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(54) MULTISTAGE PROCESS FOR COMBUSTING FUEL MIXTURES

MEHRSTUFENVERFAHREN FÜR DIE VERBRENNUNG VON BRENNSTOFFMISCHUNGEN

PROCEDE MULTI-ETAGE POUR LA COMBUSTION DES MELANGES COMBUSTIBLES

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Description

This invention is a combustion process having a series of stages in which a fuel/oxygen-gas-containing mixture is combusted stepwise using a series of specific catalysts and catalytic structures and, optionally, a final homogeneous combustion zone to produce a combusted gas at a selected temperature preferably between 1050° and 1700°C. Depending upon the pressure of operation, there may be two or three discrete catalytic stages. The choice of catalysts and the use of specific structures, including those employing integral heat exchange, results in a catalyst and its support which are stable due to their comparatively low temperature, do not deteriorate, and yet the product combustion gas is at a temperature suitable for use in a gas turbine, furnace, boiler, or the like, but has low NO_x content. Neither fuel nor air is added to the combustion process except in the initial stage.

With the advent of modern antipollution laws in the United States and around the world, significant and new methods of minimizing various pollutants are being investigated. The burning of fuel, be the fuel wood, coal, oils, or natural gas, likely causes a majority of the pollution problems in existence today. Certain pollutants such as SO_2, which are created as the result of the presence of a contaminant in the fuel source, may be removed either by treating the fuel to remove the contaminant or by treating the exhaust gas eventually produced to remove the resulting pollutant. Pollutants such as carbon monoxide, which are created as the result of incomplete combustion, may be removed by post-combustion oxidation or by improving the combustion process. The other principal pollutant, NO_x (an equilibrium mixture mostly of NO, but also containing very minor amounts of NO_2), may be dealt with either by controlling the combustion process to minimize its production or by later removal. Removal of NO_x once produced once it is a difficult task because of its relative stability and its low concentration in most exhaust gases. One solution used in automobiles is the use of carbon monoxide chemically to reduce NO_x to nitrogen while oxidizing the carbon monoxide to carbon dioxide. However, the need to react two pollutants also speaks to a conclusion that the initial combustion reaction was inefficient.

It must be observed that unlike the situation with sulfur pollutants where the sulfur contaminant may be removed from the fuel, removal of nitrogen from the air fed to the combustion process is clearly an impractical solution. Unlike the situation with carbon monoxide, improvement of the combustion reaction would likely increase the level of NO_x produced due to the higher temperatures then involved.

Nevertheless, the challenge to reduce combustion NO_x remains and several different methods have been suggested. The process chosen must not substantially conflict with the goal for which the combustion gas was created, i. e., the recovery of its heat value in a turbine, boiler, or furnace.

Many recognize that a fruitful way of controlling NO_x production is to limit the localized and bulk temperatures in the combustion zone to something less than 1800°C. See, for instance, U.S. Patent No. 4,731,989 to Furuya et al. at column 1, lines 52-59 and U.S. Patent No. 4,088,135 to Hindin et al. at column 12.

There are a number of ways to control the temperature, such as by dilution with excess air, controlled combustion using one or more catalysts, or staged combustion using variously lean or rich fuel mixtures. Combinations of these methods are also known.

One widely attempted method is the use of multistage catalytic combustors. Most of these processes utilize multisection catalysts with metal oxide or ceramic catalyst carriers. Typical of such disclosures are:

Country	Document	1st Stage	2nd Stage	3rd Stage
Japan	Kokai 60-205129	Pt-group/Al_2O_3&SiO_2	La/SiO_2·Al_2O_3	
Japan	Kokai 60-147243	La&Pd&Pt/Al_2O_3	ferrite/Al_2O_3	
Japan	Kokai 60-66022	Pd&Pt/ZrO_2	Ni/ZrO_2	
Japan	Kokai 60-60424	Pd/-	CaO&Al_2O_3&NiO&w/noble metal	
Japan	Kokai 60-51545	Pd/*	Pt/*	$LaCoO_3$/*
Japan	Kokai 60-51543	Pd/*	Pt/*	
Japan	Kokai 60-51544	Pd/*	Pt/*	base metal oxide/*
Japan	Kokai 60-54736	Pd/*	Pt or Pt-Rh or Ni base metal oxide or $LaCO_3$/*	
Japan	Kokai 60-202235	MoO_4/-	CoO_3&ZrO_2&noble metal	
Japan	Kokai 60-200021	Pd&Al_2O_3/+*	Pd&Al_2O_3/**	Pt/**
Japan	Kokai 60-147243	noble metal/heat resistant carrier	ferrite/heat resistant carrier	
Japan	Kokai 60-60424	La or Nd/Al_2O_3 0.5%SiO_2	Pd or Pt/NiO&Al_2O_3& CaO 0.5%SiO	
Japan	Kokai 60-14938	Pd/?	Pt/?	
Japan	Kokai 60-14939	Pd&Pt/refractory	?	?
Japan	Kokai 61-252409	Pd&Pt/***	Pd&Ni/***	Pd&Pt/***
Japan	Kokai 62-080419	Pd&Pt	Pd,Pt&NiO	Pt or Pt&Pd
Japan	Kokai 62-080420	Pd&Pt&NiO	Pt	Pt&Pd
Japan	Kokai 63-080848	Pt&Pd	Pd&Pt&NiO	Pt or Pt&Pd
Japan	Kokai 63-080849	Pd,Pt,NiO/?	Pd&Pt(orNiO)/?	Pt or Pd&Pt/?

*alumina or zirconia on mullite or cordierite

**Ce in first layer; one or more of Zr, Sr, Ba in second layer; at least one of La and Nd in third layer.

***monolithic support stabilized with lanthanide or alkaline earth metal oxide

Note: the catalysts in this Table are characterized as "a"/"b" where "a" is the active metal and "b" is the carrier

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The use of such ceramic or metal oxide supports is clearly well-known. The structures formed do not readily melt or oxidize as would a metallic support. A ceramic support carefully designed for use in a particular temperature range can provide adequate service in that temperature range. Nevertheless, many such materials can undergo phase changes or react with other components of the catalyst system at temperatures above 1100°C, e.g., the gamma alumina phase changes to the alpha alumina form in that region. In addition, such ceramic substrates are olefin fragile, subject to cracking and failure as a result of vibration, mechanical shock, or thermal shock. Thermal shock is a particular problem in catalytic combustors used in gas turbines. During startup and shutdown, large temperature gradients can develop in the catalyst leading to high mechanical stresses that result in cracking and fracture.

Typical of the efforts to improve the high temperature stability of the metal oxide or ceramic catalyst supports are the inclusion of an alkaline earth metal or lanthanide or additional metals into the support, often in combination with other physical treatment steps:

Country	Document	Assignee or Inventor
Japan	Kokai 61-209044	(Babcock-Hitachi KK)
Japan	Kokai 61-216734	(Babcock-Hitachi KK)
Japan	Kokai 62-071535	(Babcock-Hitachi KK)
Japan	Kokai 62-001454	(Babcock-Hitachi KK)
Japan	Kokai 62-045343	(Babcock-Hitachi KK)
Japan	Kokai 62-289237	(Babcock-Hitachi KK)
Japan	Kokai 62-221445	(Babcock-Hitachi KK)
U.S.	Pat. No. 4,793,797	(Kato et al.)
U.S.	Pat. No. 4,220,559	(Pliknki et al.)
U.S.	Pat. No. 3,870,455	(Hindin et al.)
U.S.	Pat. No. 4,711,872	(Kato et al.)
Great Britain	1,528,455	Cairns et al.

However, even with the inclusion of such high temperature stability improvements, ceramics are fragile materials. Japanese Kokai 60-053724 teaches the use of a ceramic columnar catalyst with holes in the column walls to promote equal distribution of fuel gas and temperature amongst the columns lest cracks appear.

High temperatures (above 1100°C) are also detrimental to the catalytic layer resulting in surface area loss, vaporization of metal catalysts, and reaction of catalytic components with the ceramic catalyst components to form less active or inactive substances.

Of the numerous catalysts disclosed in the combustion literature may be found the platinum group metals: platinum, palladium, ruthenium, iridium, and rhodium; sometimes alone, sometimes in mixtures with other members of the group, sometimes with non-platinum group promoters or co-catalysts.

Other combustion catalysts include metallic oxides, particularly Group VIII and Group I metal oxides. For instance, in an article by Kaiji et al, COMPLETE OXIDATION OF METHANE OVER PEROVSKITE OXIDES, Catalysis Letters I (1988) 299-306, J.G. Baltzer A.G. Scientific Publishing Co., the authors describe a set of perovskite oxide catalysts suitable for the oxidation of methane which are generically described as ABO_3, particularly oxides formulated as $La_{1-x}Me_xMnO_3$, where Me denotes Ca, Sr, or Ba.

Similarly, a number of articles by a group associated with Kyushu University describe combustion catalysts based on $BaO{\cdot}6Al_2O_3$:

1. PREPARATION AND CHARACTERIZATION OF LARGE SURFACE AREA $BaO{\cdot}6Al_2O_3$, Machida et al, Bull. Chem. Soc. Jpn., 61, 3659-3665 (1988),

2. HIGH TEMPERATURE CATALYTIC COMBUSTION OVER CATION-SUBSTITUTED BARIUM HEXAALUMINATES, Machida et al, Chemistry Letters, 767-770, 1987,

3. ANALYTICAL ELECTRON MICROSCOPE ANALYSIS OF THE FORMATION OF $BaO{\cdot}6Al_2O_3$, Machida et al, J. Am. Ceram. Soc., 71 (12) 1142-47 (1988),

4. EFFECT OF ADDITIVES ON THE SURFACE AREA OF OXIDE SUPPORTS FOR CATALYTIC COMBUSTION, J. Cat. 103, 385-393 (1987), and

5. SURFACE AREAS AND CATALYTIC ACTIVITIES OF Mn-SUBSTITUTED HEXAALUMINATES WITH VARIOUS

CATION COMPOSITIONS IN THE MIRROR PLANE, Chem. Lett., 1461-1464, 1988.

Similarly, U.S. Patent No. 4,788,174, to Arai, suggests a heat resistant catalyst suitable for catalytic combustion having the formula $A_{1-x}C_xB_xAl_{12-y}O_{19-a}$, where A is at least one element selected from Ca, Ba, and Sr; C is K and/or Rb; B is at least one from Mn, Co, Fe, Ni, Cu, and Cr; z is a value in the range from zero to about 0.4; x is a value in the range of 0.1-4, y is a value in the range of about x-2x; a is a value determined by the valence X, Y, and Z of the respective element A, C, and B and the value of x, y, and z and it is expressed as $a=1.5\{X-z(X-Y)+xZ-3y\}$.

In addition to the strictly catalytic combustion processes, certain processes use a final step in which any remaining combustibles are homogeneously oxidized prior to recovering the heat from the gas.

A number of the three stage catalyst combination systems discussed above also have post-combustion steps. For instance, a series of Japanese Kokai assigned to Nippon Shokubai Kagaku ("NSK") (62-080419, 62-080420, 63-080847, 63-080848, and 63-080549) disclose three stages of catalytic combustion followed by a secondary combustion step. As was noted above, the catalysts used in these processes are quite different from the catalysts used in the inventive process. Additionally, these Kokai suggest that in the use of a post-combustion step, the resulting gas temperature is said to reach only "750°C to 1100°C". In clear contrast, the inventive process when using the post catalyst homogeneous combustion step may be seen to reach substantially higher adiabatic combustion temperatures.

Other combustion catalyst/post-catalyst homogeneous combustion processes are known. European Patent Application 0,198,948 (also issued to NSK) shows a two or three stage catalytic process followed by a post-combustion step. The catalyst used in the first stage must be palladium and platinum or palladium, platinum and a nickel oxide. The temperature of the post-combusted gas was said to reach 1300°C with an outlet temperature from the catalyst (approximately the bulk gas phase temperature) of 900°C. The catalyst structures disclosed in the NSK Kokai are not, however, protected from the deleterious effects of the combustion taking place within the catalytic zones and consequently the supports will deteriorate.

