zones. The larger injector of Figs. 4 and 5 is more resistant to fouling, and thus is preferred to the extent that residence time limits within the injector are not exceeded. Injectors dimensioned as discussed for Figure 2 represent preferred designs for a catalytic partial oxidation (CPO) process, particularly for CPO reactors that include a gas distribution gap and/or refractory heat-shield between the face surface 25 of the injector means 11 and the inlet to the reaction zone 12 of the reactor, because their smaller size results in a shorter residence time within the injector means 11 and closer injector spacing which reduces gap dimension, all of which facilitates the distribution of the gaseous premix to the fixed catalyst inlets in a minimum of residence time, e.g., less than about 9 milliseconds.

It will be apparent to those skilled in the art that the specific dimensions of the mixing nozzles of Figs. 1 to 5 can be varied depending upon the particular syngas-producing process being conducted and the dimensions of the reactor being used in association with the injector, and the size of the latter. For example the cup 50, preferably cylindrical, can have a diameter up to about one inch, preferably up to about one-half inch, and a depth, down to the methane inlets, which is up to about two inches. At these maximum dimensions, the diameter or width of the exit orifice of each oxygen inlet conduit 53 and of the exit orifices of the methane inlet conduits 51

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and 52 of Figs. 4 and 5 will have dimensions larger than those discussed, in order to provide sufficient gas volumes and pressures to maintain a methane-to-oxygen ratio which is greater than 1, to avoid over oxidation, especially CO<sub>2</sub> formation, in all areas of the reactor before combustion begins.

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 steps 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 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 and reduction gas used for the production of sponge iron, etc.

In a conventional HCS process, liquid and gaseous hydrocarbon products are formed by contacting the present syngas comprising a mixture of H<sub>2</sub> 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

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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., C<sub>10+</sub> 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), a lubricating, industrial or mechanical 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, hydrosomerization (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 (where virtually all, e.g., less than 10 wt.% and preferable less than 5 wt. % of the feed remains uncovered) 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.

## CLAIMS:

1. A process for the partial oxidation of hydrocarbons to useful synthesis gas containing hydrogen and carbon monoxide, comprising providing individual streams of desired proportions of a hydrocarbon gas and oxygen or an oxygen-containing gas, each stream being at independent elevated pressure and temperature, injecting said individual streams into admixture with each other through an injector means having a plurality of mixing nozzles to form a gaseous premix having a pressure at least 3% lower than the lowest upstream pressure of either of the streams of the individual gases, passing said gaseous premix from the plurality of mixing nozzles into a partial oxidation reaction zone to form a said useful synthesis gas, and recovering said synthesis gas.

2. The process of claim 1 in which the gaseous premix has a pressure at least 5% lower than the lowest upstream pressure of either of the streams of the individual gases.

3. The process of claim 1 wherein the mixing nozzles are mixing cups recessed below the face surface of the injector means, into which cups the gas streams are separately introduced through individual gas orifices and impinged to form the gaseous premix.

4. The process of claim 3 in which one of the gases is injected from at least one axial gas orifice having a diameter ( $D_{AX}$ ) as at least one axial stream having a momentum and the other gas is injected from one or more radial gas orifices as at least one radial stream having a momentum, which impinges upon the axial stream to form the gaseous premix.

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5. The process of claim 4 wherein the ratio of the momentum of the radially injected stream(s) to the momentum of the axial stream(s) is within the range of 0.5 - 4.0 to 1.0.

6. The process of claim 4 wherein the oxygen or oxygen containing gas is injected as a single axial stream and the hydrocarbon containing gas is injected as two opposed somewhat radial streams.

7. The process of claim 4 wherein the efficiency of the mixing ( $E_m$ ) of the individual gases is at least 75% when the gaseous premix is at a distance (L) which is up to ten times the diameter ( $D_{AX}$ ) of the gas orifice of the axial stream.

8. The process of claim 1 wherein each of the mixing nozzles comprises a tubular cup recessed in the face surface of the injector means, injecting one of the gases into the cup as an axial stream through an axial orifice having a diameter ( $D_{AX}$ ) in the bottom of the cup, and injecting the other gas into the cup as at least two opposed somewhat radial streams through opposed 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 up to about one to six times the diameter ( $D_{AX}$ ) of the axial gas orifice.

9. The process according to claim 8 which comprises introducing said somewhat radial gas streams as opposed but offset streams which impinge the axial stream tangentially to produce a swirling gas mixture within the mixing cups.

