Final Technical Report

Award Number: DE-EE0003491

Project Title: Catalyzed Ceramic Burner Material

Project Period: Aug 15, 2010 to March 31, 2012

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Date of Report: Jun 1, 2012

Acknowledgment, Disclaimer and Proprietary Data Notice

Acknowledgment: This report is based upon work supported by the U.S. Department of Energy under Award No.DE-EE0003491.

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List of Acronyms

BEI: backscattered electron imaging

BET: Brunauer-Emmett-Teller surface area measurement method

DTA: differential thermal analysis

EA: excess air

FID: flame ionization detector

GC: gas chromatograph

GHSV: gas hourly space velocity

NESCAUM: Northeast States for Coordinated Air Use Management

NO_x: nitrogen oxide (NO and NO₂)

SEM: scanning electron microscopy

T₅₀: the light-off temperature, as determined when 50% of the input fuel has been oxidized.

TGA: thermogravimetric analysis

VOC: volatile organic compound

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1.0 Executive Summary

Catalyzed combustion offers the advantages of increased fuel efficiency, decreased emissions (both NO_x and CO), and an expanded operating range. These performance improvements are related to the ability of the catalyst to stabilize a flame at or within the burner media and to combust fuel at much lower temperatures. This technology has a diverse set of applications in industrial and commercial heating, including boilers for the paper, food and chemical industries. However, wide spread adoption of catalyzed combustion has been limited by the high cost of precious metals needed for the catalyst materials.

The primary objective of this project was the development of an innovative catalyzed burner media for commercial and small industrial boiler applications that drastically reduce the unit cost of the catalyzed media without sacrificing the benefits associated with catalyzed combustion. The scope of this program was to identify both the optimum substrate material as well as the best performing catalyst construction to meet or exceed industry standards for durability, cost, energy efficiency, and emissions. It was anticipated that commercial implementation of this technology would result in significant energy savings and reduced emissions. Based on demonstrated achievements, there is a potential to reduce NO_x emissions by 40,000 TPY and natural gas consumption by 8.9 TBtu in industries that heavily utilize natural gas for process heating. These industries include food manufacturing, polymer processing, and pulp and paper manufacturing. Initial evaluation of commercial solutions and upcoming EPA regulations suggests that small to midsized boilers in industrial and commercial markets could possibly see the greatest benefit from this technology. While out of scope for the current program, an extension of this technology could also be applied to catalytic oxidation for volatile organic compounds (VOCs).

Considerable progress has been made over the course of the grant period in accomplishing these objectives. Our work in the area of Pd-based, methane oxidation catalysts has led to the development of highly active catalysts with relatively low loadings of Pd metal using proprietary coating methods. The thermal stability of these Pd-based catalysts were characterized using SEM and BET analyses, further demonstrating that certain catalyst supports offer enhanced stability toward both PdO decomposition and/or thermal sintering/growth of Pd particles. When applied to commercially available fiber mesh substrates (both metallic and ceramic) and tested in an open-air burner, these catalyst-support chemistries showed modest improvements in the NO_x emissions and radiant output compared to uncatalyzed substrates. More significant, though, was the performance of the catalyst-support chemistries on novel media substrates. These substrates were developed to overcome the limitations that are present with commercially available substrate designs and increase the gas-catalyst contact time. When catalyzed, these substrates demonstrated a 65-75% reduction in NO_x emissions across the firing range when tested in an open air burner. In testing in a residential boiler, this translated into NO_x emissions of <15 ppm over the 15-150 kBtu/hr firing range.

2.0 Introduction

The primary objective of this project is to develop a cost-effective burner based on a high-activity, low-loading catalyst technology that dramatically exceeds industry standards for boiler performance. Table 1 quantifies these performance standards based on surveys of boiler OEMs conducted by 3M and serves as a benchmark for achievement in this project.

Table 1. Project Objectives

Parameter	Target
Price (\$/ft ²)	< 100
NO _x emissions (ppm)	< 5
Excess oxygen (%)	2
Thermal efficiency improvement (%)	2
Turndown ratio	10:1
Power density (kBtu/hr/ft ²)	120
Pressure drop (psi)	<1
Thermal shock resistance	high
Lifetime (years)	15-20

The technical approach for the program has been separated into three parts: catalyst, support, and substrate development. It is well known in the patent and technical literature that palladium-based catalysts are highly active in the combustion/oxidation of methane and/or natural gas fuels. Such catalysts may provide lower overall light-off temperatures at the point of combustion such that the overall amount of nitrogen oxide (NO_x) production via thermal NO_x pathways are minimized. Our studies in the area of Pd-based, methane oxidation catalysts have revealed highly active catalyst-support systems. The catalysts are deposited using proprietary methods for coating onto various support chemistries and maintain relatively low loadings of Pd metal. Certain catalyst supports have been identified that offer enhanced stability toward both PdO decomposition and/or thermal sintering/growth of Pd particles. For substrate development, the experimental approach has been to (1) modify existing burner mesh materials to incorporate a catalyst material and (2) introduce novel media constructions that overcome limitations that are present with existing burner substrate designs. Attractive combinations of catalyst-support chemistries and substrate constructions are tested in an open-air burner over a range of firing conditions, with the primary outputs of interest being NO_x emission, radiant emission, and media temperature. Based on these results, the best performing samples are then tested in a boiler environment.