The patent to Furuya et al. (U.S. Patent No. 4,731,989) discloses a single stage catalyst with injection of additional fuel followed by post-catalyst combustion. In this case, the low fuel/air ratio mixture feed to the catalyst limits the catalyst substrate temperature to 900°C or 1000°C. To obtain higher gas temperatures required for certain processes such as gas turbines, additional fuel is injected after the catalyst and this fuel is burned homogeneously in the post catalyst region. This process is complicated and requires additional fuel injection devices in the hot gas stream exiting the catalyst. The inventive device described in our invention does not require fuel injection after the catalyst; all of the fuel is added at the catalyst inlet.

An important aspect in the practice of our inventive process is the use of integral heat exchange structures -- preferably metal and in at least in the latter catalytic stage or stages of combustion. Generically, the concept is to position a catalyst layer on one surface of a wall in the catalytic structure which is opposite a surface having no catalyst. Both sides are in contact with the flowing fuel-gas mixture. On one side reactive heat is produced; on the other side that reactive heat is transferred to the flowing gas.

Structures having an integral heat exchange feature are shown in Japanese Kokai 59-136,140 and 61-259,013. Similarly, U.S. Patent No. 4,870,824 to Young et al. shows a single stage catalytic combustor unit using a monolithic catalyst with catalysts on selected passage walls. In addition to a number of other differences, the structures are disclosed to be used in isolation and not in conjunction with other catalyst stages. Additionally, the staged use of the structure with different catalytic metals is not shown in the publications.

None of the processes shown in this discussion show a combination catalyst system in which the catalyst supports are metallic, in which the catalysts are specifically varied to utilize their particular benefits, in which integral heat exchange is selectively applied to control catalyst substrate temperature, and particularly, in which high gas temperatures are achieved while maintaining low NO_x production and low catalyst (and support) temperatures.

The process of the invention is a combustion process in which the fuel is premixed at a specific fuel/air ratio to produce a combustible mixture having a desired adiabatic combustion temperature. The combustible mixture is then reacted in a series of catalyst structures and in a homogeneous combustion zone. The combustion is staged so that catalyst and bulk gas temperatures are controlled at a relatively low value by catalyst choice and structure.

We have found that as the pressure of operation increases, the temperature at which the palladium catalyst "self-limits" rises and the temperature at which the fuel mixture undergoes homogeneous combustion decreases. At above about ten atmospheres, for most practical fuel/air ratios, the palladium catalyst self-limiting temperature and the homogeneous combustion initiation temperature are equal or are sufficiently compatible that a "hot end" combustion catalyst stage may be eliminated.

The process produces an exhaust gas of a very low NO_x concentration but at a temperature suitable for use in a gas turbine, boiler, or furnace.

Figure 1 is a graph showing the relationship of pressure to homogeneous combustion temperature and palladium temperatures.

Figures 2A and 2B show close-up, cutaway views of a catalyst structure wall having catalyst only on one side.

Figures 3A, 3B, 3C, 4A, 4B, 5, 6A, and 6B all show variations of the integral heat exchange catalyst structure which may be used in the catalytic stages of the inventive process.

Figure 7 is a schematic representation of the three stage catalyst test reactor used in the examples.

Figures 8 and 9 are graphs of various operating temperatures as a function of preheat temperature.

Figure 10 is a graph of various operating temperatures during a long term steady state operation test.

Figure 11 is a graph of various operating temperatures during a typical start up procedure.

The process of the invention is a combustion process in which the fuel is premixed at a specific fuel/air ratio to produce a combustible mixture having a desired adiabatic combustion temperature. The combustible mixture is then reacted in two or more discrete catalyst structures and in a homogeneous combustion zone. The combustion is staged so that catalyst and bulk gas temperatures are controlled at a relatively low value through catalyst choice and structure. More particularly, the present invention provides a process comprising:

(a) contacting a combustible mixture comprising fuel and an oxygen-containing gas, necessary to reach a desired temperature upon combustion, with a catalytic structure in which catalyst is arranged in two or more catalytic stages, wherein the catalytic structure comprises a catalyst support having multiple longitudinal passageways for the passage of the combustible mixture and in which only a portion of the passageways have catalyst situated therein so that a portion of the combustible mixture is inhibited in its contact with the catalyst so that only a portion of the fuel is combusted within the catalytic structure and the temperature of partially combusted combustible mixture leaving the catalytic structure is below the desired temperature and wherein palladium is the only catalyst present in the first stage of the catalytic structure; and

(b) combusting the remainder of the fuel left in the combustible mixture outside of the catalytic structure to raise its temperature to the desired temperature.

The desired temperature after combustion is between 1050°C and 1700°C. In one embodiment of the invention the catalytic structure comprises a catalyst support, preferably a corrugated metal structure, having catalyst with a diffusion barrier situated thereon so that a portion of the combustible mixture is inhibited in its contact with catalyst.

As the pressure of operation increases, the temperature at which the palladium catalyst "self-limits" rises and the temperature at which the fuel mixture undergoes homogeneous combustion decreases. As is shown in Figure 1, the partial pressure of O_2 rises (be it through an increase in overall pressure or increase in O_2 concentration), the theoretical pressure needed to complete homogeneous combustion (to a level of carbon monoxide less than about 10 ppm) declines to a level where the palladium catalyst will initiate that combustion. The two lines meet between four and five atmospheres. When air is compressed to a level above about four to five atmospheres, the homogeneous combustion reaction will completely combust in about eleven microseconds. At above four to five atmospheres, for most practical fuel to air ratios, the palladium limiting temperature and the homogeneous combustion temperature area equal or sufficiently compatible that a third stage "hot end" combustion catalyst may, if so desired, be eliminated.

The process produces an exhaust gas of a very low NO_x concentration but at a temperature suitable for use in a gas turbine, boiler, or furnace.

This process may be used with a variety of fuels and at a broad range of process conditions.

Although normally gaseous hydrocarbons, e.g., methane, ethane, and propane, are highly desirable as a source of fuel for the process, most fuels capable of being vaporized at the process temperatures discussed below are suitable. For instance, the fuels may be liquid or gaseous at room temperature and pressure. Examples include the low molecular weight hydrocarbons mentioned above as well as butane, pentane, hexane, heptane, octane, gasoline, aromatic hydrocarbons such as benzene, toluene, ethylbenzene; and xylene; naphthas; diesel fuel, kerosene; jet fuels; other middle distillates; heavy distillate fuels (preferably hydrotreated to remove nitrogenous and sulfurous compounds); oxygen-containing fuels such as alcohols including methanol, ethanol, isopropanol, butanol, or the like; ethers such as diethylether, ethyl phenyl ether, MTBE, etc. Low-BTU gases such as town gas or syngas may also be used as fuels.

The fuel is typically mixed into the combustion air in an amount to produce a mixture having a theoretical adiabatic combustion temperature greater than the catalyst or gas phase temperatures actually occurring in the catalysts employed in this inventive process. Preferably the adiabatic combustion temperature is above 900°C, and most preferably above 1000°C. Non-gaseous fuels should be vaporized prior to their contacting the initial catalyst zone. The combustion air may be at atmospheric pressure or lower (-0.25 atm of air) or may be compressed to a pressure of 35 atm or more of air. Stationary gas turbines (which ultimately could use the gas produced by this process) often operate at gauge pressures in the range of eight atm of air to 35 atm of air. Consequently, this process may operate at a pressure between -0.25 atm of air and 35 atm of air, preferably between zero atm of air and 17 atm of air. In a preferred embodiment, the oxygen-containing gas is air and is compressed to a pressure of at least 4 atmospheres (gauge). In an alternative embodiment, the pressure is zero to 35 atm. (gauge) of air.

First Catalytic Zone

The fuel/air mixture supplied to the first zone should be well mixed and heated to a temperature high enough to initiate reaction on the first zone catalyst; for a methane fuel on a typical palladium catalyst a temperature of at least about 325°C is usually adequate. This preheating may be achieved by partial combustion, use of a pilot burner by heat exchange, or by compression.

The first zone in the process contains a catalytic amount of palladium on a monolithic catalyst support offering low resistance to gas flow. The support is preferably metallic. Palladium is very active at 325°C and lower for methane oxidation and can "light-off" or ignite fuels at low temperatures. It has also been observed that in certain instances, after palladium initiates the combustion reaction, the catalyst rises rapidly to temperatures of 750°C to 800°C at one atm of air or about 940°C at ten atm total pressure of air. These temperatures are the respective temperatures of the transition points in the thermogravimetric analysis (TGA) of the palladium/palladium oxide reaction shown below at the various noted pressures. At that point the catalytic reaction slows substantially and the catalyst temperature moderates at 750°C to 800°C or 940°C, depending on pressure. This phenomenon is observed even when the fuel/air ratio could produce theoretical adiabatic combustion temperatures above 900°C or as high as 1700°C.

One explanation for this temperature limiting phenomenon is the conversion of palladium oxide to palladium metal at the TGA transition point discussed above. At temperatures below 750°C at one atm of air, palladium is present mainly as palladium oxide. Palladium oxide appears to be the active catalyst for oxidation of fuels. Above 750°C, palladium oxide converts to palladium metal according to this equilibrium:

$$PdO \rightarrow Pd + \tfrac{1}{2} O_2$$

Palladium metal appears to be substantially less active for hydrocarbon combustion so that at temperatures above 750°C to 800°C the catalytic activity decreases appreciably. This transition causes the reaction to be self-limiting: the combustion process rapidly raises the catalyst temperature to 750°C to 800°C where temperature self-regulation begins. This limiting temperature is dependent on O_2 pressure and will increase as the O_2 partial pressure increases.

Some care is necessary, however. The high activity of palladium can lead to "runaway" combustion where even the low activity of the palladium metal above 750°C can be sufficient to cause the catalyst temperature to rise above 800°C and even to reach the adiabatic combustion temperature of the fuel/air mixture as noted above; temperatures above 1100°C can lead to severe deterioration of the catalyst. We have found that runaway combustion can be controlled by adding a diffusion barrier layer on top of the catalyst layer to limit the supply of fuel and/or oxidant to the catalyst. The diffusion barrier layer greatly extends the operating range of the first stage catalyst to higher preheat temperatures, lower linear gas velocities, higher fuel/air ratio ranges, and higher outlet gas temperatures. We have also found that limiting the concentration of the palladium metal on the substrate will prevent "runaway" but at the cost of relatively shorter catalyst life.

This self-limiting phenomenon maintains the catalyst substrate temperature substantially below the adiabatic combustion temperature. This prevents or substantially decreases catalyst degradation due to high temperature operation.

The palladium metal is added in an amount sufficient to provide significant activity. The specific amount added depends on a number of requirements., e.g., economics, activity, life, contaminant presence, etc. The theoretical maximum amount is likely enough to cover the maximum amount of support without causing undue metal crystallite growth and concomitant loss of activity. These clearly are competing factors: maximum catalytic activity requires higher surface coverage, but higher surface coverage can promote growth between adjacent crystallites. Furthermore, the form of the catalyst support must be considered. If the support is used in a high space velocity environment, the catalyst loadings likely should be high to maintain sufficient conversion even though the residence time is low. Economics has as its general goal the use of the smallest amount of catalytic metal which will do the required task. Finally, the presence of contaminants in the fuel would mandate the use of higher catalyst loadings to offset the deterioration of the catalyst by deactivation.

The palladium metal content of this catalyst composite is typically quite small, e.g., from 0.1% to about 25% by weight, and preferably from 0.01% to about 20% by weight.

The palladium may be incorporated onto the support in a variety of different methods using palladium complexes, compounds, or dispersions of the metal. The compounds or complexes may be water or hydrocarbon soluble. They may be precipitated from solution. The liquid carrier generally needs only to be removable from the catalyst carrier by volatilization or decomposition while leaving the palladium in a dispersed form on the support. Examples of the palladium complexes and compounds suitable in producing the catalysts used in this invention are palladium chloride, palladium diammine dinitrite, palladium tetrammine chloride, palladium 2-ethylhexanoic acid, sodium palladium chloride, and other palladium salts or complexes.