10. The process of claim 1 which comprises passing the formed gaseous premix into the reaction zone at a velocity between about 25 and 1000 feet/sec.



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11. The process according to claim 1 in which said stoichiometric molar proportions of oxygen ( $O_2$ ) per number of carbon atoms in the hydrocarbon gas are between 0.3 and 0.8 to 1.

12. The process according to claim 11 wherein up to about 25% of predetermined mixing nozzles inject a gaseous premix having stoichiometric molar proportions of oxygen per carbon atom lower than 0.3 to 1 and/or higher than 0.8 to 1 to provide a minority of nozzles in predetermined areas of the injector which burn at temperatures cooler and/or hotter, respectively, than the majority of the mixing nozzles.

13. The process according to claim 1 which comprises passing the gaseous premix in less than 2 milliseconds after the mixture is formed.

14. The process according to claim 1 which comprises the step of rapidly cooling the gas after a short residence time in the partial oxidation zone, to produce a multicomponent syngas.

15. The process according to claim 1 which comprises the step of injecting the individual streams through an injector means having a gas manifold assembled from a plurality of thin metal plates forming therebetween or therein and/or therethrough a plurality of segregated gas passages for supplying said individual streams through orifices into said mixing nozzles which are recessed cup areas at the face surface of the injector means.

16. The process according to claim 15 which comprises providing a plurality of said gas passages beneath and parallel to the plate forming the face surface of the injector means, and circulating at least one of the gases through said gas passages to cool the face surface of the injector means by heat exchange.

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17. The process according to claim 1 which comprises the step of further processing the recovered syngas via the Fischer-Tropsch reaction to produce liquid hydrocarbons.

18. The process according to claim 17 which comprises the further step of reacting said liquid hydrocarbons by hydroconversion to produce useful products.

19. An apparatus for the partial oxidation of hydrocarbon gas to convert such gas to useful synthesis gas containing hydrogen and carbon monoxide, comprising an injector means, a reactor having a partial oxidation reaction zone, and a syngas recovery means, said injector means having a manifold containing a plurality of segregated passages for injecting heated and pressurized individual streams of the hydrocarbon gas and oxygen or an oxygen-containing gas into admixture with each other in the desired molar proportions through exit orifices opening said passages into a plurality of mixing nozzles which are spaced over the face of the injector means while producing a drop in the pressure of said gases, through said injector means, to a pressure at least 3% lower than the lowest upstream pressure of either of the individual gas streams, and for passing the formed gaseous premix into said partial oxidation reaction zone, for reacting the gaseous premix to produce said useful syngas, and means for recovering said syngas.

20. An apparatus according to claim 19 in which said injector means is adapted to produce a gaseous premix having a pressure drop of at least 5% relative to the lowest upstream pressure of either of the gases.

21. An apparatus according to claim 19 comprising means for injecting the gaseous premix into the partial oxidation reaction zone within about 9 milliseconds after the mixture is formed.

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22. An apparatus according to claim 21 comprising means for injecting the gaseous premix into the partial oxidation reaction zone within about 2 milliseconds after the mixture is formed.

23. An apparatus according to claim 19 in which said partial oxidation zone comprises means for rapidly cooling the gas after a short residence time therein to produce a multicomponent syngas.

24. An apparatus according to claim 19 in which said partial oxidation zone opens into a steam reforming zone comprising catalyst retained in fixed arrangement.

25. An apparatus according to claim 19 in which each of said mixing nozzles comprises a cylindrical mixing cup having a bottom orifice having a diameter ( $D_{AX}$ ) for admitting an axial flow of oxygen or an oxygen-containing gas having a momentum and having opposed side orifices for admitting somewhat radial flows of the hydrocarbon gas having a summed momenta to form the gaseous premix.

26. The apparatus according to claim 25 in which said opposed side orifices are radially-offset relative to each other so that the somewhat radial flows of the hydrocarbon gas impinge the axial flow tangentially to cause the formed gas mixture to swirl within each cup.