This technology has direct application in the commercial and small industrial boiler market, with little to no modifications necessary to the boiler to incorporate the proposed burner technology. Within the industrial market, small packaged boilers are showing strong market growth, replacing larger steam boilers. These small boilers are more efficient, safer to operate, less costly to maintain, and provide the customers with system redundancy to help minimize the effects of productivity losses during maintenance downtime. Several industries today heavily utilize these smaller water boilers, including the food, chemical, and fabricated metal industry. In the commercial sector, small boilers represent the largest portion of the market, with the exception of the healthcare sector. Therefore, this technology could broadly impact the

commercial sector. In addition to the product having applicability in several industrial and commercial markets, the proposed performance improvements directly align with the objectives of several boiler manufacturers who are seeking to differentiate their products by demonstrating lower emissions and higher efficiency. There is a potential to reduce NO_x emissions by 40,000 TPY and natural gas consumption by 8.9 TBtu in these industries.

The present report begins with a review of the open literature on catalyst-support (p.12) and substrate (p.13) technologies for methane oxidation. This is followed by the experimental approach (p.17), results and discussion (p.22), and benefits assessment (p.54). At the end of the report, there is a plan for commercialization (p.57), summary of the accomplishments (p.58), conclusions (p.59), and recommendations (p.60).

3.0 Background

3.1 Catalyst and support development

The catalyst support material activates and supports the active catalyst (catalyst material) on the burner substrate. The catalyst support material will be a durable, refractory metal oxide that is compatible with the burner substrate material so as to provide long life without spalling or deactivation through sintering. The work will include development of low cost methods to uniformly deposit the catalyst support onto the active areas of the burner substrate material.

The catalyst material will be composed of nanoparticle active sites that catalyze the oxidation of the hydrocarbon gas. This site must be durable with respect to long term usage, high temperature and exposure to low levels of sulfur and other catalyst poisons. Catalyst materials examined include nanoparticle precious metals, nanoparticle alloys of precious metals, transition metal oxides, and rare earth oxides. Co-catalysts and oxidation accelerators such as alkaline metal and alkaline earth metal oxides, rare earth oxides, and phosphates are to be also examined.

A technical and patent literature review was performed in the area of catalytic methane oxidation/combustion to identify potential candidate catalyst systems for catalyzed radiant burner applications. The results of the search revealed two main areas of methane combustion catalysts: low operating temperature (~350-450 °C) and high operating temperature (~750-850 °C) catalysts (Ersson, 2006; Gelin & Primet, 2002; Choudhary, Banerjee, & Choudhary, 2002; Ciuparu, 2002; Marchetti & Forni, 1998; Eguchi & Arai, 1996; Li & Hoflund, 2003; Carroni, Schmidt, & Griffin, 2002). The former group typically contains precious metal catalysts supported on various oxide supports, with Pd being the most active of the precious metals for this application (Gelin & Primet, 2002; Ciuparu, 2002), while higher temperature catalysts include various active metal oxides (e.g., Co_3O_4 , CeO_2) (Liotta, 2005; Tschöpe, 1995) and complex oxides (e.g., perovskites, hexaaluminates) (Ersson, 2006; Yeh, 2004). In general, the lower operating temperature catalysts are more active toward methane oxidation, but less stable to thermal deactivation than the higher operating temperature catalysts.

The most active catalysts, based on low light-off temperatures, contain PdO as the active phase, and changes in the catalyst support can significantly influence the overall activity and stability of PdO-based systems. Active Pd supported catalysts typically have loading levels greater than 1 wt% of the combined weight of support and carrier (Li & Hoflund, 2003), while significant increases in activity are commonly observed with an increase of Pd loading (Gelin & Primet, 2002) up to 10 wt%. Some of the most active support phases include Al_2O_3 , ZrO_2 and CeO_2 , with the most commonly found systems in both patent and technical literature being based on Pd/ Al_2O_3 and Pd/ ZrO_2 (Narui, 1998; Mouaddib, 1992; Thevenin, 2003). Catalyst promoters are also used to enhance the activity and selectivity (e.g., SnO_2 , CeO_2) (Sekizawa, 2000; Thevenin, 2003), as well as thermal/chemical stability (e.g., NiO, Rare earth oxides) (Widjaja, 1999; Colussi, 2004). Often times mixtures of metal oxide catalyst supports are used to produce synergistic effects that enhance both activity and stability of the catalyst (Widjaja,

1999). Perovskites have been studied extensively as inexpensive alternatives to Pd and Pt based methane combustion catalysts, and have in some cases shown comparable activities to Noble metal based systems (Marchetti & Forni, 1998; Arai, 1986; McCarty & Wise, 1990; Ferri & Forni, 2001; Ciambelli, 2001; Alifanti, 2004). Some of the more commonly studied perovskite systems for methane combustion are based on the LaMO_3 families, where $\text{M} = \text{Fe}^{3+}$, Co^{3+} or Mn^{3+} (Arai, 1986). Many of the recent studies in combustion catalysts have focused on hexaaluminate-based catalysts (e.g. Mn-hexaaluminates), for high temperature applications where catalysts exhibiting high thermally stability are required (e.g., gas turbines) (Ersson, 2006; Eguchi & Arai, 1996; Yeh, 2004; Zheng, 2009; Groppi, 1993; Jang, 1999; Sidwell, 2003; Svensson, Boutonnet, & Jaras, 2008).

