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**Catalytic
Combustion
Technology
For Stationary
Gas Turbines**

**Prepared For
Minerals Management Service
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**CATALYTIC COMBUSTION TECHNOLOGY FOR
STATIONARY GAS TURBINES**

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1.0 INTRODUCTION

The Minerals Management Service of the Department of the Interior is formulating a long-term technology program to develop advanced NO_x control techniques for offshore oil and gas production operations. Implementation of effective NO_x control measures could resolve air quality issues that hinder development of Outer Continental Shelf (OCS) resources. Under this program, funding is being provided to develop those technologies that are likely to be successfully demonstrated within about five years and will have a significant impact on NO_x emissions. For technologies that may require longer than five years because of significant technical hurdles, but may offer effective long-term solutions, development progress is being monitored under this program. Catalytic combustors for gas turbines fall into this latter category, since breakthroughs in materials science will be required to produce durable catalysts.

Arthur D. Little, Inc., has been assisting the Minerals Management Service in the development and implementation of their NO_x control program. As part of this effort, ADL was commissioned to evaluate the status of catalytic combustion technology for gas turbines. Our findings are documented in this report. Specifically, the study defined the current status of catalyst materials and combustor technology, identified areas in which technical progress is required, and recommended a role for the Minerals Management Services in the development of this technology. The report is organized as follows:

- Section 2: Provides background information on environmental issues, offshore operations, and NO_x control technologies.
- Section 3: Summarizes the findings and recommendations of this evaluation.
- Section 4: Describes operating principles and configurations for catalytic combustors applied to gas turbine engines.
- Section 5: Describes the state-of-the-art in available materials for catalytic combustors.
- Section 6: Documents recent materials and combustor development activities and identifies technical progress still required.

2.0 BACKGROUND

2.1 Environmental Issues

Oxides of nitrogen (NO_x) emitted from combustion sources are precursors to the photochemical formation of ozone near ground level. This impact from engines used on platforms and boats has posed an obstacle to the development of outer continental shelf (OCS) reserves near California. Many areas in the vicinity of OCS developments are in non-attainment with federal and state standards for ambient ozone concentrations. These regions include the areas around Los Angeles, Ventura, and Santa Barbara.

The extent to which NO_x emissions generated offshore impact onshore air quality has not been clearly defined, despite extensive dispersion and photochemical modeling. However, reductions in these emissions are viewed by local and state government agencies as an important element in attaining acceptable air quality.

2.2 Sources of NO_x Emissions In OCS Operations

NO_x emissions associated with OCS operations result from the combustion of fossil fuels in engines that are utilized to produce mechanical or electrical power. Specific applications are as follows:

- Platform gas turbines
- Supply boat engines
- Crew boat engines
- Exploratory drilling rig engines
- Platform crane engines
- Tanker engines
- Platform fired heaters
- Platform construction equipment engines

This report focuses on catalytic combustion, a potentially effective technology for control of NO_x emissions from gas turbines.

Gas turbine engines are used to generate electrical power for most production platforms. Currently, these engines utilize injection of water into the combustor to control NO_x emissions. While this technique is relatively effective (NO_x emissions reductions of 60 to 70% from uncontrolled levels are achieved), turbines equipped with water injection are still responsible for a significant portion of total NO_x emissions from many OCS projects. Consequently, further improvements in gas turbine NO_x control would be desirable.

The duty cycle characteristic of gas turbines on production platforms presents a challenge to the successful implementation of most advanced NO_x control techniques. Since the gas turbines are generally the primary source of power on these platforms, turbine firing rate must respond to shifts in platform electric

demand. During phases of drilling operations, rapid shifts of significant magnitude in turbine load are required. NO_x control technologies must be capable of tracking these variations without compromising turbine performance, safety or emission control capability.

2.3 Significance Of Catalytic Combustion

In general, NO_x emissions from combustion sources (such as gas turbines) can be reduced by modifying the combustion process, by treating exhaust gas to remove NO_x, or by switching to fuels that inherently produce lower NO_x levels. Of these, combustion modifications are generally the least costly solutions and have minimal adverse impact on platform design and operation. However, the degree of NO_x control achievable with current modification techniques is insufficient to meet demanding air quality requirements. Catalytic combustion is a future combustion modification technique which may prove to be both highly effective and reasonably priced.

Commercialization of catalytic combustion for stationary gas turbines, if possible, is expected to result in NO_x emissions from these engines below 10 ppm (dry, corrected to 15% O₂) which would comply with the most strict regulations currently in effect or being planned. For comparison, current water injected gas turbines generate NO_x emissions of about 25 to 42 ppm. Achieving the 10 ppm NO_x level currently requires equipping gas turbines with both combustor water injection and selective catalytic reduction (SCR). SCR is a relatively expensive exhaust gas NO_x removal process that has been applied to onshore turbines, but has not been demonstrated for the demanding duty cycles in offshore applications. Thus, catalytic combustion is viewed as a technology that may compete with SCR for future gas turbine NO_x control applications.

Clearly, strong economic and environmental incentives exist for developing catalytic combustion. However, as discussed in this report, significant technical barriers place the horizon for commercialization of this technology at least five to ten years away.

3.0 SUMMARY/CONCLUSIONS

Currently, local regulations in certain areas of the U.S. mandate NO_x emissions below 10 ppm (dry, at 15% O₂) for new onshore gas turbines. This level has also been proposed as a target for the next generation of controls for offshore turbines. Use of a catalyst to promote and stabilize combustion would allow operation of stationary gas turbine combustors at lower fuel/air ratios and lower peak temperatures than is possible with any other combustion modification technique. Consequently, the catalytic combustor has the greatest potential for attaining ultra low thermal NO_x emissions. For gaseous fuels and low nitrogen content liquid fuels, the catalytic combustion process is capable of attaining NO_x levels below 10 ppm, as has been demonstrated in bench and full scale tests. Thus, successful application of this technology would obviate the need for the relatively expensive exhaust gas treatment systems which are now required in certain onshore applications to achieve NO_x levels below 10 ppm. Other combustion modification techniques being developed, such as the lean premixed and rich-quench-lean processes, may eventually be able to achieve emissions approaching 10 ppm. However, their potential for controlling emissions is not as great as catalytic combustion.

Many technical problems must be resolved before catalytic combustion can be applied to stationary gas turbines. The most significant area is the development of materials, both active catalysts and structural components, that can survive the operating temperatures and transients experienced in stationary gas turbine applications. Noteworthy progress has been made in the development of active monoliths, where catalytic elements or compounds are incorporated directly into the substrate material and in mixed metal oxide catalytic compounds that are potentially more stable at elevated temperatures. However, none of the catalysts developed to date has demonstrated the ability to satisfy the durability requirements of stationary turbines. Structural failures (cracking of substrates) resulting from temperature gradients during on-off cycles or load swings is the most significant problem. Additionally, loss of activity due to volatilization, migration, or sintering of catalytic materials is a deficiency that must be resolved. Clearly, research breakthroughs are required in catalytic combustor materials.

Other issues facing developers are in the areas of controls and fuel-air mixing. The overall fuel-air ratio and total gas volume throughput must be maintained within ranges that yield stable combustor operation during load swings. Under all conditions, relatively uniform fuel air mixtures are required at the combustor inlet in order to avoid local overheating of the catalyst. These problems are amenable to solution through extension of existing control and mixing technologies.

Alternative catalytic combustor configurations to the conventional single stage approach may lessen the maximum temperature demands on catalysts. One hybrid combustor concept being developed involves operating the catalyst bed at lower temperatures using a portion of the fuel and injecting additional fuel downstream of the bed to achieve the required turbine inlet temperature. This technique results in improved active material stability and allows the use of substrate materials that are better able to withstand thermal shock. However, the contribution of secondary fuel injection to NO_x emissions may be significant and catalyst durability has yet to be adequately demonstrated, even with this system's lower temperatures.

Based on the status of catalytic combustion technology and the challenges remaining to be addressed, it appears that commercial application of catalytic combustor to stationary gas turbines is at least five to ten years away. The limited magnitude of catalytic combustor research and development activities in the

The Minerals Management Service's offshore NO_x control program is targeting demonstration of advanced NO_x control techniques within about 5 years. This timeframe is dictated by the need to resolve environmental issues related to existing and near-term OCS development activities. Based on this review, catalytic combustion appears to have a low probability for commercial application to stationary turbines soon enough to have the desired impact. However, because of the significant benefits this technology could provide should a materials breakthrough occur, it is recommended that MMS monitor research progress over the next two years. This could be accomplished through brief annual surveys of active R&D progress and the preparation of addenda updating this report. If significant improvements in catalytic materials are adequately demonstrated within this timeframe, MMS could redirect or supplement program funding to support development activities required to apply catalytic combustion technology to offshore gas turbines.

4.0 CATALYTIC COMBUSTION PRINCIPLES

All catalytic combustion processes are based on heterogeneous oxidation reactions that can occur in the presence of a catalytic surface. These reactions have activation energies that are considerably lower than the corresponding homogeneous reactions. Thus, in the presence of a catalyst, oxidation rates are higher when operating temperatures are low. In practice, this allows fuels to be burned with high combustion efficiency when temperatures are below levels required to ignite and stabilize a conventional flame or when fuel-air ratios are outside flammability limits.

Two generic classes of catalytic combustion processes exist:

- *Heterogeneous catalytic reactions* in which surface reactions dominate. This process is characterized by lower operating temperatures and volumetric heat release rates. Examples include gas fueled radiant space heaters and liquid fueled hand warmers.
- *Catalytically stabilized gas phase reactions* in which surface reactions serve to promote gas phase oxidation reactions. This process can achieve very high heat release rates since most of the oxidation process occurs in the gas phase at higher temperatures. Only catalytically stabilized combustion processes are practical for gas turbine applications due to the need for relatively compact combustors.