The preferred supports for this catalytic zone are metallic. Although other support materials such as ceramics and

the various inorganic oxides typically used as supports: silica, alumina, silica-alumina, titania, zirconia, etc., and may be used with or without additions such as barium, cerium, lanthanum, or chromium added for stability. Metallic supports in the form of honeycombs, spiral rolls of corrugated sheet (which may be interspersed with flat separator sheets), columnar (or "handful of straws"), or other configurations having longitudinal channels or passageways permitting high space velocities with a minimal pressure drop are desirable in this service. They are malleable, can be mounted and attached to surrounding structures more readily, and offer lower flow resistance due to the thinner walls that can be readily manufactured in ceramic supports. Another practical benefit attributable to metallic supports is the ability to survive thermal shock. Such thermal shocks occur in gas turbine operations when the turbine is started and stopped and, in particular, when the turbine must be rapidly shut down. In this latter case, the fuel is cut off or the turbine is "tripped" because the physical load on the turbine--e.g, a generator set--has been removed. Fuel to the turbine is immediately cut off to prevent overspeeding. The temperature in the combustion chambers, where the inventive process takes place, quickly drops from the temperature of combustion to the temperature of the compressed air. This drop could span more than 1000°C in less than one second. In any event, the catalyst is deposited, or otherwise placed, on the walls within the channels or passageways of the metal support in the amounts specified above. The catalyst may be introduced onto the support in a variety of formats: the complete support may be covered, the downstream portion of the support may be covered, or one side of the support's wall may be covered to create an integral heat exchange relationship such as that discussed with regard to the later stages below. The preferred configuration is complete coverage because of the desire for high overall activity at low temperatures but each of the others may be of special use under specific circumstances. Several types of support materials are satisfactory in this service: aluminum, aluminum containing or aluminum-treated steels, and certain stainless steels or any high temperature metal alloy, including nickel alloys where a catalyst layer can be deposited on the metal surface. The preferred materials are aluminum-containing steels such as those found in U.S. Patent Nos. 4,414,023 to Aggen et al., 4,331,631 to Chapman et al., and 3,969,082 to Cairns, et al. These steels, as well as others sold by Kawasaki Steel Corporation (River Lite 20-5 SR), Vereinigte Deutchse Metallwerke AG (Alumchrom I RE), and Allegheny Ludlum Steel (Alfa-IV) contain sufficient dissolved aluminum so that, when oxidized, the aluminum forms alumina whiskers or crystals on the steel's surface to provide a rough and chemically reactive surface for better adherence of the washcoat.

The washcoat may be applied using an approach such as is described in the art, e.g., the application of gamma-alumina sols or sols of mixed oxides containing aluminum, silicon, titanium, zirconium, and additives such as barium, cerium, lanthanum, chromium, or a variety of other components. For better adhesion of the washcoat, a primer layer may be applied containing hydrous oxides such as a dilute suspension of pseudo-boehmite alumina as described in U.S. Patent 4,729,782 to Chapman et al. Desirably, however, the primed surface is then coated with a zirconia suspension, dried, and calcined to form a high surface area adherent oxide layer on the metal surface.

The washcoat may be applied in the same fashion one would apply paint to a surface, e.g., by spraying, direct application, dipping the support into the washcoat material, etc.

Aluminum structures are also suitable for use in this invention and may be treated or coated in essentially the same manner. Aluminum alloys are somewhat more ductile and likely to deform or even to melt in the temperature operating envelope of the process. Consequently, they are less desirable supports but may be used if the temperature criteria can be met.

Once the washcoat and palladium have been applied to the support and calcined, one or more coatings of a low or non-catalytic oxide may then be applied as a diffusion barrier to prevent the temperature "runaway" discussed above. This barrier layer can be alumina, silica, zirconia, titania, or a variety of other oxides with a low catalytic activity for combustion of the fuel or mixed oxides or oxides plus additives similar to those described for the washcoat layer. Alumina is the least desirable of the noted materials. The barrier layer can range in thickness from 1% of the washcoat layer thickness to a thickness substantially thicker than the washcoat layer, but preferably from 10% to 100% of the washcoat layer thickness. The preferred thickness will depend on the operating conditions of the catalyst, including the fuel type, the gas flow velocity, the preheat temperature, and the catalytic activity of the washcoat layer. It has also been found that the application of the diffusion barrier coating only to a downstream portion of the catalyst structure, e.g., 30% to 70% of the length, can provide sufficient protection for the catalyst under certain conditions. Preferably, the first stage combustion catalyst comprises palladium on a metallic support and additionally a barrier layer covering at least a portion of the palladium. In this embodiment the barrier layer is preferably zirconia.

As with the washcoat, the barrier layer or layers may be applied using the same application techniques one would use in the application of paint.

This catalyst structure should be made in such a size and configuration that the average linear velocity through the channels in the catalyst structure is greater than about 0.2 m/second and no more than about 40 m/second throughout the first catalytic zone structure. This lower limit is an amount larger than the flame front speed for methane and the upper limit is a practical one for the type of supports currently commercially available. These average velocities may be somewhat different for fuels other than methane.

The first catalytic zone is sized so that the bulk outlet temperature of the gas from that zone is no more than about

800°C, preferably in the range of 450°C to 700°C and, most preferably, 500°C to 650°C.

Second Catalytic Zone

The second zone in the process takes partially combusted gas from the first zone and causes further controlled combustion to take place in the presence of a catalyst structure having heat exchange capabilities. The catalyst may comprise materials selected from Mendelev Groups IB, VI, VIII noble metals. Desirably, the second stage catalyst comprises palladium, particularly if the pressure of the process is higher than about four atmospheres. Whatever the pressure, the catalyst comprises a Group VIII noble metal such as platinum or palladium. If the catalyst contains palladium it may optionally contain up to an equivalent amount of one or more catalyst adjuncts selected from Group IB or Group VIII noble metals. The preferred adjunct catalysts are silver, gold, ruthenium, rhodium, platinum, iridium, or osmium. Most preferred are silver and platinum. This zone may operate adiabatically with the heat generated in the partial combustion of the fuel resulting in a rise in the gas temperature. Neither air nor fuel is added between the first and second catalytic zone.

The catalyst structure in this zone is similar to that used in the first catalytic zone except that the catalyst preferably is applied to at least a portion of only one side of the surface forming the walls of the monolithic catalyst support structure. Figure 2A shows a cutaway of a the high surface area metal oxide washcoat (10), and active metal catalyst (12) applied to one side of the metal substrate (14). This structure readily conducts the reaction heat generated at the catalyst through interface between the washcoat layer (10) and gas flow (16) in Figure 2B. Due to the relatively high thermal conductivity of the washcoat (10) and metal (14), the heat is conducted equally along pathway (A) as well as (B), dissipating the reaction heat equally into flowing gas streams (16) and (18). This integral heat exchange structure will have a substrate or wall temperature given by equation (1):

$$T_{wall} = \frac{T_{gas\ inlet} + T_{adiabatic}}{2} \quad (1)$$

The wall temperature rise will be equal to about half the difference between the inlet temperature and the theoretical adiabatic combustion temperature.

Metal sheets coated on one side with catalyst, and the other surface being non-catalytic, can be formed into rolled or layered structures combining corrugated (20) and flat sheets (22) as shown in Figures 3A through 3C to form long open channel structures offering low resistance to gas flow. A corrugated metal strip (30) coated on one side with catalyst (32) can be combined with a separator strip (34) not having a catalytic coating to form the structure shown in Figure 4A.

Alternatively, corrugated (36) and flat strips (38) both coated with catalyst on one side prior to assembly into a catalyst structure can be combined as shown in Figure 4B. The structures form channels with catalytic walls (40 in Figure 4A and 42 in Figure 4B) and channels with non-catalytic walls (44 in Figure 4A and 46 in Figure 4B). Catalytic structures arranged in this manner with catalytic channels and separate non-catalytic channels are termed limited-integral-heat-exchange structures ("L-IHE"). These structure have the unique ability to limit the catalyst substrate temperature and outlet gas temperature.

The corrugated (42) and flat sheets (44) coated on one side with catalyst can be arranged according to Figure 5 where the catalytic surface of each sheet faces a different channel so that all channels have a portion of their walls' catalyst coated and all walls have one surface coated with catalyst and the opposite surface non-catalytic. The Figure 5 structure will behave differently from the Figure 4A and Figure 4B structures. The walls of the Figure 5 structure form an integral heat exchange but, since all channels contain catalyst, there is then a potential for all the fuel to be catalytically combusted. As combustion occurs at the catalyst surface, the temperature of the catalyst and support will rise and the heat will be conducted and dissipated in the gas flow on both the catalytic side and the non-catalytic side. This will help to limit the temperature of the catalyst substrate and will aid the palladium temperature limiting to maintain the wall temperature at 750°C to 800°C at one atm of air or about 930°C at ten atm of air. For sufficiently long catalysts or low gas velocities, a constant outlet gas temperature of 750°C to 800°C would be obtained for any fuel/air ratio with an adiabatic combustion temperature above approximately 800°C at one atm of air or about 930°C at ten atm of air.

The structures shown in Figures 4A and 4B have equal gas flow through each of the catalytic channels and non-catalytic channels. The maximum gas temperature rise with these structures will be that produced by 50% combustion of the inlet fuel.

The structures shown in Figures 4A and 4B may be modified to control the fraction of fuel and oxygen reacted by varying the fraction of the fuel and oxygen mixture that passes through catalytic and non-catalytic channels. Figure 6A shows a structure where the corrugated foil has a structure with alternating narrow (50) and broad (52) corrugations. Coating this corrugated foil on one side results in a large catalytic channel (54) and a small non-catalytic channel (56).

In this structure approximately 80% of the gas flow would pass through catalytic channels and 20% through the non-catalytic channels. The maximum outlet gas temperature would be about 80% of the temperature rise expected if the gas went to its adiabatic combustion temperature. Conversely, coating the other side of the foil only (Figure 6B) results in a structure with only 20% of the gas flow through catalytic channels (58) and a maximum outlet gas temperature increase of 20% of the adiabatic combustion temperature rise. Proper design of the corrugation shape and size can achieve any level of conversion from 5% to 95% while incorporating integral heat exchange. The maximum outlet gas temperature can be calculated by equation 2 below:

$$T_{gas\ max} = T_{gas\ inlet} + [T_{adiabatic} - T_{gas\ inlet}] \times \frac{\text{catalytic gas flow}}{\text{non-catalytic gas flow}} \quad (2)$$

To illustrate the operation of this integral heat exchange zone, assume that a partially combusted gas from the first catalytic zone flows into the Figure 4A structure in which the gas flow through the catalytic channels is 50% of the total flow.

Approximately half of the gas flow will pass through channels with catalytic walls (42) and half will flow through channels with non-catalytic walls (46). Fuel combustion will occur at the catalytic surface and heat will be dissipated to the gas flowing in both the catalytic and non-catalytic channels. If the gas from zone (1) is 500°C and the fuel/air ratio corresponds to a theoretical adiabatic combustion temperature of 1300°C, then combustion of the fuel in the catalytic channels will cause the temperature of all of the flowing gases to rise. The heat is dissipated into gas flowing in both the catalytic and non-catalytic channels. The calculated L-IHE wall temperature is:

$$T_{wall} = \frac{500°C + 1300°C}{2} = 900°C$$

The calculated maximum gas temperature is:

$$T_{gas\ max} = 500°C + [1300°C\text{-}500°C]\ .5 = 900°C$$

However, the palladium at one atm of air pressure will limit the wall temperature to 750°C to 800°C and the maximum outlet gas temperature will be about <800°C. As can be seen in this case, the palladium limiting is controlling the maximum outlet gas temperature and limiting the wall temperature.

The situation is different at ten atmospheres of air pressure. The palladium limiting temperature is about 930°C. The wall will be limited to 900°C by the L-IHE structure. In this case, the L-IHE structure is limiting the wall and gas temperature.