Durability of methane combustion catalysts is also a topic of great interest in many of the reviews, where additives and modifiers are regularly used to provide added protection toward poisoning, sintering and/or chemical transformation of active phases. One common method of improving both SO_2 resistance and sintering of Pd based catalyst is the addition of Pt, the latter being known to possess higher SO_2 and sintering resistance versus other Noble metals (Yu & Shaw, 1998) (Yu & Shaw, 1998; Persson, 2006). It was also found that the use of nitrate-based Pd precursors produced more active catalysts than catalysts prepared using chloride-based Pd precursors, believed to be due to the poisoning effects of halides on Noble metal active sites (Roth, 2000). Deactivation of Pd-based methane combustion catalysts are often due to the transformation of PdO to Pd metal which typically occurs near 750-800 °C. Extending the range of PdO stability on various supports has been an area of active interest, and a strong dependence between support type and the PdO decomposition temperature has been established (Farrauto, Catalytic chemistry of supported palladium for combustion of methane, 1992). Thermal sintering and subsequent loss of surface area is also of concern, and hexaaluminates are widely regarded as one of the best material systems for providing resistance toward thermal sintering at elevated temperatures (Svensson, Boutonnet, & Jaras, 2008). The challenge with hexaaluminates continues to be the low inherent surface areas and activity, and significant efforts are focused on new synthetic methods to generate higher surface area hexaaluminates without compromising the properties of high thermal stability (Bai, 2009; Wang, 2003; Zhai & Li, 2006; Xu, 2003).

The patent literature appears to be focused predominantly on the precious metal-based material systems, and is frequently directed toward methane abatement in pollution control applications. Based on the reviewed literature as summarized above, selected combinations of active metal oxide supports along with precious metal active phases were synthesized as potential candidates for complete, low temperature combustion of methane.

3.2 Substrate development

A technical and patent literature review was performed in the area of porous radiant burner media with and without the addition of a catalyst to identify potential candidate constructions (geometry and composition) for catalyzed radiant burner applications. The search revealed an extensive amount of previous work, both theoretical and experimental. It would not be possible

to discuss all of the published literature in this report so a summary will be provided. Several comprehensive review articles are available that summarize the work for various focused areas of study around porous radiant burners (Wood & Harris, 2008; Mujeebu, 2009; Howell, 1996).

With regards to materials for porous radiant combustion, both ceramic and metal compositions have extensively been explored and a review of the most common materials are provided (Wood & Harris, 2008) and (Howell, 1996). For ceramics, the most common materials are cordierite, mullite, alumina, silicon carbide, zirconia or combinations of these. Ceramic materials demonstrate excellent temperature stability, making them attractive for porous radiant burners. Alumina and ZrO_2 both have a low thermal conductivity, which can be attractive for certain media designs, particularly in upstream locations, but they suffer from high thermal expansion coefficients and poor to moderate thermal shock resistance. Alumina has been used as beads in packed beds or lamella structures while ZrO_2 is mostly used as a foam (Wood & Harris, 2008). Silicon carbide (SiC) materials are sensitive to oxidation at around 600°C but this oxide layer on the surface can protect the material in higher temperature applications. The thermal conductivity of SiC is quite high and thermal expansion coefficient low compared to other ceramics. SiC has mostly been explored as a reticulated foam for radiant burner applications but also has been examined in packed beds.

Cordierite is known for its low thermal expansion coefficient and is often used as a perforated plate burner. (Garcia, 2004) examined the degradation of a perforated cordierite plate during thermal cycling. The author reported localized degradation at the outer most surface (combustion surface) due to the loss of the glassy phase and decomposition of cordierite to mullite due to monatomic hydrogen species. This resulted in a decrease in elastic modulus at the outer surface of the burner.

Metals are also very commonly used in both commercial and experimental applications for porous burners, including high temperature stainless steels, FeCrAlY alloy, and NiCrAl alloy. Metals are usually as fibers in mat form or as foams and are most commonly used as surface burners, where the flame is stabilized on the downstream surface of the burner rather than within the media matrix. There are concerns about rapid degradation of the metal due to thermal load if the flame was confined within the media (Howell, 1996). The FeCrAl alloy panels show good oxidation resistance at high temperatures due to the formation of an $\alpha\text{-Al}_2\text{O}_3$ layer on the outer surface. (Cerri, Pavese, Saracco, & Specchia, 2003) demonstrated that preheating of the fibers to 900°C allowed the aluminum to migrate from the core of the fibers to the surface and forms a uniform $\alpha\text{-Al}_2\text{O}_3$ coating.

With regard to geometry, a variety of different constructions have been explored. Common forms are foams, beads, fibers in woven or nonwoven mats, and ported plates. The relative performance of each construction is heavily dependent on application and burner design. Below we will discuss a few of the most relevant literature studies with an emphasis on new geometrical configurations and ceramic foams.

The primary configuration for premixed radiant burners consists of a cylindrical, square or rectangular “plate” of material with the premixed gases flowing through the media. A radial design with the same porous media was proposed by (Mohammad, 2005). The radial burners demonstrated a consistent gas and solid phase temperature, independent of inlet velocities. In contrast, for the axial (plate) burner, the gas and solid phase temperatures increased with increasing inlet velocity. In both of these configurations, the excess air was held constant at a stoichiometric ratio. The radial design was also able to stabilize the flame on the media surface at a much higher inlet velocity (8 m/s) compared to an axial burner (0.3 m/s) at the same excess air conditions. In the radial design, increasing inlet velocities shift the flame to a position of greater surface area (increase radius with the media), keeping the flux almost constant. The radial design also stabilized the flame over a larger range of excess air ratios (0 to 1.2) compared to the axial design which demonstrated flame blow-out at excess air ratios greater than 0.8.