4.1 Catalytically Stabilized Combustion Process

The general configuration of a catalytically stabilized combustor is illustrated in Figure 4-1. Three steps are involved in the process: mixing of fuel and combustion air, preheating of the fuel/air mixture to a temperature sufficient for ignition by the catalyst, and oxidation of the fuel within the catalyst bed. Mixture preheating is achieved through the gas turbine's air compression process and by burning a portion of the fuel upstream of the catalyst bed. For gas turbines, the bed is usually in the form of a honeycomb structure with catalytic material dispersed on the surfaces of the passages. Detailed considerations regarding catalytic combustor configurations are provided following a discussion of catalytic combustor reactions.

Catalytic combustion systems can operate in three different rate controlling regimes, as shown in Figure 4-2. When catalyst surface temperatures are low, reactions occur only on the catalytic surface and the overall rate of oxidation is controlled by heterogeneous reaction rates (Region A). Upon increasing surface temperature, reaction rates increase until a transition occurs to a mass transfer limited regime (Region B). Here the mass transfer rates of reactants from the bulk gas to the surface and products from the surface to the bulk gas limit the overall oxidation rate. Within this range, reactions still occur primarily at the catalyst surface and increases in temperature have little impact on the overall reaction rate. However, at sufficiently high surface temperatures homogeneous gas phase combustion initiates in the boundary layer and then in the bulk gas (Region C). This results in a dramatic increase in overall reaction rate, sufficient to provide volumetric heat release rates compatible with gas turbine combustors. The catalytically stabilized homogeneous reaction regime is characterized by most reactions occurring in the gas phase. The role of the catalytic surface is to support these homogeneous reactions by supplying both energy and active radical species. Without the presence of a catalytic surface the homogeneous reactions would not be self-sustaining.

Processes that occur in the entrance region of one channel in a catalytically stabilized combustor are illustrated in Figure 4-3. Near the inlet surface reactions occur and the rates are mass transfer controlled. Further downstream homogeneous combustion initiates in the boundary layer as a result of energy and active species generated at the surface. The boundary layer then expands leading to homogeneous reactions throughout the channel. Oxidation reactions proceed to completion with combustion products exhausted

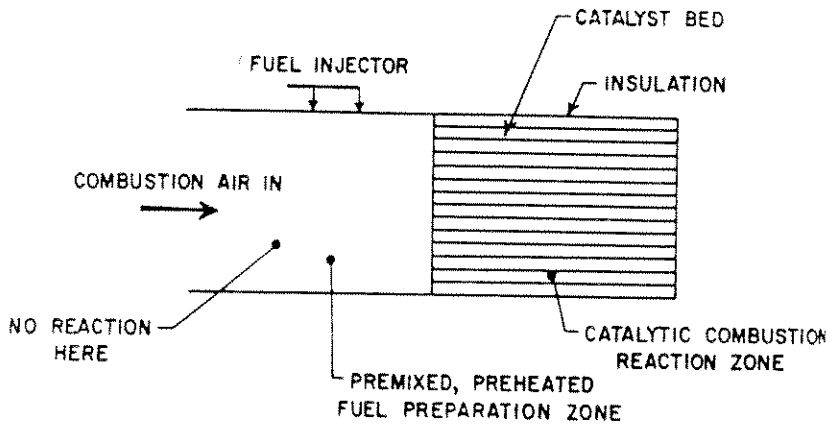


Figure 4-1. A Schematic Diagram of a Catalytic Combustor

(From Reference 23)

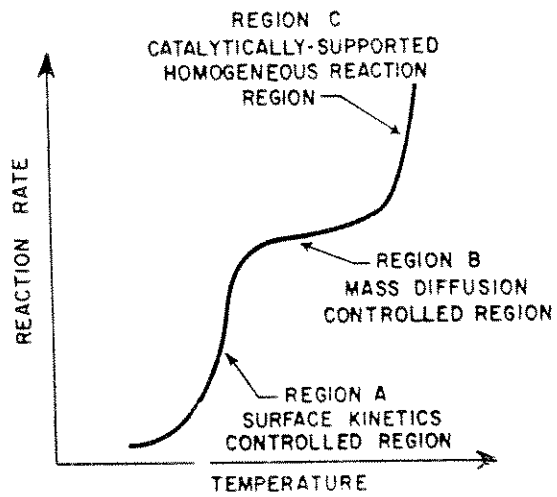


Figure 4-2. Catalytic Combustion Operating Regimes

(From Reference 23)

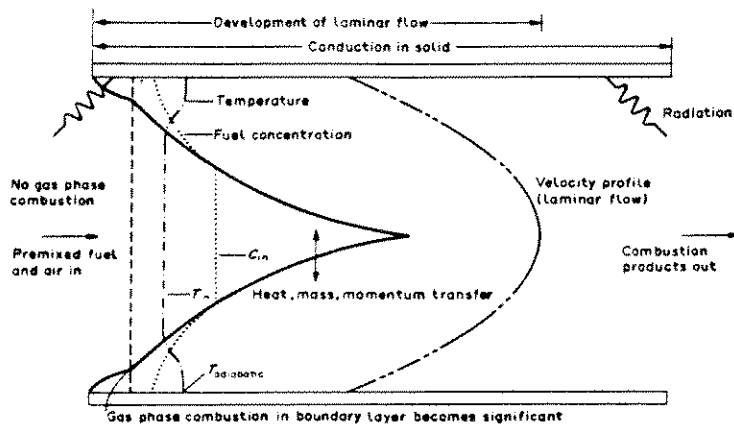


Figure 4-3. Processes in Channel of Catalytic Combustor

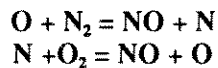
(From Reference 20)

from the channel exit. Increasing the flow rate of gases entering the channel can lead to a loss of combustion stability due to cooling of the catalytic surfaces at the inlet. If reactions are extinguished at the inlet, the process continues down the channel resulting in combustor blow out.

The primary mechanisms determining wall temperature with a catalytically stabilized combustor are the rate of reaction at the surface and the rate of convection heat transfer from the surface. Conduction through the wall is minimal since symmetric thermal conditions exist on the opposite side and, except for regions near the entrance and exit, radiation heat losses are low. As surface reactions are mass transfer limited, the balance between heat and mass transfer generally results in wall temperatures within catalytically stabilized combustors that are close to the adiabatic flame temperature of the entering fuel-air mixture.

4.2 NO_x Control With Catalytic Combustors

When burning fuels low in bound nitrogen (e.g. natural gas), NO_x is primarily formed through fixation of molecular nitrogen and oxygen in the combustion air. This formation of "thermal" NO_x is approximately described by the Zeldovich mechanism.



A simplified rate equation derived from these reactions is shown below:

$$d(\text{NO})/dt = 2 A \exp(-E_A/RT) (\text{O}_2)^{1/2} (\text{N}_2)$$

where (NO) = NO_x concentration, (O₂) = oxygen concentration, (N₂) = nitrogen concentration, t = time, A = pre-exponential constant, E_A = activation energy, R = gas constant, T = temperature.

Since the activation energy for this process is high, the formation rate increases strongly with combustion temperature. This equation also illustrates the dependence of thermal NO_x formation on oxygen concentration, nitrogen concentration, and residence time.

Combustion in a conventional gas turbine occurs in the form of a diffusion flame. In this flame structure, the temperature must, somewhere, approach that of a stoichiometric flame. It is in these regions that the peak combustor temperatures are attained and high NO_x formation rates are experienced. In a catalytic combustor, fuel and air are premixed prior to ignition. Furthermore, the mixture can be significantly leaner than that attainable with non catalytic premixed combustors. As a result, flame temperatures throughout the catalytic combustor can be maintained below the threshold at which the rate of thermal NO_x formation becomes significant - about 2800°F.

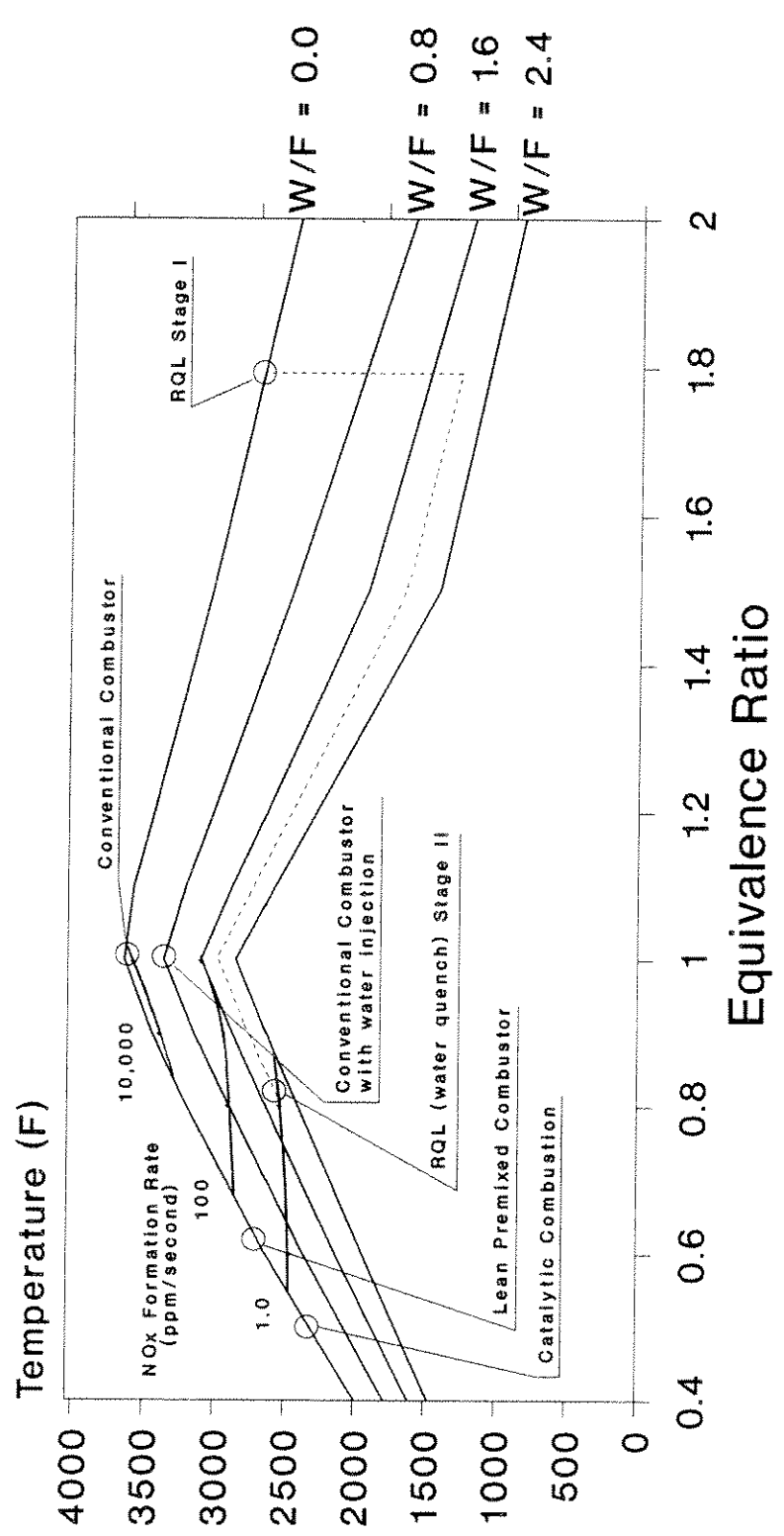
To add perspective to the NO_x control capability of catalytic combustors, the approximate design operating points of conventional combustors and Low-NO_x combustor concepts are shown on Figure 4-4, a plot of adiabatic flame temperature versus equivalence ratio¹ for various levels of water injection. Contours of constant NO_x formation rate are overlaid on this figure. The combustors shown are described below:

