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Catalytic combustion reactor design and test results

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Abstract

Engelhard Corporation has been investigating catalytic combustion for low NO_x applications since the 1970s [1]. Reactor systems have been developed for various applications including, gas turbines, boilers and automobiles. This paper will discuss the generic reactor system, its design and chemistry. An overview which shows the temperatures within the catalyst bed and the design parameter flexibility will be presented. The window of operation of the various reactors will be discussed as will life test data. Finally, the effect of fuel and temperature turndown and pressure will be discussed which demonstrate the feasibility of catalytically supported thermal combustion for natural gas fueled gas turbines.

Keywords: Combustion; NO_x; Reactor design and test results

1. Introduction

Since the 1970s, Engelhard has continued its development of catalytic supported thermal combustion for low NO_x applications such as gas turbines, boilers and automobiles. A number of systems have been developed, extensive testing has been done with gas turbines, boiler and low emission automobile manufacturers, and advanced field testing is currently in progress.

Within the last five years significant progress in both catalysts and monolithic supports has been made which allowed the technology to move closer to commercial reality. The recognition of the role of PdO and Pd in the catalytic oxidation of methane, the major component in natural gas, has been a key to developing new and improved catalysts [2,3]. The development of suitable monolithic compositions and structures capable of maintaining mechanical integrity for thousands of hours of operation, for both steady state and transient operations has been of vital importance to the technology requirements. Both of these developments have been summarized in a recent publication by Farrauto et al. [4]. Alternative approaches to catalytic combustion to those described here have also been summarized [5].

This paper will first describe the fundamental principles of catalytically supported thermal combustion, followed by a summary of the chemistry of a typical bed design for application in a natural gas combustor, and some of the important operational design parameters such as the window of operation, the effects of fuel/temperature turndown and pressure. Finally, some demonstrated laboratory life tests will be described which are currently being confirmed in a number of different field tests.

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2. Principles of catalytically supported thermal combustion

A fuel air mixture must be in the flammable composition range in order to generate a stable flame. This fundamental principle of combustion technology results in an adiabatic flame temperature well within the range for the nitrogen fixation reaction;

$$N_2 + O_2 \rightarrow 2NO \tag{1}$$

For example, starting with an 8% natural gas–air mixture an adiabatic temperature well beyond the 1 400°C necessary for reaction (1) to occur is reached. Furthermore, the inlet to a gas turbine can not tolerate temperatures in excess of about 1 400°C with modern blade material technology and thus the combustion product gas must be cooled. This is demonstrated by the dotted line of Fig. 1. Here the gas combustion temperature is plotted as a function of distance down the combustor length. The adiabatic temperature clearly exceeds 1 400°C and is shown to reach a maximum flame temperature of 2 500°C after which cooling air is added to reduce the temperature to the turbine inlet. Obviously, this results in high NO generation. Although modern gas turbine designs are mitigating this problem by a series of combustion modifications, unwanted NO is still generated. Selective catalytic reduction of NO_x using NH_3 as a reductant is now finding use to bring turbines into environmental compliance [5].

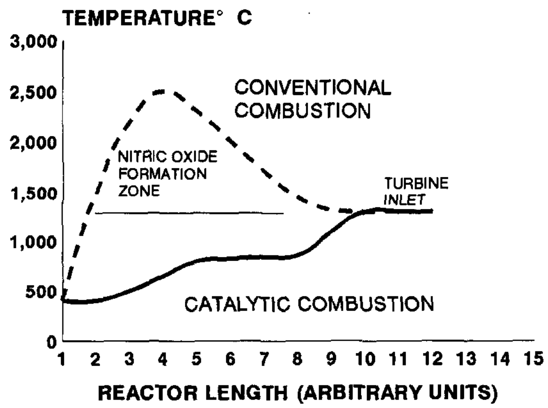

Fig. 1. Conventional and catalytic combustion.

A catalyst can oxidize fuel–air mixtures with composition lower than that required for a stable flame. For traditional catalytic processes the maximum temperature and conversion is limited by bulk mass transfer control. This condition is shown as the solid line in Fig. 1. At an inlet temperature of less than 500°C conversion (temperature) of natural gas in air begins to rise as oxidation proceeds to the first plateau. Provided the catalyst and operating conditions are correct, the heat generated at the surface of the washcoated monolithic catalyst can bring the partially combusted mixture to a condition which results in complete thermal combustion shown as the last plateau in Fig. 1. Under steady state conditions, the thermal combustion occurs downstream of the catalyst, provided the catalyst exit temperature is about 800°C. Thus, thermal combustion is supported by catalytic oxidation. The combustion products contain virtually no NO_x since the adiabatic temperature is below that required for reaction (1). The mixture is sufficiently lean so that no CO or UHC is generated. Thus, catalytically supported thermal combustion produces a temperature sufficient for operation of the gas turbine but with no unwanted pollutants. The process requires suitable design of catalysts and their monolith supports (to minimize pressure drop), inlet temperature, fuel composition and process conditions.