The temperature of gas leaving the second stage, is typically between 750 and 950°C, for example between 750 and 800°C.

The catalyst structure in this zone should have the same approximate catalyst loading, on those surfaces having catalysts, as does the first zone structure. It should be sized to maintain flow in the same average linear velocity as that first zone and, if a third catalytic stage is desired, sized to reach a bulk outlet temperature of no more than 800°C, preferably in the range of 600°C to 800°C and most preferably between 700°C and 800°C. The catalyst can incorporate a non-catalytic diffusion barrier layer such as that described for the first catalytic zone.

If a process utilizing only two discrete catalystic structures is desired, as a design matter, the second catalytic zone should be designed such that the bulk temperature of the gas exiting the zone is above its autoignition temperature (if the homogenous combustion zone is desired). The support and catalyst temperature are maintained at the moderation temperature mandated by the relative sizing of the catalytic and non-catalytic channels, the inlet temperature, the theoretical adiabatic combustion temperature, and the length of the second zone. The linear velocity of the gas in the second catalytic zone is the same as that of the first zone.

Third Catalytic Zone

The process of the invention may additionally comprise combusting any remaining uncombusted fuel in a third stage to produce a gas having a temperature greater than that of the gas leaving the second stage but no greater than about 1700°C. When utilized, the third zone in the process takes the partially combusted gas from the second zone and causes a further controlled combustion to take place in the presence of a catalyst preferably having integral heat exchange capabilities and, desirably, comprising a metal-oxygen catalytic material or comprising platinum as the catalytic material. In an embodiment of the invention, the first and/or third stage combustion catalyst is on a support having integral heat exchange surfaces.

The metal-oxygen material desirably contains one or more metals selected from those found in Mendelev Group VIII and Group I. These materials are desirable because of their reactive stability at the higher temperatures. Other combustion catalysts such as palladium, rhodium, osmium, iridium, and the like, may be used in place of or in addition to platinum. The zone may be essentially adiabatic in operation and, by catalytic combustion of at least a portion of the fuel, further raises the gas temperature to a point where homogeneous combustion may take place or where the gas may be directly used in a furnace or turbine.

The catalyst structure in this zone may be the same as used in the second zone. As noted above, the catalyst used in this zone desirably comprises a metal-oxygen catalytic materials or platinum. Suitable metal-oxygen catalytic materials include those selected from Mendelev Group V (particularly Nb or V), Group VI (particularly Cr), Group VIII transition (particularly Fe, Co, Ni), and first series lanthanides (particularly Ce, Pr, Nd, Sa, Tb, La) metal oxides or mixed oxides. Additionally, the catalytic materials may be chosen from Perovskite-form materials of the form ABO_3 where A is selected from Group IIA or IA metals (Ca, Ba, Sr, Mg, Be, K, Rb, Na, or Cs); and B is selected from Group VIII transition metals, Group VIB, or Group IB (particularly Fe, Co, Ni, Mn, Cr, Cu). We have not yet found that the manner in which these materials are formulated is critical. Impregnation of the support with a solution of salts or complexes of the desired metal or metals followed by a calcination step, as has been suggested in the literature, is suitable. These materials are typically active as combustion catalysts only at temperatures above 650°C but exhibit reasonable stability in that range. These materials do not show temperature limiting behavior as does palladium; the catalyst substrate can rise to temperatures above 800°C if no precautions are taken.

In one embodiment the second and third stage catalysts comprise palladium. In another embodiment the third stage catalyst preferably comprises palladium, rhodium, osmium, iridium or platinum.

If the L-IHE catalyst structure of Figure 6 has 50% of the gas flow through catalytic channels (3) in and 50% through non-catalytic channels (4) and if combustion is complete in the catalytic channels, then the outlet gas temperature of the third zone will be the average of the inlet temperature and the adiabatic combustion temperature as described earlier. The wall temperature and gas temperature will be limited to equations (1) and (2) given earlier. Incomplete reaction in the catalytic channels will result in a lower outlet gas temperature.

If the exhaust gas from the second zone is at a temperature of about 800°C or more and the fuel/air mixture has a theoretical adiabatic combustion temperature of 1300°C and 50% of the gas mixture is completely combusted in the catalytic channels, then the outlet temperature from the third zone will be 1050°C (i.e., the average 800°C and 1300°C). This exit gas temperature will result in rapid homogeneous combustion.

The structure of the third zone may take many forms and the catalyst can be applied in a variety of ways to achieve at least partial combustion of the fuel entering the third zone. As an example, use of the structures described above with regard to Figure 6A and 6B would result respectively in the conversion of 80% or 20% of the gas mixture entering the third zone. The outlet gas temperature from the third zone may be adjusted by catalyst support design.

As a design matter, therefore, the third zone should be designed such that the bulk temperature of the gas exiting the third zone is above its autoignition temperature (if the fourth zone homogenous combustion zone is desired). The support and catalyst temperature are maintained at the moderate temperature mandated by the relative sizing of the catalytic and non-catalytic channels, the inlet temperature, the theoretical adiabatic combustion temperature, and the length of the third zone. The linear velocity of the gas in the third catalytic zone is in the same range as those of the first and second zones although clearly higher because of the higher temperature. Typically the temperature of the combustible mixture discharged from the first stage is between 500°C and 650°C, that discharged from the second stage is between 750° and 800°C, and that discharged from the third stage is between 850° and 1050°C.

Homogenous Combustion Zone

The gas which has exited the earlier combustion zones may be in a condition suitable for subsequent use if the temperature is correct; the gas contains substantially no NO_x and yet the catalyst and catalyst supports have been maintained at a temperature which permits their long term stability. However, for many uses, a higher temperature is required. For instance, many gas turbines are designed for an inlet temperature of about 1260°C. Consequently, an homogeneous combustion zone may be an appropriate addition. Thus, the process of the invention may additionally comprise the step of combusting any remaining uncombusted fuel in a fourth zone to produce a gas having a temperature greater than that of the gas leaving the third stage but no greater than about 1700°C.

The homogenous combustion zone need not be large. The gas residence time in the zone normally should not be more than about eleven or twelve milliseconds to achieve substantially complete combustion (i.e., <ten ppm carbon monoxide) and to achieve the adiabatic combustion temperature.

The Table below shows calculated residence times both for achievement of various adiabatic combustion temperatures (as a function of fuel/air ratio) as well as achievement of combustion to near completion variously as a function of fuel-(methane)/air ratio, temperature of the bulk gas leaving the third catalyst zone, and pressure. These reaction times were calculated using a homogeneous combustion model and kinetic rate constants described by Kee et al.

(Sandia National Laboratory Report No. SAND 80-8003).

TABLE

Calculated Homogeneous Combustion Times
[time to T_{ad} & (time to CO < 10ppm) in milliseconds]

F/A >	0.043	0.043	0.037	0.037	0.032	0.032
T_{ad} ->	1300°C	1300°C	1200°C	1200°C	1100°C	1100°
Inlet Temp.	1 atm.	10 atm.	1 atm.	10 atm.	1 atm.	10 atm.
800°C	--	19.7 (21.0)	--	--	--	--
900°C	--	3.5 (4.8)	--	3.3 (6.2)	--	3.7 (10.2)
1000°C	6.5 (14.5)	1.0 (2.5)	5.0 (16.0)	1.0 (3.9)	--	1.0 (8.1)
1050°C	3.6 (11.7)	0.6 (2.1)	3.5 (13.5)	0.6 (3.6)	--	0.5 (7.7)
1100°C	2.5 (10.3)	--	--	--	--	--

T_{ad} = adiabatic combustion temperature less 20°C
F = methane
F/A = fuel to air ratio

Clearly, for a process used in support of a gas turbine, (e.g., a catalyst zone gas bulk exit temperature=900°C, F/A ratio of 0.043, pressure = ten atm of air), the residence time to reach the adiabatic combustion temperature and complete combustion is less than five milliseconds. A bulk linear gas velocity of less than 40 m/second (as discussed earlier in regard to the catalytic stages) would result in a homogeneous combustion zone of less than 0.2 m in length.

In summary, the process uses a number of carefully crafted catalyst structures and catalytic methods to produce a working gas which contains substantially no NO_x and is at a temperature comparable to normal combustion processes. Yet, the catalysts and their supports are not exposed to deleteriously high temperatures which would harm those catalysts or supports or shorten their useful life.

EXAMPLES

Example 1

This example shows the assembly of a three stage catalyst system.

Stage 1

The first stage was prepared as follows:

A 3% palladium/ZrO_2 sol was prepared. A sample of 145 g of ZrO_2 powder with a surface area of 45 m^2/gm was impregnated with 45 ml of a palladium solution prepared by dissolving $Pd(HN_3)_2(NO_2)_2$ in HNO_3 containing 0.83 g palladium/ml. This solid was dried, calcined in air at 500°C, and loaded into a polymer lined ball mill with

230 ml H_2O, 2.0 ml concentrated HNO_3, and cylindrical zirconia media. The mixture was milled for eight hours.

To 50 cc of this sol (containing about 35% solids by weight) 36 ml of palladium solution was added. The pH was adjusted to about nine and 1.0 ml of hydrazine added. Stirring at room temperature resulted in the reduction of the palladium. The final palladium concentration was 20% palladium/ZrO_2 by weight.

A cordierite monolithic ceramic honeycomb structure with 100 square cells per square inch (SCSI) was immersed in the palladium/ZrO_2 sol and the excess sol blown from the channels. The monolith was dried and calcined at 850°C. The monolith contained 6.1% ZrO_2 and 1.5% palladium. This monolith was again dipped in the same palladium/ZrO_2 sol but only to a depth of ten mm, removed, blown out, dried, and calcined. The final catalyst had 25% ZrO_2 and 6.2% palladium on the inlet 10.0 mm portion.

Stage 2

The second stage catalyst was prepared as follows:

A ZrO_2 colloidal sol was prepared. About 66 g of zirconium isopropoxide was hydrolyzed with 75 cc water and then mixed with 100 g of ZrO_2 powder with a surface area of 100 m^2/gm and an additional 56 ml of water. This slurry was ball milled in a polymer lined ball mill using ZrO_2 cylindrical media for eight hours. This colloidal sol was diluted to a concentration of 15% ZrO_2 by weight with additional water.

An Fe/Cr/Al alloy foil was corrugated in a herringbone pattern and then oxidized at 900°C in air to form alumina whiskers on the foil surface. The ZrO_2 sol was sprayed on the corrugated foil. The coated foil was dried and calcined at 850°C. The final foil contained twelve mg ZrO_2/cm^2 foil surface.

Palladium 2-ethylhexanoic acid was dissolved in toluene to a concentration of 0.1 g palladium/ml. This solution was sprayed onto one side only of the ZrO_2 coated metal foil and the foil dried and calcined at 850°C in air. The final foil contained about 0.5 mg palladium/cm^2 of foil surface.

The corrugated foil was rolled so that the corrugations did not mesh to form a final metal structure of two inch diameter and two inch length with longitudinal channels running axially through the structure and containing about 150 cells per square inch. The foil had palladium/ZrO_2 catalyst on one surface only and each channel consisted of catalytic coated and non-catalytic surfaces such as those shown in Figure 3A.

Stage 3

The third stage catalyst was prepared as follows:

An alumina sol was prepared. About 125 g of a gamma alumina with a surface area of 180 m^2/g, 21 ml of concentrated nitric acid, and 165 ml of water were placed in a half gallon ball mill with cylindrical alumina grinding media and milled for 24 hours. This sol was diluted to a solid concentration of 20%.

An Fe/Cr/Al alloy foil was corrugated to form uniform straight channels in the foil strip. When rolled together with a flat foil strip, the spiral structure formed a honeycomb structure with straight channels. The corrugated strip was first sprayed with a 5% colloidal boehmite sol and then with the alumina sol prepared above. A flat strip of metal foil was sprayed in a similar fashion. Only one surface of each foil was coated in this manner. The foils were then dried and calcined at 1100°C.