- Conventional combustor - design operating point has primary zone fuel-air ratio close to stoichiometric

$$1 \quad \text{Equivalence Ratio} = \frac{\left(\frac{\text{Fuel}}{\text{Air}}\right)_{\text{actual}}}{\left(\frac{\text{Fuel}}{\text{Air}}\right)_{\text{stoichiometric}}}$$

Combustion Modification Techniques

Figure 4-4



Fuel Gas: Methane

Note: Combustion Air Temp. = 600 F, relative humidity = 60% (at 60 F and 1 atm pressure), pressure = 10 atm

- Conventional combustor with water injection - water injection at a rate equal to 0.8 lb per lb of fuel
- Rich-quench-lean (RQL) - two stage combustion process (first stage fuel rich, second stage fuel lean) with water injection (2.0 lb/lb fuel) between stages
- Lean premixed - fuel and air are premixed at an equivalence ratio of about 0.6 prior to ignition
- Catalytic combustion - fuel and air premixed at an equivalence rates of about 0.5 prior to ignition

Of these options, catalytic combustion has the ability to achieve the lowest peak flame temperatures and to provide the best control of thermal NO_x .

Catalytic combustion is not nearly as attractive when burning fuels that contain significant levels of bound nitrogen (e.g. heavy liquid fuels), because other NO_x formation mechanisms must be considered. Under lean combustion conditions, fuel nitrogen is rapidly converted to HCN which is subsequently oxidized (usually with high efficiency) to "Fuel NO_x ." Control of fuel NO_x in catalytic combustion is difficult, requiring either a fuel-rich stage or special catalytic materials with a selectivity that minimizes the formation of fuel NO_x . Although some positive experimental results have been reported in these areas, the long-term outlook for catalytic combustion is much more favorable for natural gas and other nitrogen-free fuels than for heavy fuel oil.

For offshore production platforms, the primary gas turbine fuel is natural gas. No. 2 oil is used during periods when natural gas is unavailable. Both of these fuels have very low bound nitrogen contents. Thus, lean catalytic combustion processes should provide very effective NO_x control for offshore gas turbines.

4.3 Combustor Configurations

Many combustor configurations have been proposed and investigated for future application of catalytic combustion to gas turbines. Most can be categorized as one of three generic types: "single-stage," "hybrid," and "two-stage." The operating principles, performance advantages and key problems associated with each class are summarized below:

Single Stage Catalytic Combustors

Single stage catalytic combustors, as illustrated in Figure 4-5a, offer potentially the least complicated and most compact design. Primary fuel is burned in a diffusion flame at the upstream end of combustor to provide sufficient energy to attain the catalyst ignition or "light off" temperature. Downstream of the primary reaction zone, secondary fuel is mixed with the highly vitiated primary combustion products. This mixture then passes through the catalyst bed where oxidation reactions proceed to completion. Finally, dilution air can be added prior to entry into the turbine inlet vanes.

One area of concern is the primary zone diffusion flame, which burns at approximately stoichiometric air-fuel ratios and therefore produces NO_x at very high rates locally where peak flame temperatures are quite high. The engineering challenge here is to arrange for rapid mixing so that the NO_x reactions are quenched.

Catalytic Combustor Configurations

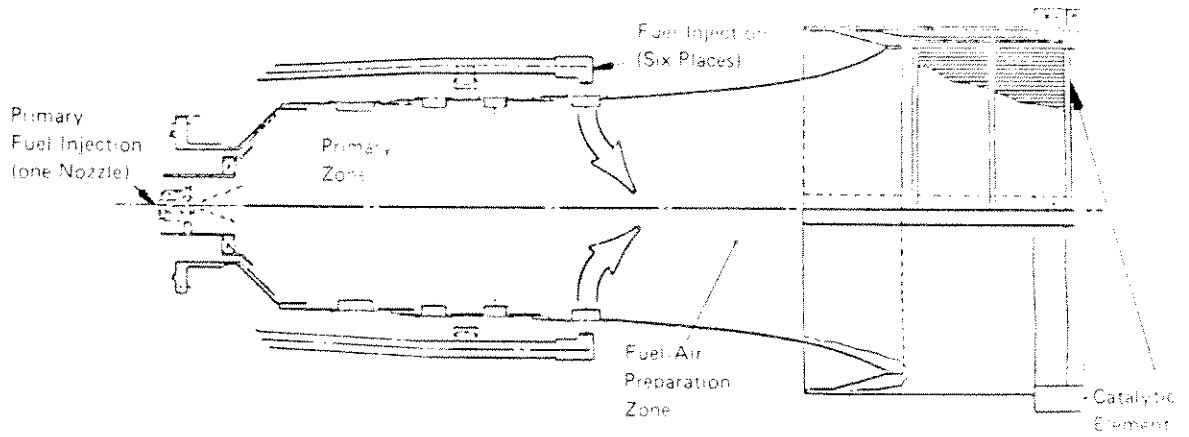


Figure 4-5a. Single-Stage Catalytic Combustor

(From Reference 21)

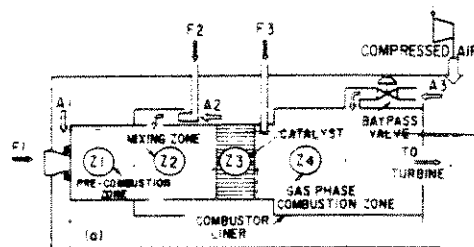


Figure 4-5b. Hybrid Catalytic Combustor

(From Reference 5)

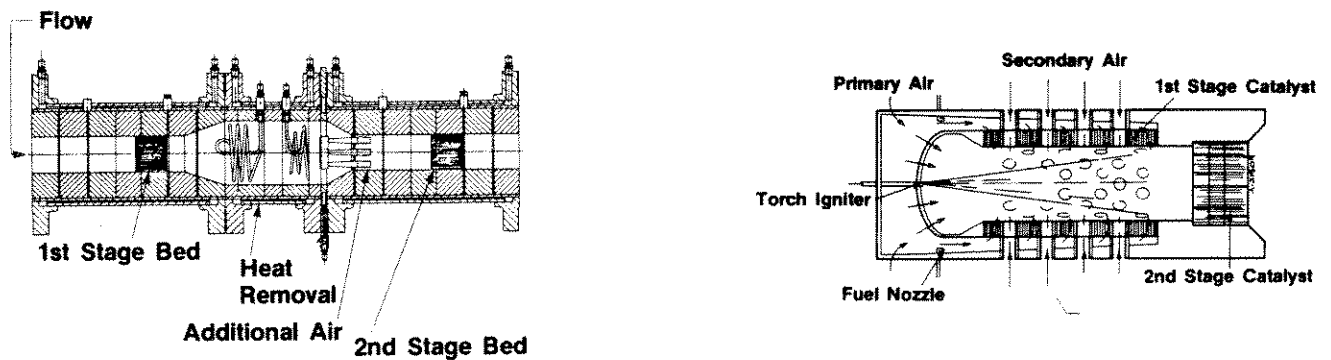


Figure 4-5c. Two-Stage Catalytic Combustor

(From Reference 16)

The secondary fuel premixing zone is also a critical area in the design of this type of combustor. Preventing ignition of the secondary fuel prior to the mixture entering the catalyst bed is clearly important. Sources of ignition include the primary flame and hot spots on the catalyst front face. An equally important requirement is the attainment of relatively uniform mixtures entering the catalyst bed. Maldistribution of secondary fuel will result in hot zones in the catalyst bed which can drastically shorten catalyst life. Furthermore, the overall fuel-air ratio entering the catalyst must be within a relatively narrow range that maintains stable combustion without overheating the catalyst. With even moderate turbine load changes, variable geometry controlling the air distribution to and around the catalyst would likely be required. Finally, in this single stage arrangement the catalyst must be capable of operating at temperatures at least equal to the turbine inlet temperature at full load.

NO_x control with this arrangement would be most promising for fuels with little or no bound nitrogen, such as natural gas or distillate oils. Combustion of heavier oil with significant bound nitrogen may result in undesirably high NO_x emissions due to the high conversion efficiency of fixed nitrogen to NO_x under lean combustion conditions.