3. Discussion

A typical Engelhard reactor design consists of three or four segments, as indicated in Table 1. These segments are an ignition catalyst section, which has high catalyst activity for light-off, resistance to catalyst deactivation, but with the ability to be regenerated in the case of transient excursions. As described in the patents and publications by Farrauto et al. [2–4]. One mode of deactivation is the conversion of the active PdO species to Pd metal shown in Eq. 2,

Table 1
Reactor bed design characteristics

	segment 1	segment 2	segment 3
Catalyst	$PdO/\gamma\text{-}Al_2O_3$	$PdO/10\%\ CeO_2+\gamma\text{-}Al_2O_3$	Pr_4PdO_7
Relative activity	High	Mid-high	Low
PdO decomposition (°C)	800	900	1200–1300
PdO reformation (°C)	600	750	1000
Exit bed temperature[a] (°C)	650	700–750	800

[a]Variable by design of the catalyst bed geometry.

$$\underset{\text{methane inactive}}{PdO} \xrightarrow{800^\circ C,\ \text{air},\ 1\ \text{atm}} \underset{\text{methane active}}{Pd + \tfrac{1}{2}O_2} \qquad (2)$$

With an inlet temperature of about 400 to 500°C, the gas exiting this segment will be at around 650°C at steady state conditions. It should be noted that where temperatures are indicated, it is the temperature of the gas that is being measured.

A key to the system design is to prevent the PdO catalyst from experiencing temperatures in excess of 800°C. This has been accomplished by carefully designing and engineering the first segment or ignition catalyst. There are many load change requirements in a gas turbine, which demand that more or less fuel be combusted. We have observed during our aging studies that these changes lead to short but rapid transients which will bring the temperature above 800°C and decomposition of the PdO occurs with a resultant loss in catalytic activity. We have also observed that Pd metal can be reoxidized by reducing the overall gas temperature to below 600°C, where the regeneration of PdO and its methane oxidation activity is achieved in accordance with Eq. 3,

$$\underset{\text{inactive}}{Pd + \tfrac{1}{2}O_2} \xrightarrow{<600^\circ C,\ \text{air},\ 1\ \text{atm}} \underset{\text{active}}{PdO} \qquad (3)$$

The second catalyst segment is designed to produce at outlet about 700–750°C, and consists of a promoter catalyst composed of PdO, whose active oxidation state of +2 is stabilized by incorporation of about 10% rare earth oxides, e.g. CeO_2, into the high surface area stabilized Al_2O_3. The rare earth oxides increase the decomposition temperature to almost 900°C. For those infrequent upset conditions temperature for regeneration is increased to about 750°C [6]. This is very favorable since it increases the temperature range for stability of the active PdO. The final segment generates only about 50–100°C, bringing the exit temperature to 800°C, which is sufficient to initiate and sustain the thermal reaction. This segment contains catalyst with active Pd^{2+} stable up to 1 300°C and regeneration temperatures close to 1 000°C [7]. Although the catalyst designs minimize exposure to temperatures usually no greater than about 800°C, we have found that these designs protect the system against upsets and transients. Table 1 summarizes the data.

The substrates used in these reactors were of two different types; both fiber reinforced ceramics. We have exposed these ceramic substrates to thermal shock testing at temperatures in excess of 1 300°C, without any detrimental effect to the substrates. A detailed discussion of the monolithic testing can be found in [4].

The exit temperature of the reactor operating at steady state is typically in the range of 800°C and approximately 30–35% of the fuel is consumed. The remainder of the fuel is combusted in the homogeneous zone downstream of the reactor. The typical adiabatic temperature is 1 300 to 1 400°C depending upon fuel concentration, inlet temperature, gas flow rate and fuel type. These temperature profiles are shown in Fig. 2 for the conditions indicated (4% CH_4, 3 atm pressure, a linear velocity of 52 ft/s and for several inlet temperatures). As can be seen, most of the temperature rise (500/600°C) occurs in the homogeneous