$Pt(NH_3)_2(NO_2)_2$ was dissolved in nitric acid to produce a solution with 0.13 g platinum/ml. This solution was sprayed onto the coated foil, the foil treated with gaseous H_2S, dried, and calcined at 1100°C. The "thickness" of the alumina coating on the metal foil was about four mg/cm^2 of flat foil surface. The platinum loading was about 20% of the alumina.

Three Stage Catalyst System

The three catalysts described above were arranged inside a ceramic cylinder as shown in Figure 7. Thermocouples were located in this system at the positions shown. The thermocouples located in the catalyst sections were sealed inside a channel with ceramic cement to measure the temperature of the catalyst substrate. The gas thermocouples were suspended in the gas stream. The insulated catalyst section of Figure 7 was installed in a reactor with a gas flow path of 50 mm diameter. Air at 150 SLPM was passed through an electric heater, a static gas mixer, and through the catalyst system. Natural gas at 67 SLPM was added just upstream of the static mixer. The air temperature was slowly increased by increasing power to the electric heater. At 368°C, exit the gas temperatures from stages 1, 2, and 3 began to rise as shown in Figure 8. Above a preheat temperature of 380°C, the gas temperature from stage 1 was constant at about 530°C, the gas exiting stage 2 was about 780°C, and the gas exiting stage 3 at approximately 1020°C. Homogeneous combustion occurred after the catalyst giving a gas temperature of about 1250°C; a temperature near the adiabatic combustion temperature of this fuel/air ratio. The substrate temperatures for the three stages are shown in Figure 9.

As was described above, the stage 1 catalyst lit off at a low temperature and substrate temperature self-limited at about 750°C. This catalyst cell density and gas flow rate produced an intermediate gas temperature of 540°C. Similarly, stage 2 also self-limited the substrate temperature to 780°C and produced a gas temperature of 750°C. Stage 3 limited the wall temperature at 1100°C.

Limiting the substrate temperature to 750°C to 780°C for stages 1 and 2 provided excellent long term catalyst stability. This stability was demonstrated for 100 hours as shown in Figure 10. This catalyst system was again ignited by holding the inlet air temperature at 400°C and increasing the fuel/air ratio by increasing the methane flow rate. This start-up procedure is shown in Figure 11. Stage 1 achieved an outlet gas temperature of 540°C at fuel/air=.033 and maintained this temperature at fuel/air ratios up to .045. Complete homogeneous combustion in the region after the catalyst was achieved at a fuel/air ratio of .045.

Claims

1. A process for burning a combustible mixture, the process comprising:

   (a) contacting a combustible mixture comprising fuel and an oxygen-containing gas, necessary to reach a desired temperature upon combustion, with a catalytic structure in which catalyst is arranged in two or more catalytic stages, wherein the catalytic structure comprises a catalyst support having multiple longitudinal passageways for the passage of the combustible mixture and in which only a portion of the passageways have catalyst situated therein so that a portion of the combustible mixture is inhibited in its contact with the catalyst so that only a portion of the fuel is combusted within the catalytic structure and the temperature of partially combusted combustible mixture leaving the catalytic structure is below the desired temperature and wherein palladium is the only catalyst present in the first stage of the catalytic structure; and
   (b) combusting the remainder of the fuel left in the combustible mixture outside of the catalytic structure to raise its temperature to the desired temperature.

2. A process according to claim 1 where the catalytic structure is divided into three stages and the second stage catalyst comprises palladium while the third stage catalyst comprises platinum.

3. A process according to claim 2 where the temperature of the combustible mixture discharged from the first stage is between 500°C and 650°C, that discharged from the second stage is between 750° and 800°C, and that discharged from the third stage is between 850° and 1050°C.

4. A process according to any preceding claim where the desired temperature after combustion is between 1050°C and 1700°C.

5. A process according to any preceding claim wherein the catalytic structure comprises a catalyst support having catalyst with a diffusion barrier situated thereon so that a portion of the combustible mixture is inhibited in its contact with catalyst.

6. A process according to any preceding claim wherein the catalytic structure is divided into three stages and the third stage catalyst comprises palladium, rhodium, osmium, iridium or platinum.

7. A process of claim 5 where the catalyst support is a corrugated metal structure.

8. A process according to any of claims 2 to 7 wherein the second stage catalyst has a support structure of corrugated or flat sheets coated on one side with catalyst arranged so that the catalytic surface of each sheet faces a different channel and all channels have a portion of their walls catalyst coated and all walls have one surface coated with catalyst and an opposite surface non-catalytic, so that as combustion occurs at the catalyst surface the temperature of the catalyst and support will rise and heat will be conducted and dissipated in the gas flow on both the catalytic and non-catalytic sides.

9. A process according to any of claims 2 to 8 wherein the second stage combustion catalyst comprises palladium.

10. A process according to claim 9 wherein the bulk temperature of the gas leaving the second stage is between 750°C and 950°C.

11. A process according to any preceding claim wherein the oxygen-containing gas is air and is compressed to a pressure of at least 4 atmospheres (gauge).

12. A process according to any of claims 2 to 11 additionally comprising combusting any remaining uncombusted fuel

in a third stage to produce a gas having a temperature greater than that of the gas leaving the second stage but no greater than about 1700°C.

13. A process according to any preceding claim wherein the first stage combustion catalyst comprises palladium on a metallic support.

14. A process according to claim 13 wherein the first stage combustion catalyst comprising palladium on a metallic support additionally comprises a barrier layer covering at least a portion of the palladium.

15. A process according to claim 14 wherein the barrier layer comprises zirconia.

16. A process according to any of claims 13 to 15 where the second stage combustion catalyst contains one or more Group IB metals or Group VIII metals.

17. A process according to any of claims 2 to 16 wherein the second stage catalytic structure is a limited-integral-heat-exchange structure.

18. A process according to claim 17 where the bulk temperature of the gas leaving the second stage is between 750°C and 800°C.

19. A process according to any of claims 4 to 18 where the third stage combustion catalyst is one or more of the metal-oxygen catalytic materials from Mendeleev Group V (particularly Nb), Group VI (particularly Cr), Group VIII transition (particularly Fe, Co, Ni), first series lanthanides (particularly Ce, Pr, Nd, Sa, Tb or La) metal oxides or mixed oxides or Perovskite-form materials of the form ABO_3 where A is a Group IIA or IA metal (Ca, Ba, Sr, Mg, Be, K, Rb, Na or Cs); and B is a Group VIII transition metal, Group VIB, or Group IB element (particularly Fe, Co, Ni, Mn, Cr or Cu).

20. A process according to any of claims 11 to 19 where the oxygen-containing gas is air and is compressed to a pressure of zero to 35 atm. (gauge) of air.

21. A process according to any of claims 2 to 20 where the first and/or third stage combustion catalyst is on a support having integral heat exchange surfaces.

22. A process according to any preceding claim additionally comprising the step of combusting any remaining uncombusted fuel in a fourth zone to produce a gas having a temperature greater than that of the gas leaving the third stage but no greater than about 1700°C.

Patentansprüche

1. Verfahren zum Verbrennen eines brennbaren Gemischs, umfassend:

(a) das In-Kontaktbringen eines brennbaren Gemischs, das Brennstoff und ein sauerstoffhaltiges Gas umfaßt, die zur Erzielung einer gewünschten Temperatur bei der Verbrennung nötig sind, mit einer katalytischen Struktur, in der Katalysator in zwei oder mehr katalytischen Stufen angeordnet ist, wobei die katalytische Struktur einen Katalysatorträger mit mehreren längsgerichteten Kanälen für den Durchtritt des brennbaren Gemischs umfaßt, und wobei nur ein Teil der Kanäle Katalysator in sich birgt, so daß ein Teil des brennbaren Gemischs am Kontakt mit dem Katalysator gehindert wird und nur ein Teil des Brennstoffs in der katalytischen Struktur verbrannt wird, und die Temperatur des partiell verbrannten, brennbaren Gemischs, das die katalytische Struktur verläßt, unter der gewünschten Temperatur liegt, und wobei Palladium der einzige Katalysator in der ersten Stufe der katalytischen Struktur ist; und
(b) das Verbrennen des restlichen, im brennbaren Gemisch verbliebenen Brennstoffs außerhalb der katalytischen Struktur, so daß seine Temperatur auf die gewünschte Temperatur erhöht wird.

2. Verfahren nach Anspruch 1, wobei die katalytische Struktur in drei Stufen aufgeteilt ist und der Katalysator der zweiten Stufe Palladium umfaßt, wohingegen der Katalysator der dritten Stufe Platin umfaßt.

3. Verfahren nach Anspruch 2, wobei die Temperatur des aus der ersten Stufe tretenden brennbaren Gemischs

zwischen 500°C und 650°C liegt, des aus der zweiten Stufe tretenden zwischen 750°C und 800°C liegt, und des aus der dritten Stufe tretenden zwischen 850°C und 1050°C liegt.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei die gewünschte Temperatur nach der Verbrennung zwischen 1050°C und 1700°C liegt.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die katalytische Struktur einen Katalysatorträger umfaßt, der einen Katalysator mit einer darauf befindlichen Diffusionsschranke besitzt, so daß ein Teil des brennbaren Gemischs am Kontakt mit dem Katalysator gehindert wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei die katalytische Struktur in drei Stufen aufgeteilt ist, und der Katalysator der dritten Stufe Palladium, Rhodium, Osmium, Iridium oder Platin umfaßt.

7. Verfahren nach Anspruch 5, wobei der Katalysatorträger eine gerippte Metallstruktur ist.

8. Verfahren nach einem der Ansprüche 2 bis 7, wobei der Katalysator der zweiten Stufe eine Trägerstruktur aus gerippten oder ebenen Platten besitzt, die auf einer Seite mit Katalysator beschichtet sind, derart angeordnet, daß die katalytische Oberfläche jeder Platte jeweils zu einem anderen Kanal gerichtet ist, und bei sämtlichen Kanälen ein Teil der Wände katalysatorbeschichtet ist, und bei sämtlichen Wänden eine Oberfläche mit Katalysator beschichtet ist und die gegenüberliegende Oberfläche nicht katalytisch aktiv ist, so daß die Temperatur des Katalysators und des Trägers steigt, wenn die Verbrennung an der Katalysatoroberfläche stattfindet, und die Wärme im Gasstrom auf die katalytisch aktive und die nicht-katalytisch aktive Seite geleitet und verteilt wird.

9. Verfahren nach einem der Ansprüche 2 bis 8, wobei der Katalysator der zweiten Stufe Palladium umfaßt.

10. Verfahren nach Anspruch 9, wobei die Gesamttemperatur des Gases, das die zweite Stufe verläßt, zwischen 750°C und 950°C liegt.

11. Verfahren nach einem der vorhergehenden Ansprüche, wobei das sauerstoffhaltige Gas Luft ist und auf einen Druck von mindestens 4 Atmosphären (Manometerdruck) komprimiert ist.

12. Verfahren nach einem der Ansprüche 2 bis 11, das zudem das Verbrennen jeglichen verbliebenen unverbrannten Brennstoffs in einer dritten Stufe umfaßt, so daß ein Gas hergestellt wird, dessen Temperatur höher als bei dem Gas ist, das die zweite Stufe verläßt, jedoch nicht höher als etwa 1700°C ist.

13. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Verbrennungskatalysator der ersten Stufe Palladium auf einem Metallträger umfaßt.

14. Verfahren nach Anspruch 13, wobei der Verbrennungskatalysator der ersten Stufe, der Palladium auf einem Metallträger umfaßt, zusätzlich eine Sperrschicht umfaßt, die zumindest einen Teil des Palladiums abschirmt.

15. Verfahren nach Anspruch 14, wobei die Sperrschicht Zirkondioxid umfaßt.

16. Verfahren nach einem der Ansprüche 13 bis 15, wobei der Verbrennungskatalysator der zweiten Stufe ein oder mehrere Gruppe-IB-Metalle oder Gruppe-VIII-Metalle enthält.