Hybrid Catalytic Combustors

Significant improvements in catalyst durability can be realized by lowering the required catalyst operating temperature. However, this must be accomplished without decreasing turbine inlet temperature in order to maintain cycle efficiency. These incentives have led to the development of a hybrid combustor concept. Figure 4-5b illustrates one type of hybrid combustor. Three combustion zones are incorporated into this design -- a diffusion flame, catalytically stabilized combustion, and a second diffusion flame. The initial sections, which consist of primary combustion zone (for preheat), secondary fuel mixing zone, and catalyst are similar in concept to the single stage catalytic combustor described previously. However the fuel-air ratio entering the catalyst bed is leaner, resulting in lower catalyst temperatures. Additional fuel is then injected downstream of the catalytic to raise gas temperature to the required turbine inlet level.

Most of the design problems described for the single stage combustor are applicable to this concept, with the exception that lower operating temperatures may provide greater tolerance to excursions in local or overall catalyst temperature. The added complication of fuel injection and combustion downstream of the catalyst raises new concerns. First, the combustion process must be controlled to rapidly quench high temperature zones where thermal NO_x forms. Also, the temperature distribution at the turbine inlet must be controlled to provide an acceptable pattern factor. Both of these requirements dictate excellent control of the mixing process in this last combustion zone.

Another hybrid concept incorporates a fuel rich homogeneous combustion stage followed by a lean catalytic stage. In this configuration the fuel rich zone can provide a means to control NO_x formed from nitrogen bound in fuel molecules. It also releases sufficient energy to maintain the required catalyst inlet temperature and may resolve fuel distribution problems. However, this concept does not provide the benefits of reduced catalyst operating temperature. Furthermore, thermal NO_x may form in significant quantities when air is added to the rich zone products.

Two Stage Catalytic Combustors

Effective control of NO_x emissions from fuels containing significant levels of bound nitrogen will probably require incorporation of an initial fuel rich combustion zone. Under optimized fuel rich combustion conditions, most of the bound nitrogen can be converted to molecular nitrogen. The two stage catalytic combustor concept was developed in part to achieve control of fuel NO_x . As shown in Figure 4-5c, this system incorporates two catalyst zones. The first catalyst is supplied with a fuel rich mixture and the fuel is partially oxidized. Sufficient air is added between stages to operate the second catalyst under very lean conditions.

Many of the design problems associated with this system are similar to those for the single stage combustor: attaining uniform fuel air ratios entering each catalyst stage, avoiding flashback in the regions upstream of each bed, controlling overall fuel/air ratio in each stage as load changes, and achieving catalyst durability in the second stage which operates close to the turbine inlet temperature. In addition, soot formation and deposition in the fuel rich stage must be limited to prevent deactivation of the catalyst.

4.4 Catalytic Combustor Materials - Overview

The catalyst bed of a gas turbine catalytic combustor must provide surface area adequate to promote reactions while minimizing pressure drop (to maintain cycle efficiency). Consequently, most are configured in the shape of a honeycomb, examples of which are shown in Figure 4-6. Approximately 100-600 cells per square inch are incorporated into these elements. The bed often consists of a substrate that provides structure, a wash coat to increase surface area and the active catalytic materials dispersed on the wash coat. Substrates can be formed from either ceramic (Figure 4-6a) or metallic (Figure 4-6b) materials. Examples of ceramics include mullite, cordierite, zircon, and silicon carbide. Metallic substrates that have been used include FeCrAlloy and Kanthal. The most common wash coat is gamma-alumina. The active catalytic materials are noble metals (primarily platinum or palladium), oxides of transition metals, or combinations of these. In general, the noble metals offer better low temperature activity while some metal oxides can tolerate higher operating temperatures. Active monoliths in which the catalytic materials are incorporated into the substrate have also been developed.

Two essential performance requirements exist for materials used in catalytic combustors. First, the activity of the catalyst must be sustained after long-term use (4000-8000 hr) at operating combustion temperatures. Second, the structural integrity of the monolith must be maintained through the thermal cycling which results from turbine start-ups, shut downs and/or load changes. ~ 1 yr

Development of catalyst bed materials that meet both these requirements is critical to the commercialization of this technology, and at the time of this review there are no materials yet discovered which the industry is confident will be satisfactory. This is one of the critical hurdles which must be passed over before catalytic combustion can be successfully applied to gas turbines. Consequently, the materials issues are explored in greater depth within the next two sections. Section 5 provides a review of available materials for gas turbine catalytic combustors while Section 6 documents development activities that have targeted improvements in this key area. It will be seen that the breakthroughs which are required in catalyst material appear to be at least five years into the future.

Catalytic Combustor Substrates

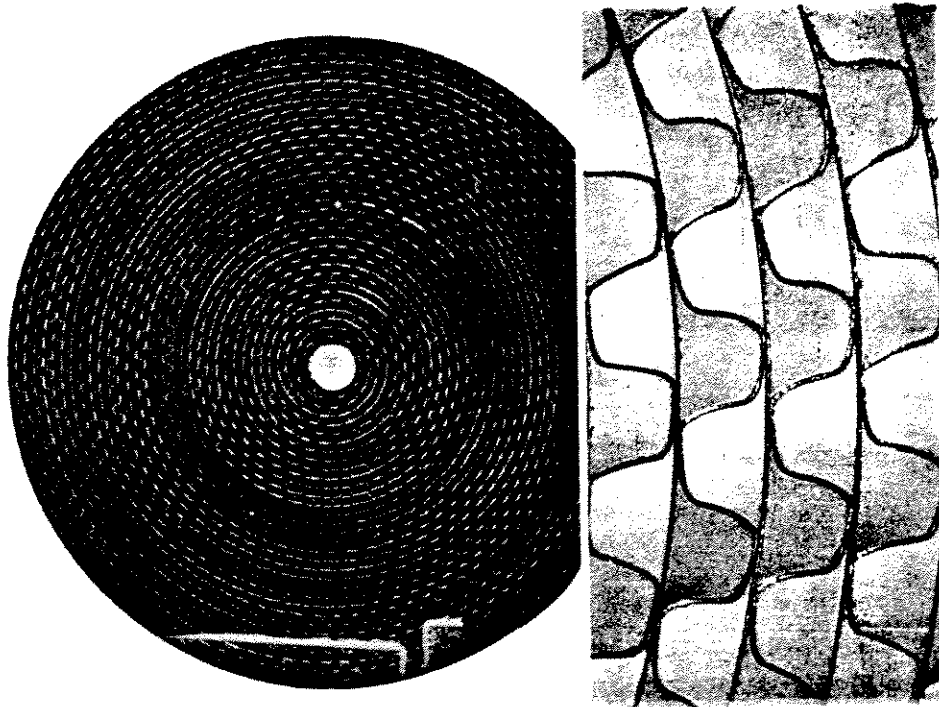


Figure 4-6a. Metallic Substrate

(From Reference 4)

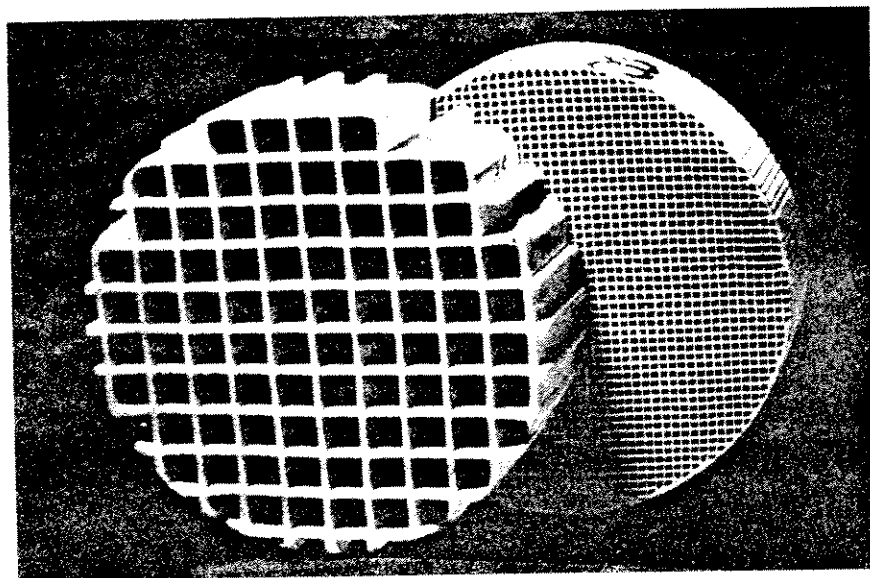


Figure 4-6b. Ceramic Substrate

(From Reference 10)

5.0 CATALYST MATERIALS TECHNOLOGY

The materials used to construct catalytic combustors are the most critical factor in the success of this technology. The following sections review available technology in the areas of catalysts, substrate materials, wash coats, and active monoliths. None of these available materials is generally felt to be satisfactory. The key materials-related hurdles that must be overcome to commercialize catalytic combustion for stationary gas turbines are subsequently identified.

5.1 Catalytic Materials

Materials that can be used to catalyze combustion reactions include noble metals and oxides of transition metals. Each class has distinct performance advantages and weaknesses. Although discussed separately below, prototype applications often employ combinations of noble metals and oxides, either uniformly distributed or segregated in order to take advantage of specific performance characteristics.

5.1.1 Noble Metals

A significant characteristic of noble metals is their high specific activity for oxidation of hydrocarbons. This characteristic can allow initiation of catalytic reactions at low mixture inlet temperatures. Within the noble metals group, ruthenium and rhodium are generally the most active, followed in order by palladium, osmium, iridium, and platinum. However, for the relatively high temperature catalytic combustors being developed for gas turbines, only palladium and platinum appear to be viable candidates. The other noble metals are generally eliminated due to their high volatility, tendency to form less active metal oxides, or limited availability.

Platinum and palladium enhance hydrocarbon combustion reactions through their ability to activate O-O, H-H, O-H and H-C bonds. This phenomenon effectively allows oxidation reactions to proceed rapidly at relatively low temperatures. Platinum is more effective in oxidizing saturated hydrocarbons, while palladium is more effective for CO. Often mixtures of the metals are used to take advantage of differences in performance.