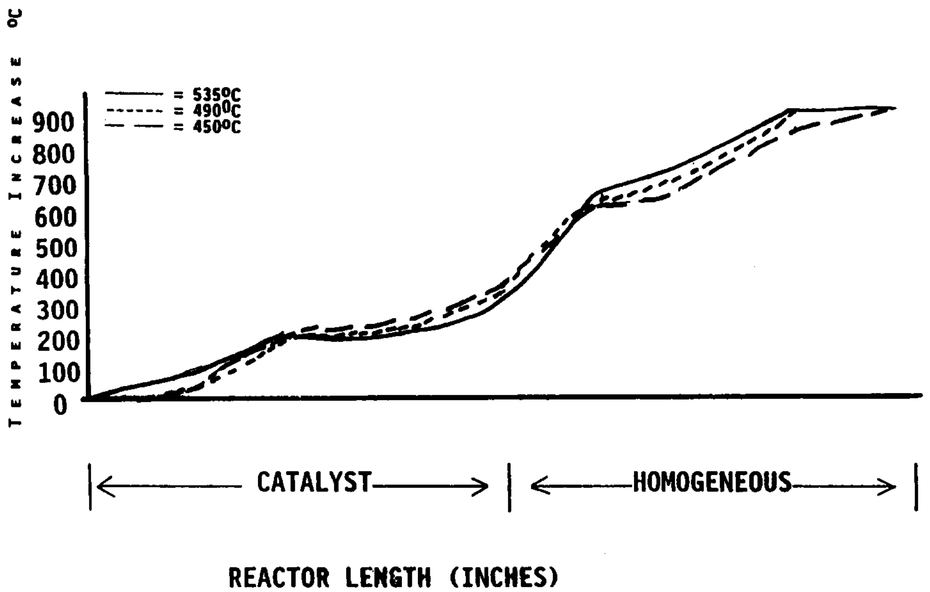

Fig. 2. Temperature increase vs. reactor length, fuel: 4% CH_4; bal air, pressure: 3 atm, linear velocity: 52 ft/s, catalyst size: 1″ diameter.

I. FUEL CONCENTRATION
- Direct effect on catalyst reaction rate
- Ignition temperature ↓ as concentration ↑

II. INLET VELOCITY
- Direct effect on surface heat removal rate
- Ignition temperature ↓ as velocity ↑

III. CATALYST GEOMETRY
- Cell shape and cell density affect the ration of catalyst surface area/gas volume
- Ignition temperature ↓ as cell density ↑

IV. CATALYST CHEMISTRY
- Metals
- Loadings

Fig. 3. Design parameter flexibility.

reaction zone behind the bed, where the majority of the combustion occurs. Thus the catalysts do not experience, for any significant period of time, the high temperatures which could deactivate them. However, as stated above upset and transient conditions do occur which require catalyst and support materials to have higher temperature resistance than that required for steady state operation.

From the extensive testing done over many years of research with different catalyzed reactors for various applications, a design parameter flexibility (Fig. 3) can be drawn. Fuel concentration has a direct effect on catalyst reaction rate with ignition temperature decreasing as fuel concentration increases. Inlet velocity affects the surface heat removal rate and as velocity decreases so does the ignition temperature. Catalyst geometry, cell shape and density, affect the active catalytic surface area available and as cell density increases, so ignition temperature decreases. Finally, the catalyst chemistry, both which metals are used and the level of metal loadings can have a great effect on reactor performance. By choosing the correct combination of substrate geometry and catalyst chemistry, reactors have been built which give very smooth controllable burning of the fuel. Also, the temperatures within the catalyst bed, and in the homogeneous area outside of the reactor are very stable.

Over the years, Engelhard has conducted tests with numerous fuels including natural gas (methane), diesel fuel, gasoline and propane. All of the

Table 2
Window of operation

Inlet gas velocity	10–90 ft/s 3–27 m/s
Inlet gas temperature	626°F–1 040°F 330°C–560°C
Inlet CH_4 level	3.5–5.6 vol.-%
Reactor pressure	15–200 psi 1–15 atm

Table 3
Life test–1244 reactor

Duration	501 h
Ignitions	70
Average IT	509°C
Low IT	494°C
Inlet velocity	50 ft/s
Fuel conc.	4.0 vol.-%
Pressure	3 atm
NO_x	< 1.5 ppm
CO	4–15 ppm
UHC	0

Table 4
Fuel turndown

Conditions		
5% fuel		4.3%
450°C	NO_x = 1.8 ppm	
46 ft/s	UHC = 0 ppm	
3 atm	CO = 5 ppm	
	CO_2 = 5.5%	
	O_2 = 11.5%	
Reignite		
5.1%		4.3%
410°C	NO_x = 1.4 ppm	
41 ft/s	HHC = 0 ppm	
3 atm	CO = 10 ppm	
	CO_2 = 5.7%	

testing to date has resulted in a series of reactors being developed which have been run within a window of operation (Table 2). It should be stated that these ranges are not the limits of operation of the various reactors, but encompass the ranges requested by the customers. Thus, while the window of operation for inlet gas velocity is 10–90 ft/s, this does not mean that catalytic reactors can not run at velocities both above and below this range. Similarly, this applies to the other parameters shown in Table 2; that is, inlet gas temperature, inlet fuel (methane) level and reactor pressure.