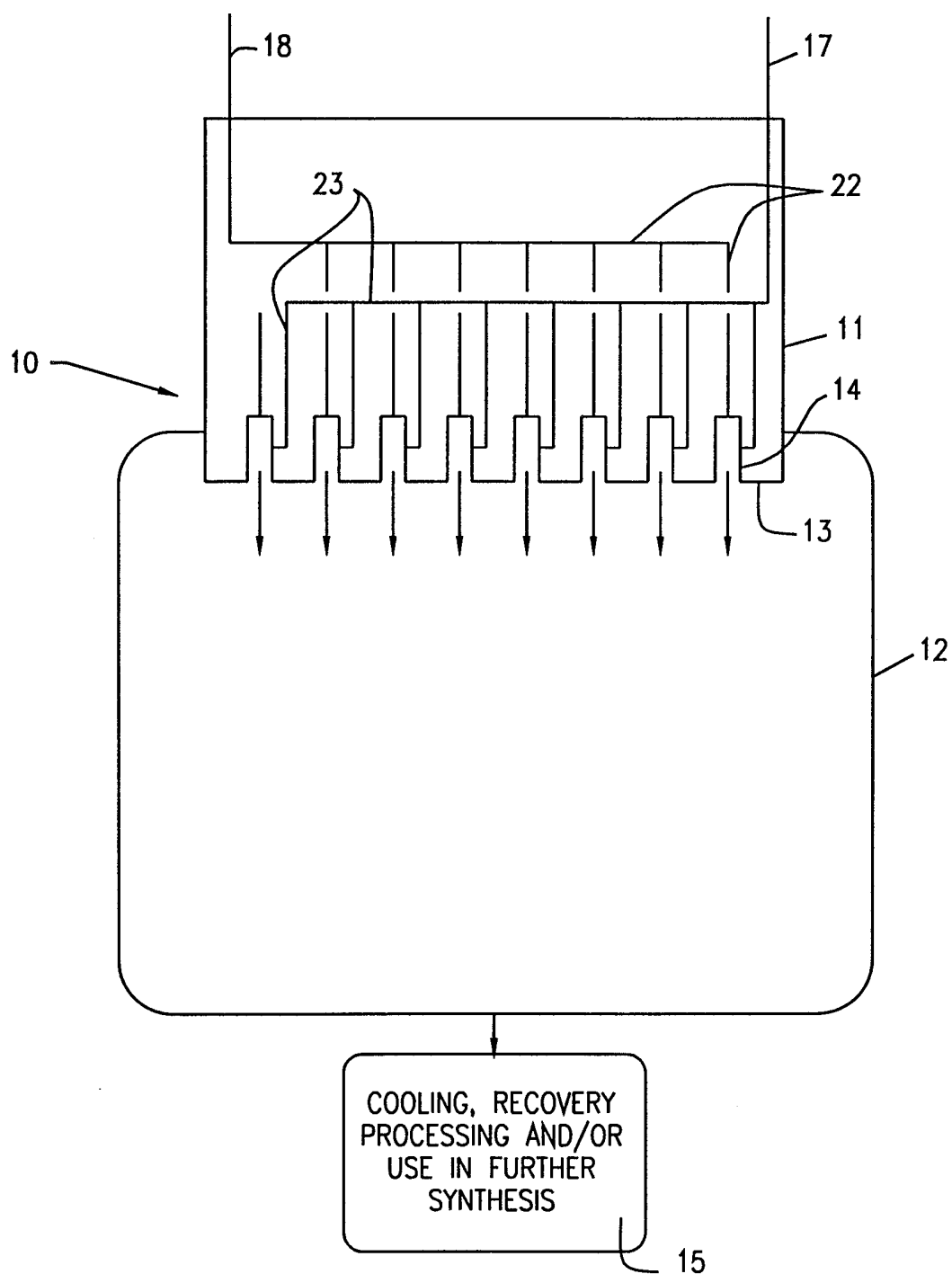
27. An apparatus according to claim 19 in which the said injector means comprises a manifold assembled from a plurality of thin metal plates forming therebetween or therein and/or therethrough a plurality of segregated passages for supplying the individual gases through gas orifices into the mixing nozzles present at the face surface of the injector means.