Relative to transition metal oxides, the noble metals offer the performance advantages of higher specific activity for hydrocarbon oxidation and less susceptibility to poisoning by sulfur at low temperatures. These are tempered by several key performance limitations. First, when operating at gas turbine combustor temperatures (1800-2500°F), the noble metals can agglomerate, resulting in a significant reduction in active sites and a decrease in activity. Furthermore, these metals are quite volatile at these temperatures, resulting in rapid depletion of the active materials. Consequently, it is unlikely that noble metals alone can be effectively applied to high temperature gas turbine combustors.

5.1.2 Transition Metal Oxides

While transition metal oxides are not as active as noble metals in the oxidation of hydrocarbons, combinations of these oxides may produce a relatively stable and active catalytic material for gas turbine combustors. Highly catalytic metal oxides materials are generally those whose metal ions exhibit multiple valance states. Potentially attractive candidates for catalytic combustors include oxides of cobalt, nickel, chromium, copper and lanthanum. However, most of these oxides alone exhibit relatively high volatility at gas turbine combustor operating temperatures. Many also form low melting point eutectics with silica, a common substrate material. Furthermore, the oxides can migrate through substrate materials, resulting in potential structural weakness.

Some mixed metal oxides solid solutions can yield higher catalytic activity and provide greater stability at elevated temperatures than their individual components. Stability benefits are realized when the solid solutions formed are non-ideal. Examples that have shown improved performance include $\text{Cr}_2\text{O}_3 - \text{CO}_3\text{O}_4$ and $\text{La}_2\text{O}_3 - \text{Cr}_2\text{O}_3$. These solutions can be used in the conventional active layer/substrate configuration or, as discussed in section 5.4, integrated into the material that is used to form the substrate.

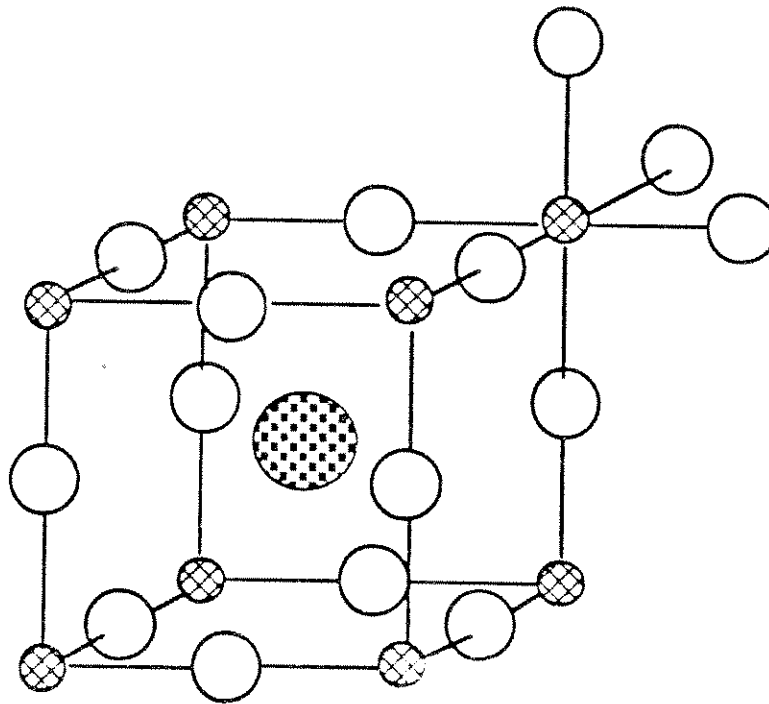
Mixed metal oxide compounds are a promising group of catalytic materials that may provide the required stability at elevated temperature. In these compounds two different metal ions are incorporated with oxygen into the unit cell structure. The general classes of these compounds include perovskites, spinels and ilmenites. Perovskites have an atomic formula of ABO_3 (where A and B are the metal ions) and assume a cubic close-packed arrangement as shown in Figure 5-1. Ilmenites have the same formula, but assume a hexagonal close packed configuration. Spinelns have a formula of AB_2O_4 and assume a cubic close packed arrangement. Examples of compounds within each of these classes are provided in Table 5-1. It is also possible to chemically bind noble metals into these structures. Addition of trace amounts of platinum to perovskites can result in significantly increased catalytic activity with reduced loss of platinum at elevated temperatures. As with solid solutions, these materials can either be coated on the substrate or incorporated into the material from which the substrate is formed.

5.2 Substrates

The most effective configuration for gas turbine combustor catalyst substrates is that of a honeycomb. This shape provides adequate catalyst surface area and acceptable combustor pressure drop within a compact volume. The substrate can be formed from either ceramics or metal alloys. Of the wide range of ceramics that have been employed, the most common are mullite, cordierite, alumina, zircon, and silicon carbide. Metals that have been used include FeCrAlloy and Kanthal.

Ceramic substrates have been most commonly used in catalytic combustor development programs. They offer high temperature capabilities and are well suited to application and retention of wash coats and catalysts. Table 5-2 provides typical properties for ceramic substrate materials. In general, materials with high maximum use temperature, low thermal expansion coefficient, and high thermal stress resistance are desirable. The ceramic elements can be formed by a number of manufacturing processes, including extrusion, slip casting, pressing, and rolling or layering corrugated sheets.

Perhaps the most significant problem preventing successful application of ceramic honeycomb catalyst supports is the difficulty in coping with thermal stresses. These stresses are induced by a combination of thermal expansion of the material and restraint to free movement. Very high stresses can be produced during transient operations, such as start-up and shut-down. Even under steady state conditions these levels can be significant. Design approaches to reducing this problem include use of materials with a low thermal coefficient of expansion and fabrication of small and/or thin parts. However, to date no ceramic structure has demonstrated the ability to survive thermal cycling representative of requirements for stationary gas turbines. Innovative and intensive development programs may resolve this problem; however, based on progress to date and the current level of activity (see Section 6), this is not likely to occur in the near future.






-  A - SITE CATION
-  B - SITE CATION
-  OXYGEN ANION

Figure 5-1. The Perovskite Structure
(From Reference 24)

Table 5-1
EXAMPLES OF MIXED OXIDE COMPOUNDS

(From Reference 11)

Spinel: AB_2O_4 (Cubic close packed)	Perovskite: ABO_3 (Cubic close packed)	Ilmenite: ABO_3 (Hexagonal close packed)
$MgAl_2O_4$	$LaCrO_3$	$FeTiO_3$
$MgCr_2O_4$	$CaTiO_3$	$NiTiO_3$
$NiCr_2O_4$	$YAlO_3$	$CoTiO_3$
$Mg_xCo_{1-x}Cr_2O_4$	$LaAlO_3$	$MgTiO_3$
$CoAl_2O_4$	$YCrO_3$	$LiNbO_2$
$NiAl_2O_4$	$YMg_{0.05}Cr_{0.95}O_3$	
$MgAl_2O_4:NiAl_2O_4$	$La_{0.95}Mg_{0.05}CrO_3$	
$Ni(Al_{0.3}Cr_{0.5}Fe_{0.2})_2O_4$	$(Th_{0.1}La_{0.9})(Fe_{0.8}Al_{0.2})O_3$	
$Ni_{0.5}Mg_{0.5}(Al_{0.5}Cr_{0.3}Fe_{0.2})_2O_4$	$SrRuO_3$	
	$(Ba_{0.1}La_{0.9})(Al_{0.9}Pt_{0.1})O_3$	

Table S-2
TYPICAL PROPERTIES OF CERAMIC SUBSTRATE MATERIALS

Material	Composition	Porosity Vol %	Melting Point		Maximum Use Temperature		Coefficient Thermal Expansion(α) $\times 10^6/^{\circ}\text{C}$	Young's Modulus (E) $\times 10^3$ psi	Fracture Strength(σ) $\times 10^3$ psi (1000 $^{\circ}\text{C}$)	Thermal Conductivity(κ) cal/s/cm 2 / $^{\circ}\text{C}$ (1000 $^{\circ}\text{C}$)	Thermal Stress Resistance ⁽¹⁾ (R)
			$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$					
<i>Ceramics:</i> Alumina (sintered)	99.8Al ₂ O ₃	3-7	2030	3685	1900	3452	8.6	53	22	0.014	0.68
Cordierite	2MgO·2Al ₂ O ₃ ·5SiO ₂		1470	2678	1300	2372	1.0	-25	11	0.0025	1.10
Mullite (sintered)	72Al ₂ O ₃ ·28SiO ₂	3-10	1810	3290	1750	3182	4.5	21	12	0.008	1.02
Spinel (sintered)	99.8MgAl ₂ O ₄	3-10	2130	3866	1850	3362	8.2	35	11	0.013	0.50
Zircon (sintered)	99.5ZrSiO ₄	5-15	2420	4388	1800	3272	4.2	30	6	0.008	0.38
Stabilized zirconia (sintered)	92ZrO ₂ ·4HF0 ₂ ·4CaO	3-10	2550	4622	2200	3992	7.2	22	15	0.005	0.47
Silicon carbide (sintered)	α -SiC(98% dense)	-	5126	9259	1530	2800	4.7	50	66	0.100	28.10
Silicon nitride (hot pressed)	Si ₃ N ₄ (98% dense)	-	3450	6242	1200	2200	3.0	40	64	0.045	24.00
Chrome alumina cermet	77Cr·23Al ₂ O ₃	2	1850	3362	1300	2372	8.9	37.5	20	0.050	3.00
Beryllia (sintered)	99.8BeO	3-7	2570	4658	1900	3452	8.9	45	10	0.046	1.15
Magnesia (sintered)	99.8MgO	3-7	2800	5072	1900	3452	13.5	30.5	12	0.016	0.46
Titania (sintered)	99.5TiO ₂	3-7	1840	3344	1600	2912	8.7	-	6	0.008	-
Thoria (sintered)	99.8ThO ₂	3-7	3050	5522	2500	4532	9.0	21	7	0.007	00.26

$$(1) \quad R = \frac{1 - \nu}{\sigma \alpha E}, \text{ where } \nu = \text{Poisson ratio}$$

(From Reference 11)

5.3 Wash Coats

In the majority of catalytic combustor designs a wash coat is applied to the substrate as a means of dispersing the catalytic material and increasing the effective surface area. The most common washcoat material is gamma alumina. However, a phase change from gamma alumina to alpha alumina occurs at gas turbine combustor temperatures, which results in a significant decrease in surface area. To minimize this effect, stabilizing additives (e.g. BaO, CeO₂, or CsO) can be utilized. Other washcoat materials that have been used include zirconia and thoria. Both are attractive due to their higher sintering resistance. However, washcoats that are able to maintain surface area at gas turbine operating conditions have yet to be successfully demonstrated.