Metal and ceramic open cell foams were examined for porous radiant burner applications (Randrianalisoa, 2009) and the level of NO_x and CO emissions as well as radiant efficiency were calculated. The author predicts that FeCrAlY with 95% porosity and cell size of 1.27 mm would have the lowest concentration of NO_x and CO at an in-flux of 100 and 300 kW/m². The NO_x level was calculated to be 7.5 mg/kWh at 100 kW/m² and 32 mg/kWh at 300 kW/m². The CO concentration increased from almost 27 mg/kWh at 100 kW/m² to 330 mg/kWh at 30 kW/m². NiCrAl with a porosity of 93% and cell size of 1.3 mm was calculated to show similar CO and NO_x concentration at the high power condition. The worst performing material from an emissions perspective at low power was PSZ (partially stabilized zirconia) with a porosity of 83% and a cell size of 0.83. This material was calculated to produce a NO_x emissions level of 8.4 mg/kWh and CO level of 32 mg/kWh. In addition to calculating emission levels, the author also looked at radiant power. At low in-flux power, the radiant emitted power was greatest for the mullite material with a porosity of 77% and pore size of 2.63 mm and at high power, the FeCrAlY alloy material was calculated to have the highest radiant emitted power. But for all materials except the most dense alumina, the calculated emitted power varied only a small amount, from 20-25 kW/m² for the low inlet power and 25-27 kW/m² for the high inlet power. The porosity of the two metals examined was significantly higher than any ceramic material examined (92 - 95% compared 67-87%). The author concludes that the best materials have the highest porosities and cell size of about 1.2-1.3 mm.

Cordierite foams fabricated by a polymeric sponge replication technique were described by (Olhero, 2008). As a media for porous burners, the author found that increased porosity was more important than decreasing thickness in achieving the lowest pressure drop through the material. A low pressure drop is desirable in porous burner applications and therefore the target of this study.

In traditional combustion (without the addition of media) staging a burner is a technique used to lower the NO_x emissions. In a two stage system, the first stage has very low excess air and partially combusts the fuel. In the second stage, it is very lean with lots of excess air, which completes the combustion at a low enough temperature to keep the NO_x levels down. For

porous burners, several studies have examined a different kind of two stage design. These staged burners consist of a small pore region upstream and a larger pore region downstream. Several researchers have explored the affect of composition, media geometry (packed bed or foams) and porosity on performance (Hsu, 1993; Mathis & Ellzey, 2003; Trimis & Durst, 1996). In these staged porous burners, the interface between the two regions often acts as a means to stabilize the combustion process over a wide range of flow conditions and the small pore region upstream can act as a flashback arrestor. (Trimis & Durst, 1996) examined spherical beads as media for a two stage porous radiant burner. The critical bead diameter to sustain combustion was found to be 9 mm. At diameters less than 9mm, the Peclet number was less than 65 and flame propagation could not be sustained, resulting in flame quenching. At bead diameters above 9 mm, a flame could be sustained. (Barra, 2003) modeled a two stage system and determined that low thermal conductivity in the upstream (small pore size) material resulted in the largest stable operating range.

Some literature is also available on the addition of a catalyst to porous material for improved burner properties. The effect of the location of a thin layer of platinum catalyst on radiant efficiency and emissions in a fiber surface radiant burner was modeled by (Rumminger, Hamlin, & Dibble, 1999). The authors concluded that only a thin layer of catalyst was needed on the downstream surface to achieve the efficiency improvements. (Cerri, Pavese, Saracco, & Specchia, 2003; Cerri, 2001) examined LaMnO_3 based materials and Pd as catalysts for a metal fiber system in radiant burners. The fibers were FeCrAl alloy and they were catalyzed with various forms of LaMnO_3 or Pd. The Pd catalyzed material showed improved performance with regards to lowering the emission levels of NO_x and CO.

Overall, the literature on burner materials and constructions attempts to improve the efficiency and/or emissions of existing designs. Of these, few have combined these changes with a catalyst material. Initial experiments were focused on catalyzed ceramic fiber mesh solutions, due to 3M's strength in Nextel alumina fibers. The analogous metal system that was also pursued are FeCrAl meshes, which are advantageous for catalyst development due to their wide spread adoption in the burner market. The second approach looked at developing novel media constructions that would overcome limitations that are present with existing burner substrate designs. These limitations include inadequate NO_x reductions in all uncatalyzed burner constructions, excessive cost and poor lifetime in catalyzed porous materials, and limited thermal shock resistance in ceramic foams.

4.0 Results and Discussion

4.1 Experimental methodology

The experimental methodology for the program has three focuses. The first is to identify catalyst-support chemistries that exhibit high activity for methane oxidation and high thermal stability and integrate the most attractive chemistries with our proprietary precious metal deposition process. Second, to develop catalyzed substrates based on the modification of existing burner mesh materials or introduce novel media constructions that maximize the gas-catalyst contact. The third focus is the integration of the catalyst-support chemistries with the substrates and testing in a burner/boiler environment, using NO_x emissions and radiant output to evaluate performance.

4.2 Technical approach

4.2.1 Catalyst-support preparation and testing

The general method for the preparation of catalyst materials involved modification of a carrier particle comprising commercial gamma alumina spherical beads (Alcoa 350 and Alcoa 450 alumina available from Alcoa Incorporated, Pittsburgh, PA and/or Sasol alumina spheres available from Sasol). The modification methods we used included impregnation of the alumina beads with a solution carrying the precursor of a modifying metal oxide material, deposition of a nanoparticle dispersion of a modifying metal oxide or oxide mixture onto the alumina beads to form a coated bead, or a combination of impregnation and coating, followed by drying and calcination of the impregnated and/or coated beads.