17. Verfahren nach einem der Ansprüche 2 bis 16, wobei die katalytische Struktur der zweiten Stufe eine Struktur mit eingeschränktem integralen Wärmeaustausch ist.

18. Verfahren nach Anspruch 17, wobei die Gesamttemperatur des Gases, das die zweite Stufe verläßt, zwischen 750°C und 800°C liegt.

19. Verfahren nach einem der Ansprüche 4 bis 18, wobei der Verbrennungskatalysator der dritten Stufe ein oder mehrere katalytische Metallsauerstoffmaterialien aus den Metalloxiden der Mendelejew-Gruppe-V (insbesondere Nb), der -Gruppe-VI (insbesondere Cr), der -Gruppe-VIII-Übergangsmetalle (insbesondere Fe, Co, Ni), der ersten Lanthanoidenreihe (insbesondere Ce, Pr, Nd, Sa, Tb oder La) oder gemischte Oxide oder perovskitartige Materialien der Form ABO_3 umfaßt, wobei A ein Gruppe-IIA- oder -IA-Metall (Ca, Ba, Sr, Mg, Be, K, Rb, Na oder Cs) ist, und B ein Gruppe-VIII-Übergangsmetall, ein Gruppe-VIB- oder ein Gruppe-IB-Element (insbesondere Fe, Co,

Ni, Mn, Cr oder Cu) ist.

20. Verfahren nach einem der Ansprüche 11 bis 19, wobei das sauerstoffhaltige Gas Luft ist und auf einen Druck von 0 bis 35 atm (Manometerdruck) Luft komprimiert ist.

21. Verfahren nach einem der Ansprüche 2 bis 20, wobei sich der Verbrennungskatalysator der ersten und/oder dritten Stufe auf einem Träger befindet, der Oberflächen für den integralen Wärmeaustausch hat.

22. Verfahren nach einem der vorhergehenden Ansprüche, zudem umfassend den Schritt des Verbrennens sämtlichen restlichen unverbrannten Brennstoffs in einer vierten Zone, so daß ein Gas hergestellt wird, dessen Temperatur größer ist als die des Gases, das die dritte Stufe verläßt, jedoch nicht höher als etwa 1700°C ist.

Revendications

1. Procédé pour brûler un mélange combustible, le procédé comportant les étapes consistant à :

(a) mettre en contact un mélange combustible comportant du carburant et un gaz contenant de l'oxygène, nécessaire pour atteindre une température voulue lors de la combustion, avec une structure catalytique dans laquelle le catalyseur est agencé en deux ou plus de deux étages catalytiques, dans lequel la structure catalytique comporte un support de catalyseur ayant de multiples voies de passage longitudinales pour le passage du mélange combustible et dans lesquelles seule une partie des voies de passage ont du catalyseur situé à l'intérieur de sorte qu'une partie du mélange combustible est empêchée de venir en contact avec le catalyseur de sorte que seule une partie du carburant entre en combustion dans la structure catalytique et la température du mélange combustible, ayant subi une combustion partielle, qui sort de la structure catalytique est située en dessous de la température voulue, et le palladium étant le seul catalyseur présent dans le premier étage de la structure catalytique, et
(b) faire subir une combustion au reste du carburant laissé dans le mélange combustible à l'extérieur de la structure catalytique pour faire monter sa température jusqu'à la température voulue.

2. Procédé selon la revendication 1, dans lequel la structure catalytique est divisée en trois étages, et le catalyseur du deuxième étage est constitué de palladium alors que le catalyseur du troisième étage est constitué de platine.

3. Procédé selon la revendication 2, dans lequel la température du mélange combustible évacué du premier étage est située entre 500°C et 600°C, celle évacuée à partir du deuxième étage est située entre 750°C et 800°C, et celle évacuée à partir du troisième étage est située entre 850°C et 1050°C.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la température voulue après combustion est située entre 1050°C et 1700°C.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la structure catalytique comporte un support de catalyseur comportant un catalyseur sur lequel est située une barrière de diffusion de sorte qu'une partie du mélange combustible ne peut venir en contact avec le catalyseur.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel la structure catalytique est divisée en trois étages et le catalyseur du troisième étage est constitué de palladium, de rhodium, d'osmium, d'iridium ou de platine.

7. Procédé selon la revendication 5, dans lequel le support de catalyseur est une structure métallique ondulée.

8. Procédé selon l'une quelconque des revendications 2 à 7, dans lequel le catalyseur du deuxième étage a une structure de support constituée de feuilles plates ou ondulées recouvertes sur un côté d'un catalyseur agencé de sorte que la surface catalytique de chaque feuille fait face à un canal différent et tous les canaux ont une partie de leurs parois recouverte d'un catalyseur et toutes les parois ont une surface recouverte d'un catalyseur et une surface opposée non-catalytique, de sorte que lorsqu'une combustion a lieu au niveau de la surface de catalyseur, la température du catalyseur et du support augmente et la chaleur est conduite et dissipée dans l'écoulement de gaz sur les deux côtés catalytique et non-catalytique.

9. Procédé selon l'une quelconque des revendications 2 à 8, dans lequel le catalyseur de combustion du deuxième étage est constitué de palladium.

10. Procédé selon la revendication 9, dans lequel la température du gaz quittant le deuxième étage est située entre 750°C et 950°C.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz contenant de l'oxygène est l'air et est comprimé jusqu'à une pression d'au moins 4 atmosphères (au manomètre).

12. Procédé selon l'une quelconque des revendications 2 à 11, comportant de plus la combustion de tout carburant restant, n'ayant pas subi de combustion, dans un troisième étage pour produire un gaz ayant une température supérieure à celle du gaz quittant le deuxième étage mais inférieure à environ 1700°C.

13. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur de combustion du premier étage est constitué de palladium sur un support métallique.

14. Procédé selon la revendication 13, dans lequel le catalyseur de combustion du premier étage constitué de palladium sur un support métallique comporte de plus une couche formant barrière recouvrant au moins une partie du palladium.

15. Procédé selon la revendication 14, dans lequel la couche formant barrière est constituée de zircone.

16. Procédé selon l'une quelconque des revendications 13 à 15, dans lequel le catalyseur de combustion du deuxième étage contient un ou plusieurs métaux du groupe IB ou métaux du groupe VIII.

17. Procédé selon l'une quelconque des revendications 2 à 16, dans lequel la structure catalytique du deuxième étage est une structure d'échange thermique, venue de matière et limitée.

18. Procédé selon la revendication 17, dans lequel la température du gaz quittant le deuxième étage est située entre 750°C et 800°C.

19. Procédé selon l'une quelconque des revendications 4 à 18, dans lequel le catalyseur de combustion du troisième étage est constitué d'un ou plusieurs matériaux catalytiques du type métal-oxygène provenant du groupe V de la classification de Mendeleïev (en particulier Nb), du groupe VI (en particulier Cr), de métaux de transition du groupe VIII (en particulier Fe, Co, Ni), des lanthanides de la première série (en particulier Ce, Pr, Nd, Sa, Tb ou La), des oxydes métalliques ou des oxydes mélangés ou des matériaux de type Perovskite ayant la forme ABO_3 où A est un métal du groupe IIA ou IA (Ca, Ba, Sr, Mg, Be, K, Rb, Na ou Cs), et B est un métal de transition du groupe VIII, du groupe VIB, ou un élément du groupe IB (en particulier Fe, Co, Ni, Mn, Cr ou Cu).

20. Procédé selon l'une quelconque des revendications 11 à 19, dans lequel le gaz contenant de l'oxygène est l'air et est comprimé jusqu'à une pression allant de zéro à 35 atmosphères d'air (au manomètre).

21. Procédé selon l'une quelconque des revendications 2 à 20, dans lequel le catalyseur de combustion du premier et/ou troisième étage est sur un support ayant des surfaces d'échange thermique venues de matière.

22. Procédé selon l'une quelconque des revendications précédentes, comportant de plus l'étape consistant à faire subir une combustion à tout carburant restant n'ayant pas subi de combustion dans une quatrième zone, pour produire un gaz ayant une température supérieure à celle du gaz quittant le troisième étage mais inférieure à environ 1700°C.

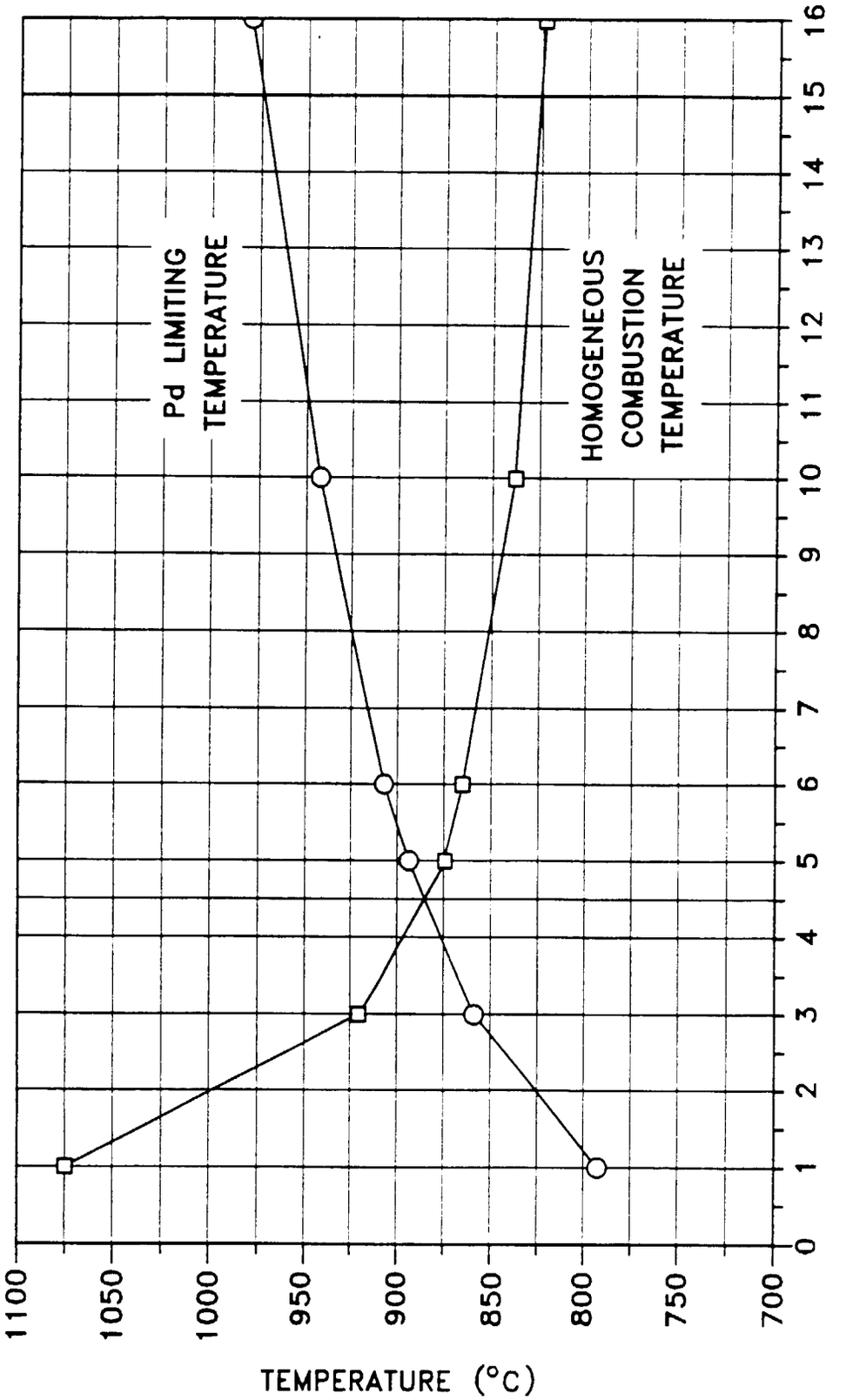
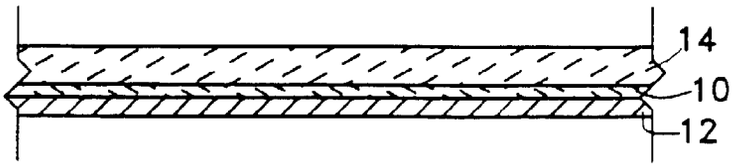