Compatibility of the catalyst washcoat and substrate material is an important consideration in developing a durable catalyst bed. Two of the more critical factors are the relative thermal expansion and chemical interaction. Significant differences in thermal expansion coefficient of the substrate and washcoat materials can result in separation of the washcoat as the bed experience changes in operating temperatures. Interaction of metal oxide catalysts in the washcoat with the substrate material can result in significant weakening of the support structure and loss of catalyst activity. This can be attributed to the formation of low melting point eutectics or the migration of metal oxides into the substrate.

The two washcoat problems discussed above have not yet been resolved. The first, loss of surface area, may not be a critical issue in the successful commercialization of catalytic combustors. Researchers have demonstrated that very high surface areas are likely not required at the elevated operating temperatures characteristic of gas turbine combustors. The second, materials compatibility, is still an important consideration for conventional washcoat/substrate configurations. However, use of an active monolith as discussed below may provide an effective solution.

5.4 Active Monoliths

A promising concept in catalytic combustor design is the incorporation of catalytic compounds or mixtures into the material from which the substrate is formed. This results in what has been coined an "active monolith". The primary advantage which this system may offer is the elimination of destructive catalyst/washcoat/substrate interactions. Active monoliths formed in part from metal oxide components may provide a catalyst system able to perform well at the expected gas turbine operating temperatures. The active monolith would have an effective surface area significantly lower than wash coat/substrate configurations. However, as noted above, it has been demonstrated that very high surface areas are likely not required for catalytically stabilized combustors. But, as described in Section 6, development work to date has not produced an active monolith that can structurally survive gas turbine operating conditions. With significant research into materials and structural design, the active monolith concept may lead to a successful catalytic combustor. However, based on progress to date, this is not likely to occur in the near future.

6.0 MATERIALS AND PROTOTYPE COMBUSTOR DEVELOPMENT PROGRAMS

Provided below are highlights of recent or ongoing materials and prototype combustor R & D activities aimed at producing viable catalytic combustors for gas turbines. While not a comprehensive review, most of the recent key efforts are described. This section was assembled through a review of the pertinent literature and through contacts with organizations active in funding or conducting catalytic combustion R&D. Only publicly disclosed information is included. This section is followed by a summary of the key technical hurdles that must be overcome to successfully commercialize catalytic combustors for stationary gas turbines.

6.1 *Research and Development Programs*

Materials and Combustor Research at Acurex

Acurex has conducted diverse and extensive development activities in the catalytic combustion field under the sponsorship of the U.S. EPA and others. Specific applications have included gas turbines and boilers. Emphasis has been placed on both materials and combustor development. Described below are portions of their gas turbine related activities.

Acurex has evaluated in a test reactor over 30 catalysts utilizing a variety of substrates with noble metal or metal oxide active materials. Over test times of about 50 hours they found that all of the noble metal catalysts experienced large decreases in activity. They concluded that bed temperatures must be limited to 2400°F. In these tests all ceramic substrates failed structurally and the one metal substrate experienced problems in retaining its coating of catalyst. Although the metal oxide catalysts were less active than the noble metal catalysts, high heat release rates were obtained at bed temperatures of 2600°F. Acurex concluded that the metal oxide catalysts should have greater durability than the noble metal counterparts. However, interaction between the catalytic and substrate materials often led to structural weakness and failure resulting from thermal shock.

Two promising developments from Acurex's work are the graded cell reactor and the active monolith catalyst. The former concept incorporates two or more catalyst substrates in series, each with different cell sizes. Use of larger cells in the front segment with cell size decreasing in subsequent segments was demonstrated to improve blowout characteristics at high throughput. As a result, significantly higher combustor loadings (heat release rate per unit volume) are possible than with uniform cell sizes. The active monolith results from incorporating active metal oxide catalytic materials directly in the substrate material before the substrate is formed. This concept was explored in part to resolve the problem of active layer/substrate interaction. Eight active monoliths were fabricated and tested by Acurex. All demonstrated acceptable activity, but failed structurally. Acurex indicated that improvements in fabrication techniques are required to resolve this problem.

Acurex has developed conceptual designs for gas turbine catalytic combustions and has tested scale models. Testing of a terbium-cerium-thorium catalyst on a graded cell ceramic substrate using propane fuel was conducted over a 1000 hour period to assess durability and performance. The catalyst survived these tests, which include 5 on/off cycles, without experiencing major cracks, loss at substrate materials, or other damage. Emission at the end of this period were as follows: NO_x - 2 ppm, CO - 12 ppm, and HC < 1 ppm.

Despite significant progress up to 1985, Acurex has concluded that further development and demonstration activities are required to resolve materials durability problems. Currently, Acurex is not active in catalytic combustion R&D.

Westinghouse Prototype Combustor Development

Under EPRI sponsorship and in conjunction with Engelhard, Westinghouse investigated application of catalytic combustion to distillate-fueled utility gas turbines. This work, which was completed in 1982, included conceptual design studies followed by performance testing in a full scale (14 in. diameter) combustor can. The catalyst bed used was developed by Engelhard and consisted of a noble metal catalyst on a magnesium - aluminum titanate substrate manufactured by NGK of Japan. The combustor configuration was that (as shown previously in Figure 4-5a) of a primary burner/secondary fuel addition single stage catalyst.

In performance testing of the combustor significant problems resulted from the secondary fuel injection process. Fuel-air ratio maldistribution entering the catalyst produced significant gradients in catalyst bed temperature. This effectively limited the maximum firing rate that could be attained without exceeding the substrate's maximum temperature of 2500°F. Furthermore, combustor exit pattern factors* of about 0.56 were measured, far in excess of the design target of 0.20. In addition, ignition of fuel upstream of the catalyst occurred during transfers of operation from primary fuel only to primary and secondary fuel. Catalyst durability could not be assessed during this work due to the limited hours of operation (the longest run was about 7 hours).

Westinghouse recommended further development activities in these critical areas: secondary fuel-air mixing, catalyst life and controls. They are currently not active in catalytic combustion R&D.

EPRI Sponsored Catalyst Durability Testing

The Electric Power Research Institute has established performance criteria that catalytic combustors must meet in order to be a viable technology for utility gas turbines. Key among these are the ability to operate without structural damage or significant loss of activity for at least one year at turbine inlet temperatures of 2300-2550°F and the ability to withstand thermal shock resulting from start-ups and shut-downs (300 cycles). To determine whether the mechanical properties of what they believed to be the best commercially available catalyst beds could meet these criteria, EPRI sponsored durability testing at Engelhard in the mid 1980's.

The honeycomb substrates selected were composed of aluminum titanate-based materials and were manufactured by NGK of Japan and Corning. Relevant characteristics of these materials are as follows:

*Pattern factor = (Peak Temperature - Average Temperature)/Average Temperature

	NGK	Corning
Material	Magnesium dioxide - Aluminum titanate Titanium dioxide	72% mullite 28% aluminum titanate
Thermal expansion coefficient	$0.5 \times 10^{-6}/^{\circ}\text{C}$	$0.5 - 1.9 \times 10^{-6}/^{\circ}\text{C}$
Melting Point	>3100°F	>3100°F
Bed Diameter	4.9 in.	4.9 in.
Cells/in ²	400-600	400-600
Web Thickness	0.15-0.20mm	0.15-0.20mm

From each material, cylindrical catalyst segments were formed by cementing extruded segments together. Each was then coated by Engelhard with a proprietary noble metal catalyst wash coat. Evaluations that were conducted included thermal cycling tests, catalytic combustion tests and 1000 hour isothermal aging tests.

The thermal cycling tests exposed the catalysts to temperature changes characteristic of turbine start-ups and shut-downs. Cracks were evident in the NGK substrate after 22 cycles and in the Corning material after 45 cycles. Both tests were terminated after 65 cycles due to significant damage. The combustion tests, which also included thermal cycling, further demonstrated substrate materials problems. The NGK substrate failed after 4 cycles, while the Corning substrate developed severe cracks throughout. The aging tests involved holding the catalysts at uniform temperatures (1600, 2000, and 2300°F) for 1000 hours each with catalyst activity measured before and after the exposures. The results revealed no loss of activity for the lower two temperatures and a moderate loss at 2300°F.

Based on the results of this work, the investigators concluded that significant improvements in substrate materials are required to meet the demanding operations of large stationary gas turbine combustors.

Engelhard Catalyst Development

Through internal funding and support from EPRI and GRI, Engelhard has been active in the development of catalysts for gas turbine combustors. They are optimistic about recent success achieved in the areas of substrates and active catalysts. Engelhard indicated that they have identified a ceramic substrate that shows promise for withstanding thermal shock and operation at gas turbine combustor temperatures. In a separate effort they have developed a noble metal-based catalytic material that is resistant to deactivation and thus shows promise for gas turbine application. Their next step is to integrate these two materials into a catalyst bed. This bed will be divided into segments, each of which is designed to achieve different performance characteristics. Specific information regarding this design is currently proprietary.

Substrate testing of Engelhard's catalyst is expected to take place at General Electric in 1989. If successful, a full scale demonstration could be initiated in the summer of 1990. The target applications for this combustor are large utility gas turbines.