The test system used for measuring the methane combustion activity is shown in Figure 1. The conditions of the test were as follows: 1000 ppm methane balance air, 5 L/min volumetric flow rate, 25 mL catalyst, gas hourly space velocity (GHSV) = 12,000 hr⁻¹. A micropump was used to sample effluent gas from the reactor in 17 minute intervals into a GC fitted with an FID detector to measure the quantity of methane in the effluent. After collection of each data point, the reactor temperature was raised 50 °C via external heating to the next requisite temperature for collection of the next data point. The reactor wall temperature was the temperature shown for each data point on the resulting graphs. During this process the inlet temperature and the outlet temperature were also measured but are not displayed on the graph. In a typical reaction test, the temperature was taken from 50 °C to 500 °C in 50 °C increments resulting in the collection of seven data points showing the percentage of methane removed (conversion %) by the catalytic process at each temperature.

Figure 1. Schematic of the activity testing setup used for screening catalyst-support chemistries.

4.2.2 Substrate testing

Catalyst systems (catalyst-support-substrate combinations) were tested both in an open-air burner and residential boiler. Open-air testing allows for greater accessibility to the sample during testing and can highlight spatial variations in a sample that may be lost in testing within an enclosure such as a boiler. However, operation in a boiler presents unique conditions, such as pressure differentials, limitations on equivalency ratios due to gas mixing, flame confinement effects, and thermal gradients due to heat exchanger design, that are difficult to reproduce in open-air burners. Since this is ultimately the environment where the performance of the catalyst systems needs to be evaluated, boiler testing was used as a complementary test method to verify the effectiveness of samples positively identified in open-air testing.

The open-air burner testing setup is shown below (see Figure 2), along with a list of major hardware (see

Table 2). Methane and clean dry air were metered using mass flow controllers and passed through a flame arrestor before reaching the burner head. The burner head was a half cylindrical geometry that mimics a common burner design used in residential boilers (see Figure 3). Sample temperature (both front and backside) were measured with thermocouples, as well as infrared surface imaging. Combustion products were sampled just downstream of the burner and passed through a chiller to remove any water vapor before being sent to a series of gas analyzers. Emissions (NO_x , CO, CO_2 , CH_4) were monitored using infrared absorption methods and were dilution corrected to 0% O_2 in the sampled gas. Radiant heat flux was measured using a set of three thermopiles, positioned 9-1/2" downstream from the burner face. Typical operating conditions was 23% excess air (EA) and firing rates of 1-16 slm, or 29-464 kBtu/hr/ft².

Figure 2. Schematic of the burner testing setup.

Table 2. Burner system components

Component	Company	Product Number	Description
Air mass flow controller	Aalborg	GFCS-011374	0-200 STD L/min calibrated for Air, 3/8" compression fittings
Methane mass flow controller	Aalborg	SKUW-325711	0-30 STD L/min calibrated for Methane, 3/8" compression fittings
Mass flow controller power supplies	Aalborg	PS-GFC-110NA-2	12VDC power supply for each mass flow controller
Sample Gas Chiller	Universal Analyzers Inc.	3080	Remove humidity from collected gas sample.
NO _x Gas Analyzer	Teledyne Technologies Incorporated	T200m	Teledyne NO _x Gas analyzer, 0-200ppm ranges and data logging.
CO Gas Analyzer	Horiba Instruments Incorporated	VIA-510	Configured for CO measurement, 0-50/100/500/1000ppm ranges.
CO ₂ Gas Analyzer	Horiba Instruments Incorporated	VIA-510	Configured for CO ₂ measurement, 0-1/2/10/20% ranges.
CH ₄ Gas Analyzer	Horiba Instruments Incorporated	VIA-510	Configured for CH ₄ measurement, 0-50/100/500/1000ppm ranges.

Figure 3. Images of a commercially available cylindrical burner head, showing (a) the perforated outer surface, (b) the coarse mesh inner surface, and (c) the 'half-can' design used in the current experiments to simulate the cylindrical head design. The red arrow in (c) gives the direction of the gas flow through the burner head.

Boiler testing was conducted in a residential sized boiler (NTI Trinity Ti150). Samples were tested at 30% EA and fired at 15-150 kBtu/hr (equivalent to input power densities of 48-480 kBtu/hr/ft²). Boiler inlet water temperature was held constant at 60°C, with a temperature rise through the boiler (outlet minus inlet temperature) of 11°C. As with the open-air testing, emission data was dilution corrected to 0% O₂ in the sampled gas. Figure 4 shows an image of the boiler-burner configuration, highlighting the orientation of the burner with respect to the heat exchanger.

Figure 4. Burner head (left) and heat exchanger (right) from a residential boiler (NTI Trinity Ti150). Image taken from NTI (http://www.nythermal.com/trinity_ti, 1/1/12).

4.2.3 Additional analytical methods

In addition to activity and burner testing, an array of analytical tools were used to characterize the catalyst samples. These included scanning electron microscopy (SEM) to visualize the morphology, BET methods to quantify surface area, and differential thermal analysis (DTA) and thermogravimetric analysis (TGA) to measure the transition temperature for Pd reduction. Experimental details for the quantitative techniques are provided below.

Samples were mounted onto double-sided carbon tape adhered onto an aluminum stub. The mounted samples, except Pd catalyst samples, were coated with Au/Pd using an SEM Coating Unit PS3 (Ted Pella, Inc., Irvine, CA) sputter coater to minimize charging effects during imaging. The coated samples were imaged in secondary electron mode using a JEOL JSM-6400 Scanning Electron Microscope (JEOL USA, Inc., Peabody, MA) with the following imaging conditions: 20 kV, 17 mm Working Distance (W.D.).

Nitrogen (N₂) specific BET surface area analysis was performed on an ASAP 2020 Micromeritics Analyzer. Approximately 200 mg of material was used for each analysis. Each sample was degassed under high vacuum at 150°C for 60 minutes (ramp to 150°C from room

temperature at 10 °C/min.) prior to starting the analysis. Surface areas were calculated based on an 11-point BET isotherm obtained between $P/P_0 = 0.05$ and 0.3.