Pd LIMITING TEMPERATURE
HOMOGENEOUS COMBUSTION TEMPERATURE
TEMPERATURE (°C)
1100
1050
1000
950
900
850
800
750
700
PRESSURE (ATM)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Fig. 1

Fig. 2A



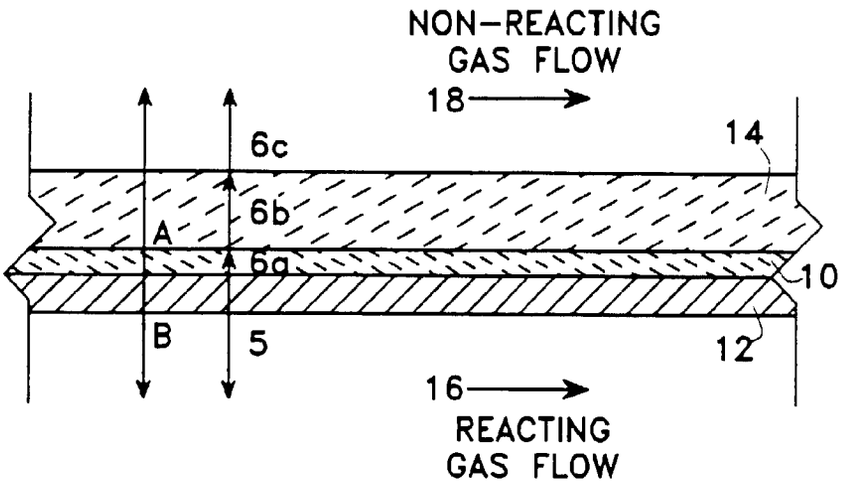


Fig. 2B

Fig. 3B

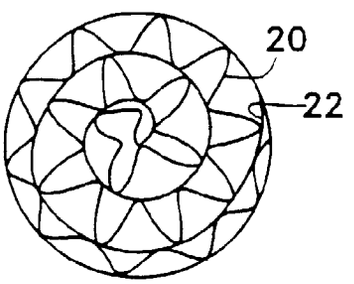
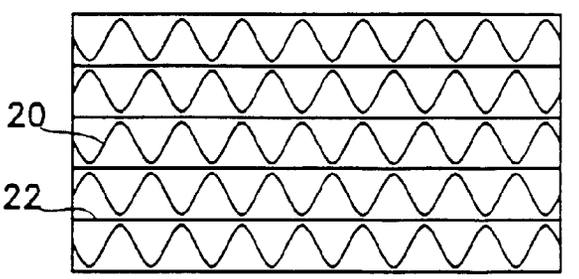


Fig. 3A



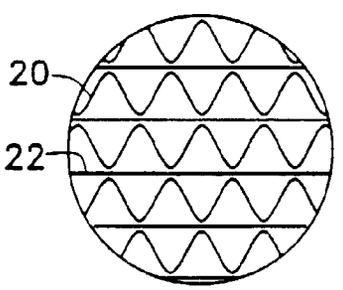


Fig. 3C

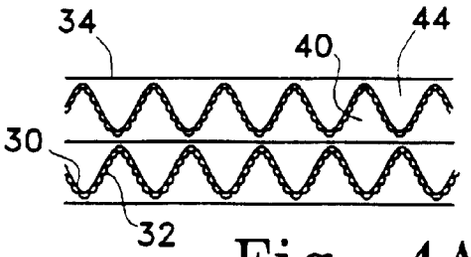


Fig. 4A

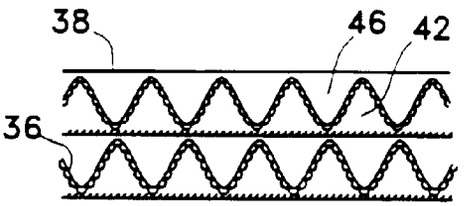


Fig. 4B

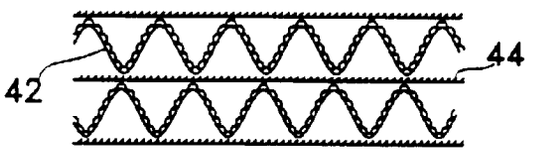


Fig. 5

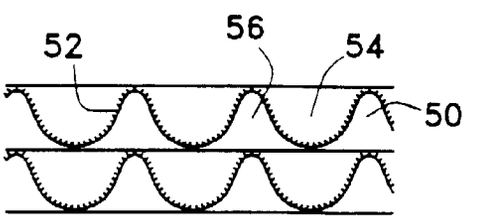


Fig. 6A

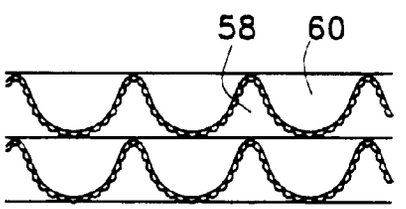


Fig. 6B

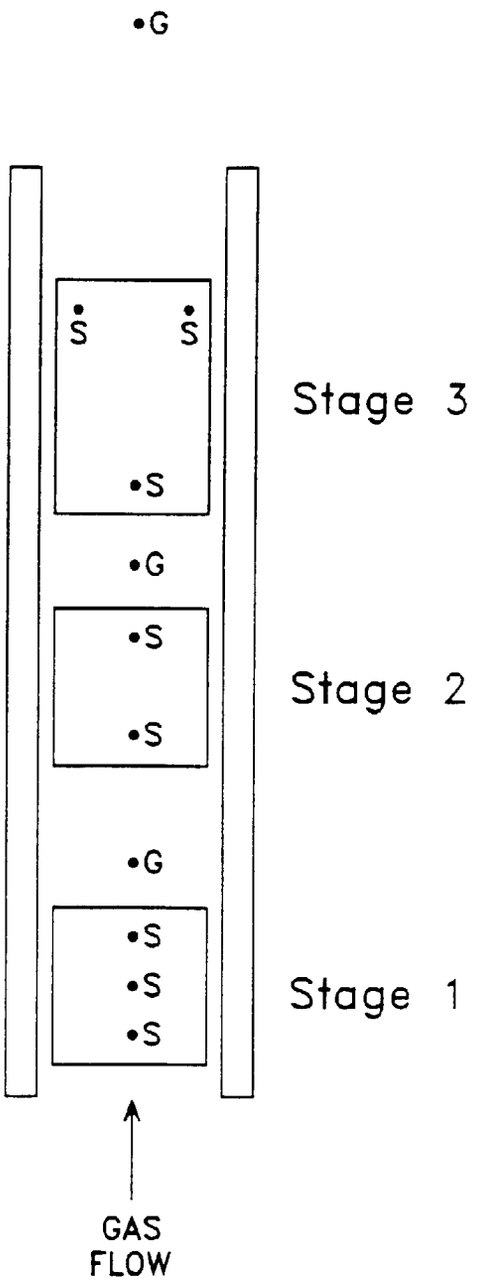


Fig. 7

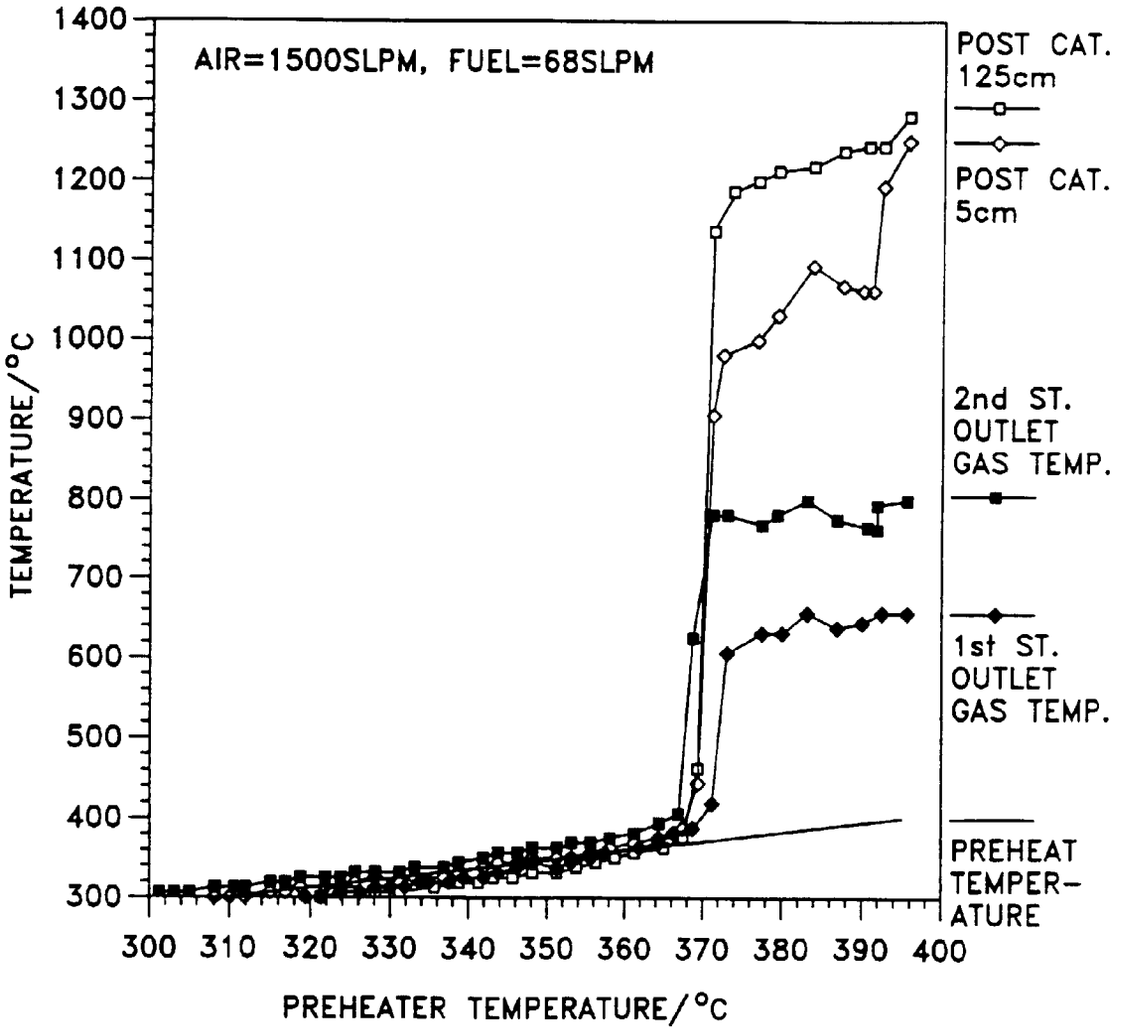

AIR=1500SLPM, FUEL=68SLPM
TEMPERATURE/°C
PREHEATER TEMPERATURE/°C
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
300 310 320 330 340 350 360 370 380 390 400
POST CAT. 125cm
POST CAT. 5cm
2nd ST. OUTLET GAS TEMP.
1st ST. OUTLET GAS TEMP.
PREHEAT TEMPER-ATURE