To measure the effects of both run time and shut-down/start up on catalyst deactivation, a reactor was run under the following conditions (Table 3); average inlet temperature 494/509°C, inlet velocity 50 ft/s, fuel concentration 4 vol.-% and 3 atm pressure. Total run duration was 501 h and during this time, the reactor was subjected to simulated emergency shut-downs 70 times (fuel is suddenly shut off, resulting in a rapid decrease in temperature). Many high temperature surges were also noted during the fuel and temperature changes. We believe that these surges were the result of pressure changes within the catalyst channels, and the subsequent result on reaction rate and hence heat generation. Additionally, because of the difference in response time of the fuel and air controllers, the fuel to air ratio would increase temporarily during these system changes. The catalyst/system was able to sustain the ther-

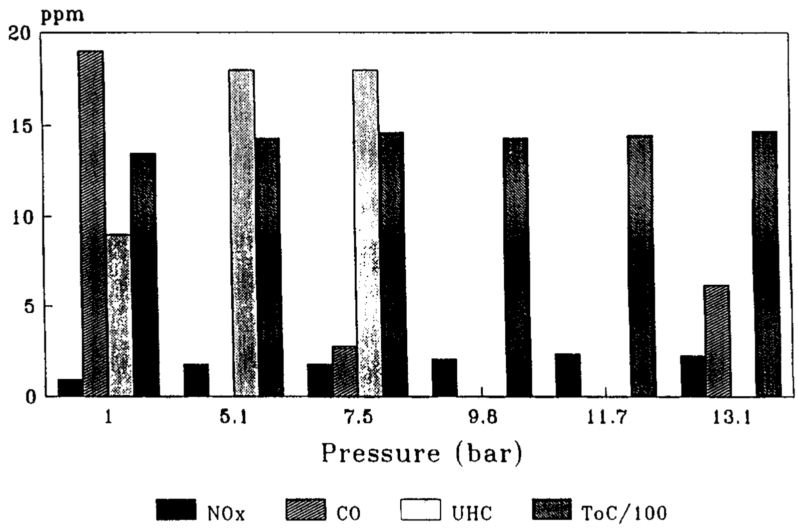

Fig. 4. High pressure testing, 438/459°C, 46/60 ft/s, 4.3/5 vol.-%.

mal reaction during the entire run with no signs of serious deactivation. Outlet gas emissions remained constant as indicated; NO_x less than 1.5 ppm, CO in the range of 4–15 ppm and unburned hydrocarbons zero. The NO_x analyzer used did not detect N_2O. Earlier work at this laboratory indicated that N_2O was not formed in the catalytic systems discussed in this paper.

Fuel turndown is very important to meet the changing demands of the turbine. Tests were conducted to observe the effect of fuel turndown on reactor performance. Table 4 shows one such test where the fuel was reduced from 5% to 4.3%, which resulted in the homogeneous reaction being extinguished. At that point, the reactor was reignited by increasing the fuel to 5.1% and again the bed and homogeneous reaction stayed lit until the fuel was reduced to 4.3%.

Similar tests have been conducted for temperature turndown. Typically, for an inlet temperature of 450°C with 4% fuel and 50 ft/s inlet velocity, the inlet temperature can be reduced to 350/360°C before the homogeneous reaction is extinguished.

The effect of pressure on reactor (catalyst) activity was measured in a series of tests, one of which is illustrated in Fig. 4. Under the conditions shown, pressure has little or no effect on gaseous emissions (NO_x, CO, UHC) nor on adiabatic flame temperature. Variation in the unburned hydrocarbon level was due to some unit flow control difficulties as the pressure was being increased.

4. Future work

Engelhard is continuing to develop and adapt its catalytic combustion reactor systems for various applications. Successful field testing is the next major milestone in bringing this technology to the commercial market.

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References

[1] W.C. Pfefferle, US Patent, 3 928 961.
[2] R.J. Farrauto, T. Kennelly, M. Hobson and E. Waterman, US Patent, 4 893 465.
[3] R.J. Farrauto, M. Hobson, T. Kennelly and E. Waterman, Appl. Catal. A, 81 (1992) 227.
[4] R.J. Farrauto, M. Larkin, J. Fu and J. Feeley, in Voss, Quick, Gadgil and Adkins (Editors), Mat. Res. Soc. Symp. Proc., 344 (1994) 101.
[5] R.M. Heck and R.J. Farrauto, Catalytic Air Pollution Control: Commercial Technology, Van Nostrand Reinhold, New York, 1995.
[6] T. Kennelly and R.J. Farrauto, US Patent, 5 216 875.
[7] T. Chou, T. Kennelly and R.J. Farrauto, US Patent, 5 169 300.