DTA and TGA were performed on several of the catalysts to determine the temperature of transition from PdO to Pd metal. The decomposition of PdO to Pd metal is well known in the literature, and is typically reported to occur near 800 °C (Nell & O'Neill, 1996). (Farrauto, 1998) used thermal gravimetric analysis to study this transition in Pd-based methane oxidation catalysts and reported significant differences in the transition temperature (as well as the reoxidation temperature upon cooling) depending on the material upon which palladium was supported.

The thermal analyses (DTA and TGA) were performed (simultaneously) using a Shimadzu TA60 TGA/DTA analyzer using alumina pans. An empty alumina pan was used as the reference. Samples and reference were heated at a rate of 20 °C/min with a constant flow of 20 mL/min of dry air from ~25 °C up to 1000-1200 °C. Data acquisition was continued for an additional 30 minutes during cooling of the samples. The cooling rate was not controlled and depended on the cooling efficiency of the cooling fan and furnace thermal properties. Thermal analysis software (TA 60, ver. 2.11) was used to analyze the data and obtain “glass transition” onset temperatures in the DTA traces for the PdO to Pd metal transition.

4.3 Results and Discussion

4.3.1 Catalyst-support development

From previous work we had discovered a family of highly efficient platinum-based catalyst for removal of both aliphatic (heptane) and aromatic (toluene) hydrocarbons. Because of the high total oxidation activity of these catalysts, we used these materials as a starting point for our work with methane oxidation.

Despite this high activity for oxidizing both toluene and heptane, this family of catalysts that was optimized for these higher hydrocarbons showed very little propensity for activating methane oxidation below 500 °C (see Figure 5). Variations on the chemistry of these catalysts were carried out by introducing a variety of different particulate and nanoparticulate supports for the nanoplatinum to attempt to increase the activity of these materials. In all these samples, the amount of platinum deposited on the samples is essentially the same as measured by unit *volume* of catalysts. Because the catalysts vary in density depending on composition and the activity is measured for a given volume of catalyst, keeping the amount of platinum incorporated constant for a given volume allows a more accurate comparison of changes in activity due to changes in the nature of the support.

Although numerous support compositions and formulations were prepared as nanoplatinum catalyst supports, the majority of these samples showed T_{50} values (where T_{50} is the temperature at which 50% of the inlet concentration of methane is combusted) greater than 500 °C. One exception was Platinum Catalyst 8, exhibiting a T_{50} near 470 °C (see Figure 6).

Figure 5. Methane combustion activity of nanoplatinum-based catalyst.

Figure 6. Methane combustion activity of modified nanoplatinum catalysts.

In addition to the Pt-based samples above, a number of alumina-bead supported catalysts with palladium were also tested under similar conditions, with the results of the analyses summarized in a typical activity graph (Figure 7) and summary table below (see Table 3). Because of the higher activities, these catalysts can be characterized by their T_{50} and T_{90} temperatures as determined from the oxidation data.

Table 3 summarizes the top 10 methane oxidation catalysts based on lowest light-off (T_{50}) temperatures. All samples reported in Table 3 were prepared with similar amounts of palladium deposited on the catalyst supports.

Figure 7. Methane combustion activity for Pd-based catalysts.

Table 3. Top 10 methane oxidation catalysts (sorted by T_{50} values)

DOE Sample	T_{50} (C)	T_{90} (C)	Testing Conditions						
			Flow Rate (L/min)	Packed Density (g/mL)	CH ₄ (ppm)	Sample Vol (mL)	Residence Time (sec)	GHSV (hr ⁻¹)	CH ₄ /O ₂ (stoich = 0.5)
Pd Catalyst 4	318	375	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 8	330	397	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 39	339	403	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 14	340	408	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 37	342	398	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 27	344	415	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 7	346	420	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 16	347	490	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 23	351	428	5	0.422	1000	25	0.3	12000	0.0048
Pd Catalyst 36	352	424	5	0.422	1000	25	0.3	12000	0.0048

The catalytic activity results for Pd-based catalysts reveal a number of potential candidate systems for use in low temperature combustion of methane, with light off temperatures as low as ~318 °C (Pd Catalyst 4). All samples were thermally processed using the same heat treatment protocol. Differences in light off temperatures between samples are believed to originate from the differences in the nature and composition of the metal/mixed metal oxide supports upon which Pd is deposited.

Many of the Pd-based catalysts are light to dark grey in color, changing in color to a light to dark brown after testing for methane combustion from 200 °C to 500 °C (see Figure 8 below). It is believed that the change in color is due to the formation of PdO phases, although the transformation onset temperatures may vary between catalyst samples.

The effect of increasing the amount of deposited palladium on a given catalyst support is shown in Figure 9. The amount of palladium in each sample in Figure 9 is less than 0.5 wt% Pd, and each sample has been normalized to the sample with the lowest wt% Pd (brown curve). Increasing the amount of palladium on the support appears to significantly increase the methane oxidation activity (decreasing T_{50} values) for loadings of 1x to 18x Pd, although less of an increase in activity was observed between loadings of 18x Pd and 39x Pd. A comparative example of a catalyst prepared by palladium nitrate solution impregnation is also plotted in Figure 9 (blue curve). Based on a similar weight percent of Pd, a palladium catalyst prepared

using our proprietary coating method (18x Pd (green curve), $T_{50} \sim 355^\circ\text{C}$) performs significantly better than the solution impregnated catalyst (26x Pd (blue curve), $T_{50} \sim 440^\circ\text{C}$).