Fig. 8

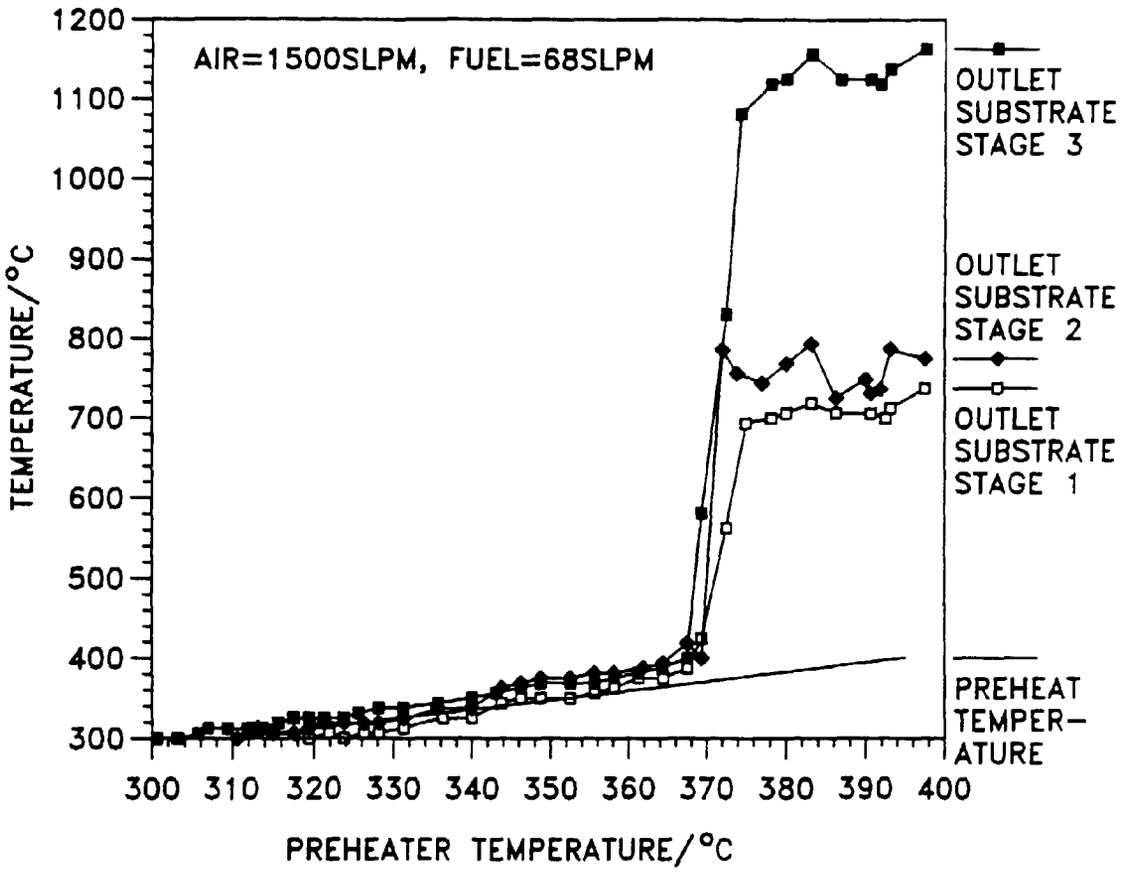

AIR=1500SLPM, FUEL=68SLPM
TEMPERATURE/°C
PREHEATER TEMPERATURE/°C
1200
1100
1000
900
800
700
600
500
400
300
300 310 320 330 340 350 360 370 380 390 400
OUTLET SUBSTRATE STAGE 3
OUTLET SUBSTRATE STAGE 2
OUTLET SUBSTRATE STAGE 1
PREHEAT TEMPER-ATURE

Fig. 9

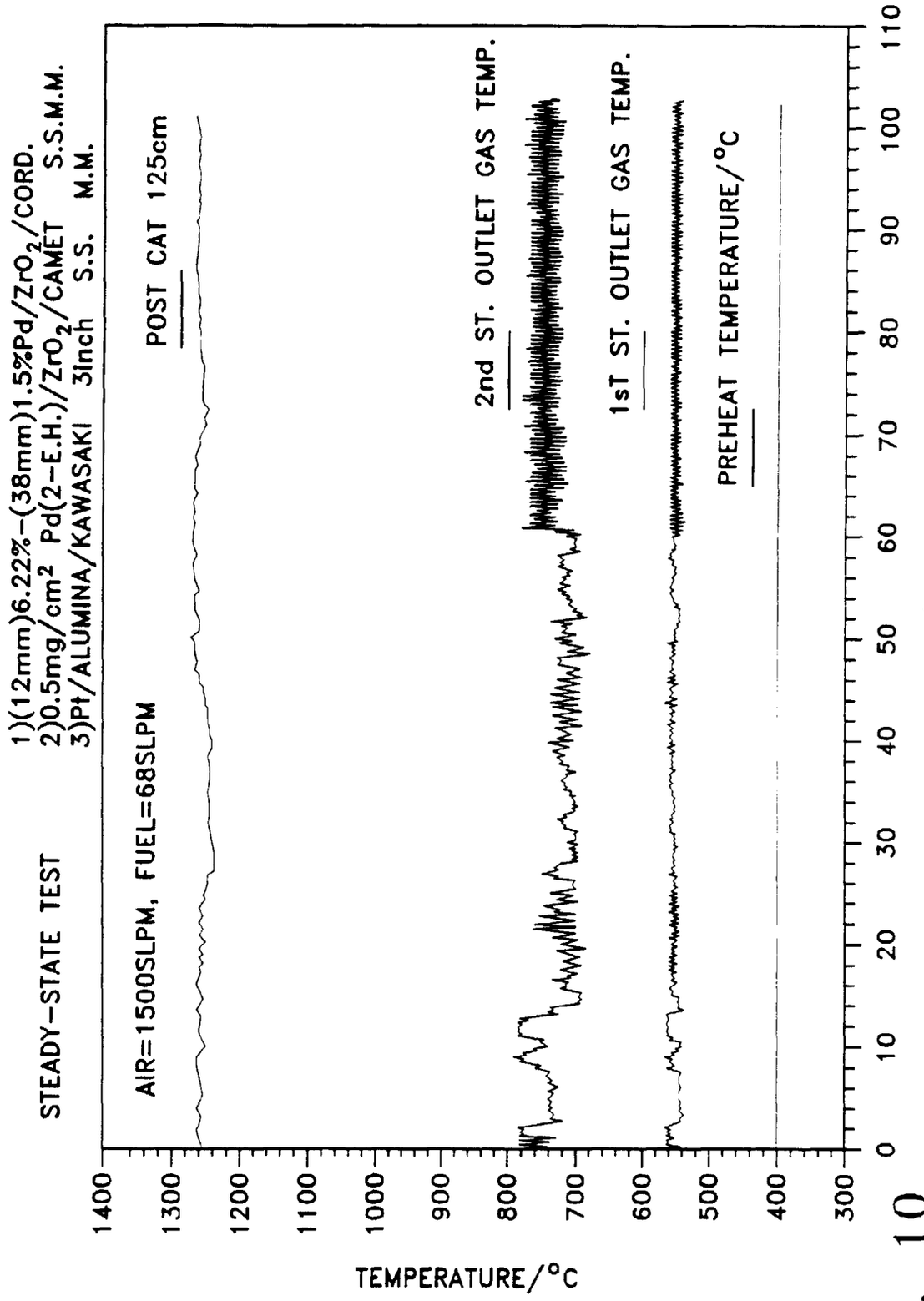

STEADY-STATE TEST
1)(12mm)6.22%-(38mm)1.5%Pd/ZrO2/CORD.
2)0.5mg/cm2 Pd(2-E.H.)/ZrO2/CAMET S.S.M.M.
3)Pt/ALUMINA/KAWASAKI 3inch S.S. M.M.
AIR=1500SLPM, FUEL=68SLPM
POST CAT 125cm
2nd ST. OUTLET GAS TEMP.
1sT ST. OUTLET GAS TEMP.
PREHEAT TEMPERATURE/°C
TEMPERATURE/°C
RUN TIME/HOUR
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
0
10
20
30
40
50
60
70
80
90
100
110

Fig. 10

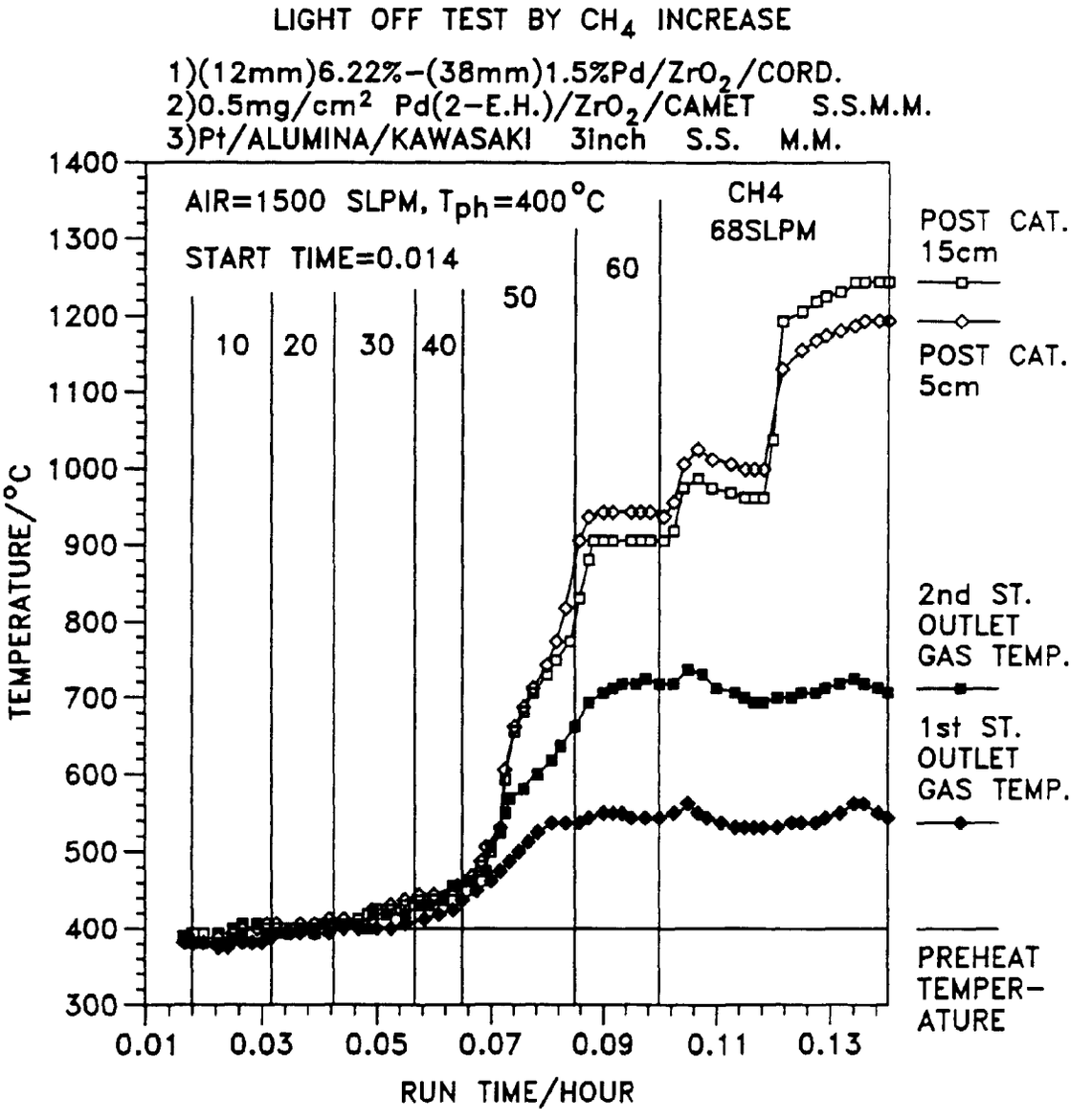

LIGHT OFF TEST BY CH_4 INCREASE
1)(12mm)6.22%-(38mm)1.5%Pd/ZrO_2/CORD.
2)0.5mg/cm² Pd(2-E.H.)/ZrO_2/CAMET S.S.M.M.
3)Pt/ALUMINA/KAWASAKI 3inch S.S. M.M.
AIR=1500 SLPM, T_{ph}=400°C
START TIME=0.014
CH4
68SLPM
10
20
30
40
50
60
TEMPERATURE/°C
RUN TIME/HOUR
POST CAT. 15cm
POST CAT. 5cm
2nd ST. OUTLET GAS TEMP.
1st ST. OUTLET GAS TEMP.
PREHEAT TEMPER-ATURE

Fig. 11