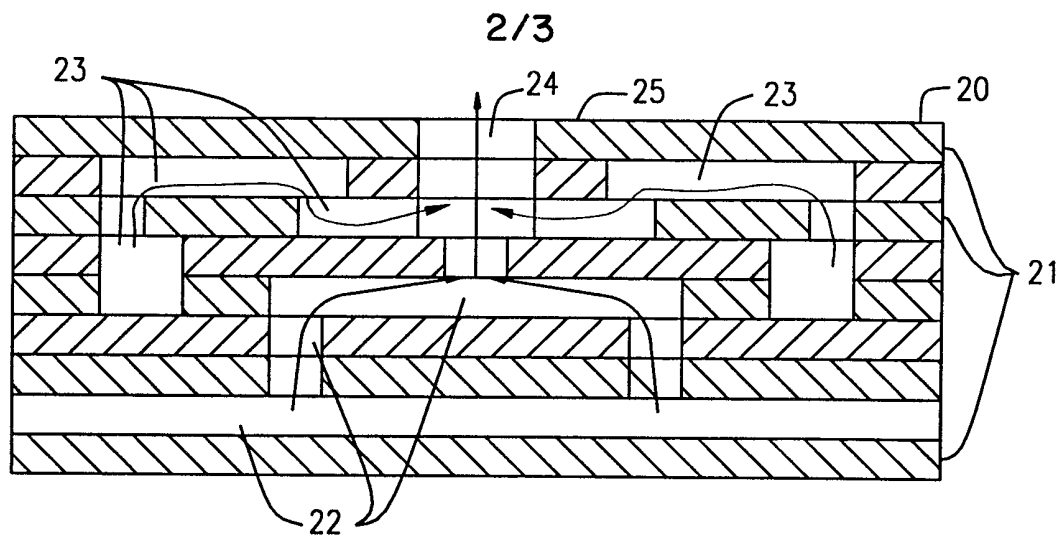
- 34 -

28. An apparatus according to claim 27 in which said manifold comprises a plurality of gas passages beneath and parallel to the plate forming the face surface thereof to cool said face surface by heat-exchange.

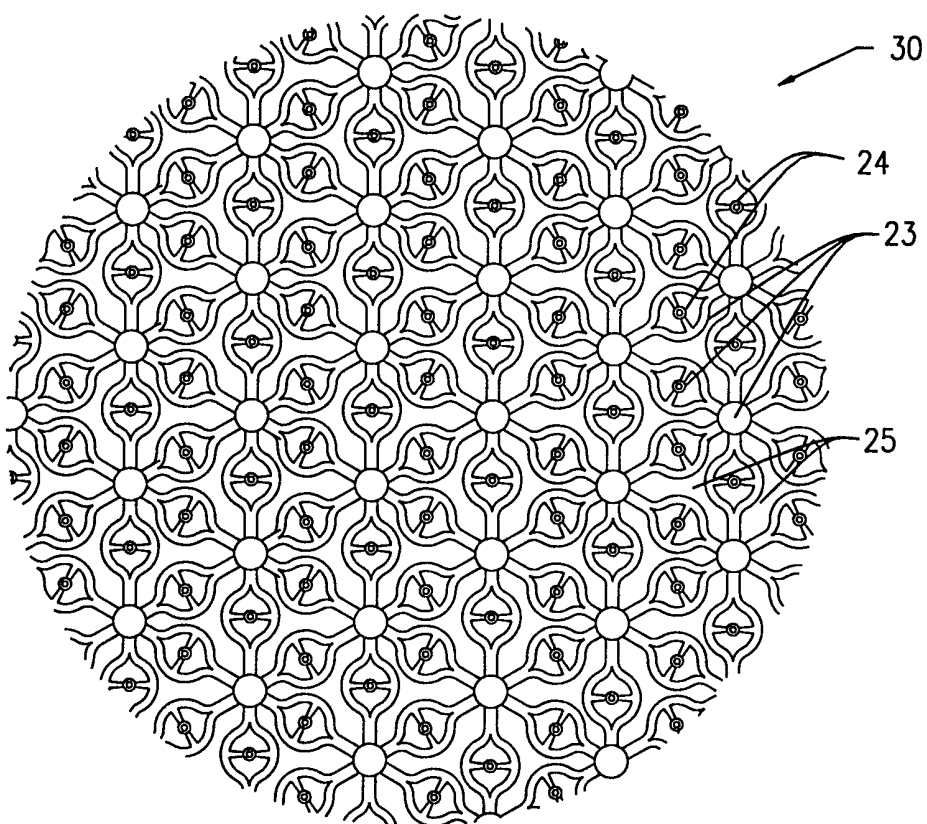
29. An apparatus according to claim 25 wherein the injector means provides an efficiency of mixing ( $E_m$ ) of the individual gases of at least 75% complete when the gaseous premix is at a distance downstream ( $L$ ) which is up to ten times the diameter ( $D_{AX}$ ) of the gas orifice of the axial stream.