Figure 8. Optical images of Pd Catalyst 3 (A) before, and (B) after methane oxidation testing.

Figure 9. Effect of Pd loading amounts on methane oxidation activity and comparison of 3M proprietary Pd coating method vs. Pd coating via solution impregnation method (blue curve)

Thermal Stability of Pd-based, methane oxidation catalysts: PdO decomposition

Thermal analysis methods (Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)) were used as a tool for determining the thermal stability of our palladium-based, methane oxidation catalysts. The use of DTA/TGA analysis in characterization of Pd/PdO based catalysts is described in the previous experimental sections. A representative plot of the TGA and DTA traces for Pd Catalyst 8 is shown in Figure 10 below.

Figure 10. DTA and TGA traces for Pd catalyst 8 under air flow and 20 °C/min heating rate.

Due to the low loadings of palladium used in our samples, the TGA trace (Figure 10, blue curve) did not show any significant weight loss commonly associated with the evolution of O₂ during PdO decomposition. The DTA trace (Figure 10, red curve), however, contained a noticeable endothermic transition near 800 °C which we believe to be related to the PdO decomposition reaction. Melting transitions are usually “peak” features and the melting point of bulk palladium (~1555 °C) is well above the temperature of the endothermic transition of Figure 10. It has also been reported that the reduction of PdO back to Pd metal is an endothermic process equal in magnitude to the enthalpy of oxidation (Gross, Appelbaum, & Gallagher, 1987). Therefore, the onset of PdO decomposition in Pd Catalyst 8 occurs near 812.81 °C, while the reoxidation of the

resulting Pd metal appears to significantly increase below ~740 °C as seen in the cooling curve portion of the DTA trace.

Other catalysts were tested using the methods described above, and analyzed where applicable. Not all catalysts showed distinct endothermic transitions in the DTA traces, however, reoxidation was observed on the cooling curve. Examples having such undeterminable transitions are noted as “N/A” for the T_{onset} as in the case of Pd Catalyst 11. Table 4 summarizes the results of the thermal analyses for Pd Catalyst samples 1-16, sorted from highest to lowest onset temperature for the PdO to Pd metal transition.

Table 4. Onset temperature for PdO decomposition: Pd Catalysts 1-16 (sorted by T_{onset})

DOE Sample	T_{onset} (C)	TGA-DTA Analysis Conditions						
		Heating Rate (C/min)	Flow Rate (mL/min)	Analysis Gas	Sample Weight (mg)	Start Temp (C)	Stop Temp (C)	Sharp Onset Temp?
Pd Catalyst 11	N/A	20	20	Dry Air	25	22	1200	No
Pd Catalyst 6	898	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 15	867	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 4	859	20	20	Dry Air	25	22	1000	No
Pd Catalyst 14	853	20	20	Dry Air	25	22	1200	No
Pd Catalyst 16	839	20	20	Dry Air	25	22	1200	No
Pd Catalyst 12	826	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 1	824	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 5	818	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 8	813	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 7	813	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 9	811	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 3	811	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 13	810	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 10	807	20	20	Dry Air	25	22	1200	Yes
Pd Catalyst 2	798	20	20	Dry Air	25	22	1200	Yes

As noted in the work by Farrauto et al.(Farrauto, 1998), we also see significant differences in the onset temperature depending on the substrate upon which palladium is supported. Four of the sixteen samples show onset temperatures for PdO decomposition above 850 °C, with Pd Catalyst 6 showing an onset temperature approaching 900 °C. Further work into identifying the stabilizing factors in these samples are required, but these initial results are encouraging for the construction of more thermally durable, high activity Pd-based methane oxidation catalysts.

Scanning electron microscopy (SEM) was used as a screening method for determining any significant changes in the microstructure of various catalyst supports (with and without palladium) after various high temperature treatments. Figure 11 and Figure 12 show SEM images of Pd Catalyst 2 and 6, respectively, before and after heating from room temperature to 800 °C at 5 °C/min and keeping at 800 °C for one hour in air before slowly cooling back to room temperature.

Figure 11. Pd Catalyst 2 before and after heating at 800 °C.

Figure 12. Pd Catalyst 6 before and after heating at 800 °C.

From our work on the differential thermal analysis of Pd catalysts presented in the previous section, Pd Catalyst 2 and Pd Catalyst 6 exhibited the lowest and highest onset temperatures for PdO decomposition, respectively. The Pd Catalyst 2 had a PdO decomposition onset temperature of 798 °C, and would therefore be expected to exhibit a notable degree of PdO decomposition during the one hour heating at 800 °C. The higher mobility of Pd metal (vs. PdO) at these temperatures would suggest a greater likelihood for sintering and growth of Pd structures on the surface of the catalyst. The SEM images for Pd catalyst 2 show the appearance of numerous bright particles dispersed on the surface which were not observed in the sample prior to heating. This observation suggests significant Pd particle growth is occurring on this sample.

On the other hand, Pd catalyst 6 has an onset temperature for PdO decomposition of ~898 °C (approximately 100 °C higher than Pd catalyst 2). Therefore, the thermal treatment at 800 °C is not expected to cause a significant amount of Pd metal to form on the surface of this catalyst, with a correspondingly smaller amount of structural reorganization being expected due to the lower surface mobility of the PdO particles. The SEM images for Pd Catalyst 6 (Figure 12) appear to confirm these ideas, where the before and after image for Pd catalyst 6 are not significantly different in morphological features.

Palladium catalysts were further thermally challenged by heating from room temperature to 900 °C or 1000 °C at 5 °C/min and keeping at 900 or 1000 °C for one hour in air before slowly cooling back to room temperature. SEM images of the catalysts after heat treatment were then compared. A representative example of the differences in Pd distribution and sizes on different catalyst supports are shown in the SEM images below in Figure 13 and Figure 14.