Catalyst Materials Research At SRI International

Under GRI sponsorship, SRI International has investigated a series of mixed metal oxides with a perovskite structure. Their objective was to examine the fundamental properties of these complex oxide catalysts. Specifically, they correlated catalytic activity with the thermodynamic stability of the metal oxide, the lattice structure, the B-cation valence and oxygen nonstoichiometry. Most of the work centered on the first row transition metal lanthanates. They found that catalytic activity for methane oxidation when normalized to surface area, increased as follows: $\text{LaCrO}_3 < \text{LaFeO}_3 < \text{LaMnO}_3 < \text{LaCoO}_3 < \text{LaNiO}_3$. This series correlates inversely with thermodynamic stability. Other fundamental properties had less significant impacts on activity.

In their experiments, sintering of the catalysts was significant, even at 1830°F. The process was one of crystal growth through merging of smaller crystals which initiated at a temperature of about one-half the melting point (absolute). Thus, they have concluded that few perovskites are likely to maintain high surface areas at operating temperatures above 1830°F.

Based on more recent work, SRI believes that metal oxides combined with nonvolatile compounds can perform successfully at temperatures as high as 2200-2400°F. Consequently, they feel that the most critical issue is substrate durability. Along this line they suggest that silicon nitride or silicon carbide passivated with a protective layer may provide the required substrate properties. They projected that with appropriate funding a workable solution for gas turbine catalytic combustors may be available in two to three years, with a full scale demonstration occurring two years later. At this time, SRI, International is completing their final report for GRI and has proposed additional work on catalysts.

ULCA Catalyst Materials Research

Under GRI sponsorship, UCLA's Chemical Engineering Department has been conducting research on noble metals for catalyzing combustion reactions. Currently they are focusing on oxidation of methane with surface temperatures below 1830°F. These conditions are found in radiant surface burners used in appliances and in industrial heaters or boilers.

UCLA's work has characterized the influence of catalyst structure on intrinsic activity of platinum and palladium at temperatures of 500 to 700°F. Catalyst supports that were used include Alpha Product's Al₂O₃, Degussa flame synthesized ZrO₂, Zicor precipitated ZrO, and Zicor precipitated 12 mol% Y₂O₃. Of these, the Degussa alumina exhibited the highest thermal stability (surface area remained constant when maintained at 1830°F in air for 2 to 48 hours).

Initially, UCLA's scope of work was to include higher temperature applications. However, they have indicated that the noble metal catalyst systems they are working with would not survive under conditions characteristic of gas turbine combustors.

Kawasaki Heavy Industries Development Program

Since 1982, Kawasaki Heavy Industries has been actively pursuing development of catalytic combustor systems for their small stationary gas turbine engines (about 200 kW output). Much of this work has been in cooperation with Nippon Shokubai Kagaku (NSK), a catalyst supplier in Japan. Their goal is to reduce NO_x emissions to a level of about 6 ppm (at 15%O₂) under baseload conditions when burning natural gas.

Their most recent accomplishments are embodied in the two catalytic combustor designs described below and shown in Figure 6-1. Both of these designs have recently been tested at full scale in Kawasaki's SIA-02 gas turbine.

Kawasaki's combustors are of the preburner, single stage design. Variable geometry dilution ports are included to maintain catalyst exit temperature at the proper level across the engine's load range. The two designs differ in the preburner design, secondary fuel premixing arrangement and catalyst bed configuration, as shown in Figure 6-1.

Catalytic elements for Kawasaki's combustors are manufactured by NSK. They consist of a cordierite substrate with noble metal catalysts dispersed on a stabilized alumina wash coat. The maximum expected temperature in the catalyst bed is less than 2370°F, with exit temperature typically about 2000°F.

In engine tests both combustors performed well with fresh catalyst: NO_x emissions were low (below 6 ppm after optimization), combustion efficiencies were high (over 98%) and exit temperature variation was low ($\pm 90^\circ\text{F}$). However, following only three hours of operation the activity of the catalyst deteriorated dramatically, to the point where combustion efficiency was unacceptable. Furthermore, all catalyst substrates were damaged at their edges. Kawasaki has concluded that significant improvements in catalyst durability is required to establish product feasibility. They are continuing to work on this problem.

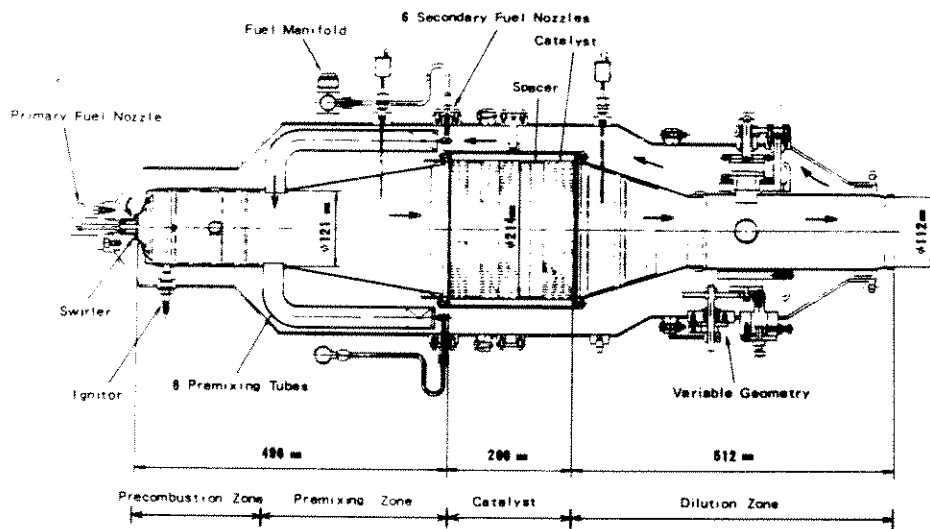
Hitachi Research on Catalyst Support Materials

Hitachi has conducted research on ceramic materials for use as support structures in gas turbine catalytic combustors. Their objective was to identify materials that provide high surface areas and are stable at combustor temperatures. In this work, Hitachi evaluated hundreds of candidate ceramics, including Al₂O₃, SiO₂, TiO₂, ZrO₂, MgO, and mixtures of these compounds.

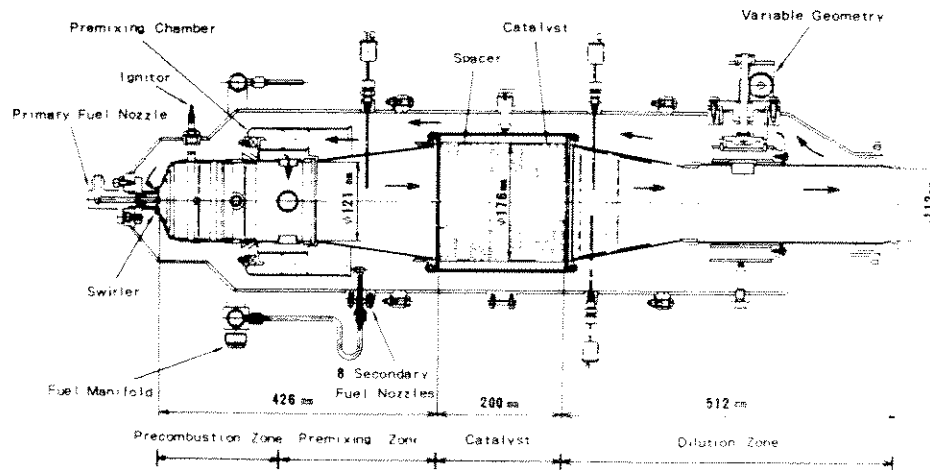
The most significant outcome of this work was the identification of La₂O₃-Al₂O₃ mixtures as promising support materials. The addition of small quantities of La₂O₃ to Al₂O₃ was found to retard the transition of gamma-alumina to alpha alumina. Consequently, surface area can be maintained at higher operating temperatures. Testing of a catalytic combustor consisting of palladium supported on lanthanum beta alumina was conducted to assess endurance characteristics. A mixture of 3 volume % methane in air was burned for a period of 100 hours. Catalyst bed temperature was about 2100°F. Over this period methane combustion efficiency was maintained above 99.5%. Similar tests using a catalyst consisting of palladium supported on alumina resulted in combustion efficiency dropping to 98%. BET surface area measurements revealed a 90% decrease in surface area for the alumina catalyst, whereas the lanthanum beta alumina supported catalyst experienced only a moderate loss of 30%.

Catalyst Specifications

Catalyst designation	Outer diameter mm	Cell density cells/cm	Wall thickness mm	Geometrical surface area cm^2/cm^3	Total cell length mm	Relative combustion loading
ULNXC-302A	220	31	0.30	19.6	160	0.65
ULNXC-302B	184	62	0.15	27.8	160	0.66
ULNXC-302	184	31	0.30	19.6	150	1.0



Type A



Type B

Figure 6-1. Kawasaki's Catalytic Combustor Configurations
(From Reference 15)

Toshiba Catalytic Combustor Development Program

Toshiba Corporation and Tokyo Electric Power Company (TEPCO) are developing a hybrid catalytic combustor for stationary gas turbines. As shown in Figure 4-5b, this system consists of a precombustion zone, a secondary fuel-air mixing zone, a catalyst bed, a tertiary fuel addition zone and a dilution zone. In this configuration the catalyst bed operates at moderate temperatures and the tertiary fuel provides energy to achieve the required turbine inlet temperatures. Projected operating temperatures are as follows: 840°F at the catalyst inlet to provide stable catalyst operation, 1830°F at catalyst outlet to improve catalyst durability, and 2190-2730°F in the tertiary fuel reaction zone to control emissions of NO_x, hydrocarbons and CO. By limiting the catalyst bed temperature to 1830°F, Toshiba believes that catalysts consisting of platinum and palladium supported on an alumina washcoat and cordierite substrate can be successfully used. Tensile stress testing and finite element modeling of cordierite substrates conducted by Toshiba have shown that from a structural perspective the concept is viable.