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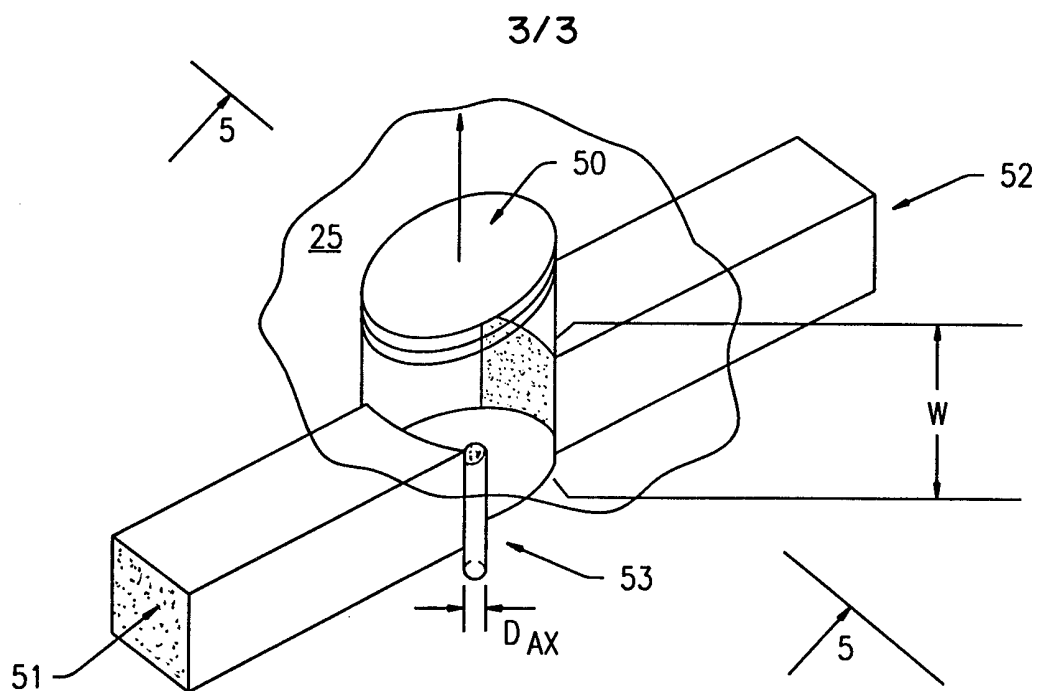
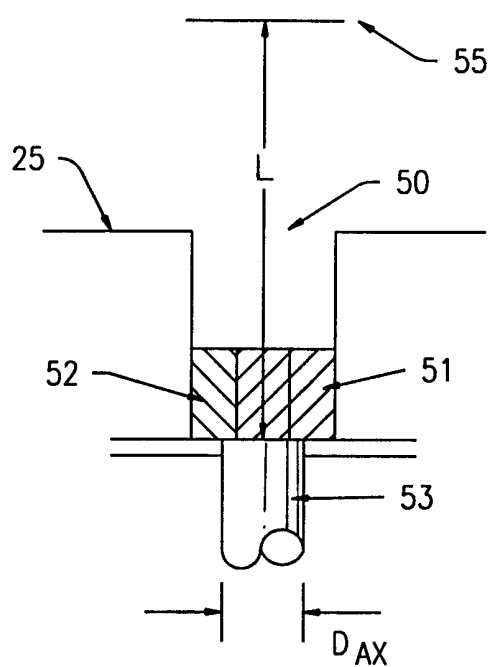
*FIG. 1*



*FIG. 2*



*FIG. 3*

*FIG. 4**FIG. 5*

# INTERNATIONAL SEARCH REPORT

Inventor's Application No

PCT/US 98/08073

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B3/36 B01J8/02 B01J4/00 F23D14/22 C01B3/38  
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 5 292 246 A (GATEAU PAUL ET AL) 8 March 1994 cited in the application see the whole document ---	1,2,10, 11,13, 19-22,24
X	EP 0 303 439 A (DAVY MCKEE CORP) 15 February 1989  see the whole document ---	1,2,10, 11,13, 19-22,24
X	US 5 492 649 A (CHRISTENSEN THOMAS S) 20 February 1996 cited in the application see the whole document ---	1,2,10, 11,13, 19-22,24
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

13 July 1998

Date of mailing of the international search report

24/07/1998

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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.
A	<p>US 4 722 181 A (YU TAI I) 2 February 1988</p> <p>see column 1, line 46 - line 68  see column 2, line 34 - column 3, line 7  see figure</p> <p>---</p>	<p>1,3,4,  8-10,19,  25</p>
A	<p>US 3 881 701 A (SCHOENMAN LEONARD ET AL) 6  May 1975  cited in the application  see the whole document</p> <p>-----</p>	<p>1,19</p>

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Information on patent family members

In. tional Application No

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