Subscale testing of the hybrid catalytic combustor has been completed at atmospheric pressure and at about 100 psig using natural gas. These results indicate that high combustion efficiency and low NO_x emissions (below 10 ppm at 15% O₂) are possible. Catalyst durability testing has not been reported. Further development activities are being planned by Toshiba and TEPCO.

General Electric Catalytic Combustor Development Program

General Electric has been actively involved in the development of catalytic combustors for utility gas turbines. Prior work has resulted in the development and successful testing of a fuel-air preparation system that meets the requirements for catalyst combustors. However, durable catalyst beds have not yet been demonstrated. GE's mixing system, shown in Figure 6-2a, has a multiple venturi arrangement that is based on earlier work at NASA. The preliminary design of a gas turbine catalytic combustor incorporating this mixing system is shown in Figure 6-2b. Atmospheric pressure rig testing of a combustor with this general configuration demonstrated that the mixing system could produce relatively uniform fuel-air mixture distributions at the catalyst inlet. The design also prevented the occurrence of flashback and flame holding upstream of the catalyst bed. However, in these tests the preburner produced unacceptable maldistributions in temperature and velocity at the catalyst inlet. According to GE, further development was expected to resolve this problem.

The most critical element remaining in their program is the development of durable catalyst elements. Currently, GE is involved in three programs that address this issue. These are summarized below.

- GE is a subcontractor to Engelhard in an EPRI/GRI-sponsored catalyst development program. This effort is focusing on high temperature catalysts that use ceramic substrates.
- GE is conducting a program to evaluate metallic substrates manufactured by Camet (a division of W.R. Grace).
- GE is working with the Imperial Chemical Industries to develop a high temperature catalyst with a ceramic substrate using materials employed in the chemicals industry.

As each of these efforts is in an early stage, no significant progress can be reported. Funding for portions of GE's work has been supplied by the Southern California Gas Company and Tokyo Electric Power Company.

General Electric's Catalytic Combustor

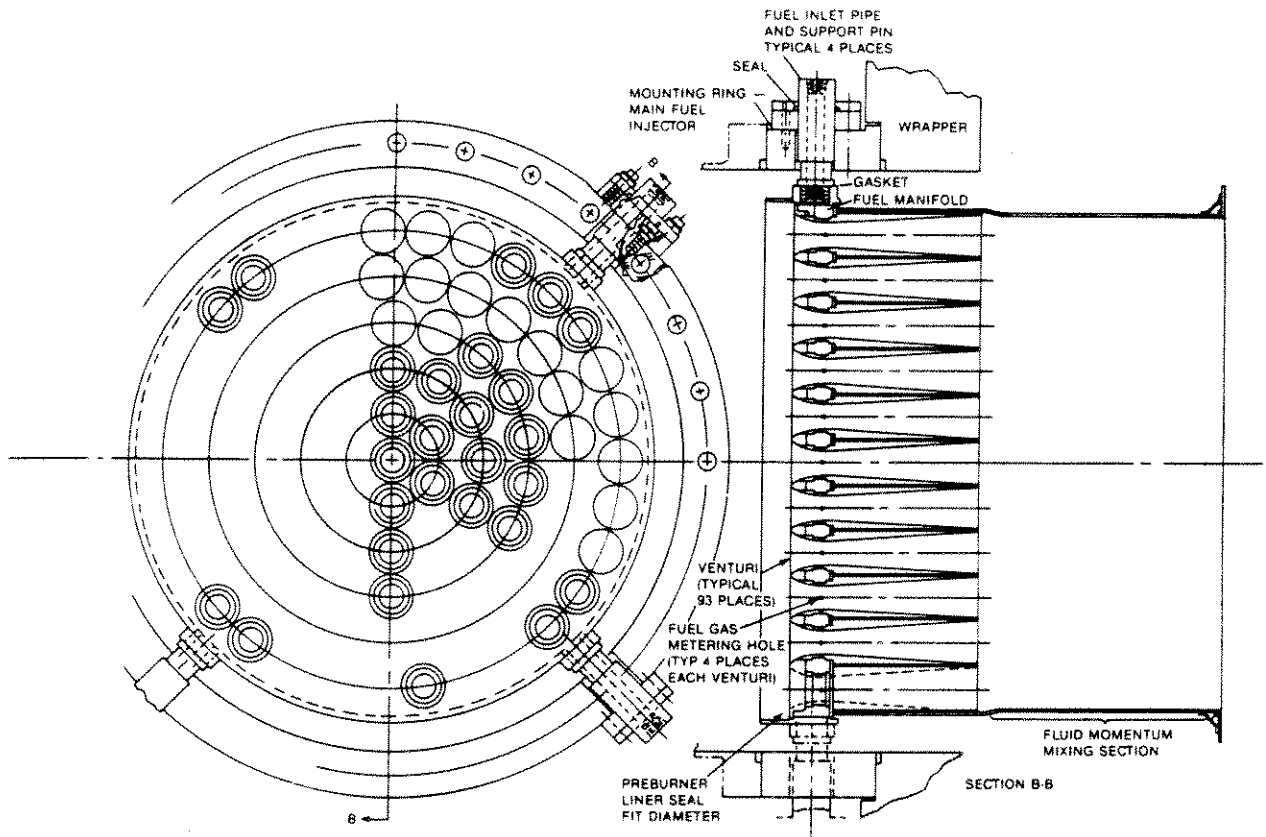


Figure 6-2a. Fuel-Air Preparation System (From Reference 3)

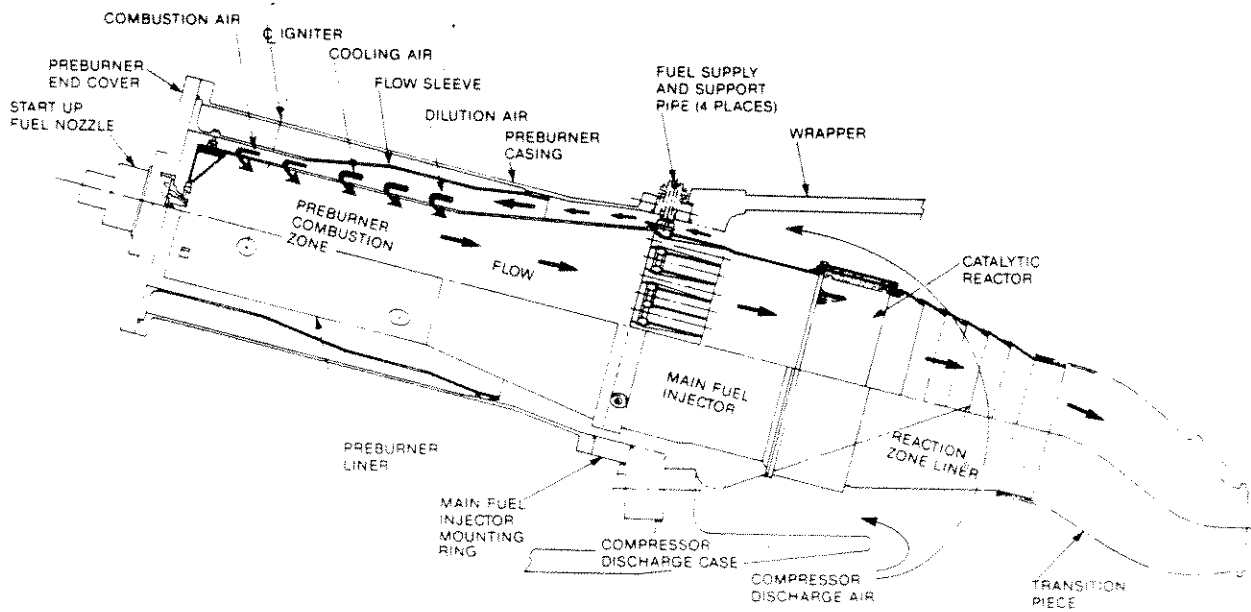


Figure 6-2b. Natural Gas-Fueled Catalytic Combustion System for a Heavy-Duty Industrial Gas Turbine

Johnson-Matthey Catalyst Development

Under GRI sponsorship, Johnson-Matthey is developing combustion catalysts for application to small (under 1000 kW), stationary natural gas-fueled gas turbines. Their prototype system utilizes noble metals (with added transition metals) on a metallic substrate. Johnson-Matthey indicated that this substrate has advantages over ceramics in two areas: lower gas pressure drop and better tolerance to thermal shock. For small turbines they have set goals of achieving a catalyst exit temperature of 1800°F and catalytic life of one year. This temperature level is close to the upper limit at which their current substrate and catalytic material can successfully perform. However, they indicated that use of more exotic substrate alloys and active materials of the perovskite or spinel structure may permit an increase in the operating temperature to about 2100°F.

Subscale testing at steady state has been conducted for a period of 500 hrs. Currently, they are seeking funds from GRI to conduct a one thousand hour durability test. With successful results, they envision commercialization of this technology for small gas turbines in about two to three years.

6.2 Technical Hurdles

Through the research and development activities described above, significant progress has been made along the path to commercialization of catalytic combustors for stationary gas turbines. However, many technical hurdles remain. The prognosis for eventually solving the important remaining technical hurdles is fair to good. However, commercialization of catalytic combustors for gas turbines is not expected until the late 1990's at the earliest. The critical areas where further development activities must focus are summarized below.

- Development of substrate materials and geometries that are capable of operating for extended periods at required combustor temperatures and that can survive repeated thermal cycling
- Discovery and application of active catalytic materials that are stable at required combustor temperatures
- Demonstration of advanced combustor concepts that reduce the required catalyst operating temperatures
- Development of fuel-air mixing techniques that...
 - supply energy for catalyst light-off
 - provide uniform fuel-air distribution to catalyst beds, and
 - prevent the occurrence of flashback
- Development of control systems to maintain stable catalyst operation as gas turbine load changes. The rapid fluctuations characteristic of offshore turbine duty cycles places added significance on this element.

The first two items will require materials-related breakthroughs and represent the most significant challenge for this technology. The mixing and control related hurdles can most likely be overcome through extensive prototype development activities.

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