Figure 13. Pd Catalyst 2 after 900 °C and 1000 °C heat treatments.

Figure 14. Pd Catalyst 4 after 900 °C and 1000 °C heat treatments.

It is clear from the comparison of Pd Catalyst 2 and Pd Catalyst 4 that the catalyst support upon which Pd is coated plays a critical role in the thermal stability of the Pd species at elevated temperatures of 900 and 1000 °C (well above the PdO decomposition temperatures of both catalysts). The Pd Catalyst 2 maintains significantly larger particles of Pd material versus the Pd Catalyst 4 sample, where the Pd is highlighted as small bright spots due to the imaging mode (backscattered electron (BEI) imaging) used in these images. Although we previously noted the effect of catalyst support differences on the PdO decomposition temperature and corresponding stabilization of Pd growth at temperatures of 800 °C, these results suggest that the underlying surface morphology and structure of the catalyst support itself may provide for enhanced stability toward Pd agglomeration and growth even at temperatures well above the PdO decomposition temperature of the catalyst. Specifically, catalyst supports with smaller surface features as observed in Pd Catalyst 4, where isolated nanostructures may exist, appear to correspondingly isolate Pd particles from further interaction and growth.

Thermal Stability of Pd-based, methane oxidation catalysts: Catalyst Support Stability

Based on the results in the previous section, further studies on the thermal stability of the catalyst support were performed at temperatures up to 1200 °C. Various solution treatments of Catalyst Support A were carried out in order to maintain the nanostructural features of the support at elevated temperatures. SEM images of the resulting products from two different support treatments after heat treating at 1000 °C for 1 hour are shown below in Figure 15 and Figure 16 (each column of images are two magnifications of the noted sample). After the high temperature heat treatment, Catalyst Support A shows indications of sintering and growth, where the surface morphology and features are on a scale greater than 100 nm (first column of images in either set of images). However, depending on the solution treatment, this sintering and growth can either be enhanced (as in the case of Catalyst Support A-4-0.5, Figure 15) or interrupted (as in the case of Catalyst Support A-2-6.5, Figure 16). Based on such image analyses, solution treatments such as Catalyst Support A-2-6 would be expected to provide a more thermally stable catalyst support surface upon which Pd species would be restricted from sintering/growth, and thereby maintain higher overall surface areas.

Figure 15. Catalyst Support A vs. A-4-0.5 after heat treatment at 1000 °C/1 hour.

Figure 16. Catalyst Support A vs. A-2-6.5 after heat treatment at 1000 °C/1 hour

Media temperatures encountered during burner operation may increase to more than 1000 °C and at times approach upwards of 1200 °C for brief periods of time. Therefore, catalyst supports were further tested for thermal stability at 1200 °C for 1 hour in air in a similar manner as described previously. Figure 17 compares SEM images of Catalyst Support A after heat treatment at 1000 °C vs. 1200 °C for 1 hour in air. Significant sintering and growth is observed for Catalyst Support A after the 1200 °C treatment when compared to the 1000 °C treatment.

Various solution treatments of Catalyst Support A were carried out in order to maintain the nanostructural features of the support at temperatures of 1200 °C. SEM images from the resulting products from three different support treatments and the control sample of Catalyst Support A after heat treating at 1200 °C for 1 hour are shown below in Figure 18 and Figure 19 (each column of images are two magnifications of the noted sample).

Previously, we identified promising solution treatments of Catalyst Support A which appeared to stabilize nanostructural features even after heating at 1000 °C for 1 hour (e.g., Catalyst Support A-2-10, Figure 18). However, increasing the temperature of heat treatment to 1200 °C for 1 hour appears to significantly decrease the stability of these nanostructural features, making Catalyst Support A-2-10 less promising for these elevated temperature conditions.

Figure 17. Catalyst Support A after 1000 °C vs. 1200 °C heat treatment for 1 hour

Figure 18. Catalyst Support A vs. A-2-10 heat treated at 1200 °C/1 hr and 1000 °C/1 hr

Figure 19. Catalyst A vs. A-51-1 and A-35-1 after heat treatment at 1200 °C for 1 hour.

Other solution treatments on Catalyst Support A (e.g., Catalyst Support A-51-1 and A-35-1) stabilize nanostructural features of the support after heat treatment at 1200 °C as shown in the SEM images in Figure 19. Based on these results, such solution treatments would be expected to provide a more thermally stable catalyst support surface (up to temperatures of 1200 °C) upon which supported Pd species may be less prone to sintering and/or growth.

Based on the above results, various multi-component, solution-modified Catalyst Support A samples were coated onto a secondary Catalyst Support B for further characterization using nitrogen BET surface area analysis. The results for several modified catalyst supports are summarized in

Table 5 along with unmodified Catalyst Support B and Catalyst Support A for comparison. All catalyst supports were heat treated to 1200 °C for 1 hour in air (5 °C/min ramp from room temperature) prior to analysis. Significantly higher surface areas were obtained for the selected multi-component based catalyst support samples compared to Catalyst Support B (B-1) or Catalyst A coated onto Catalyst Support B (B-A-1). These higher surface areas appear to correlate well with the SEM images of similarly prepared Catalyst Supports in Figure 19. One sample (B-A51-1) was further coated with Pd and did not appear to change in surface area significantly (B-A51-Pd-1).

Table 5. BET surface areas of Catalyst Supports after 1200 °C heat treatments

DOE Sample ID	BET Surface Area (m ² /g)	R ² (Correlation Coefficient.)
B-1	5.0	0.99996
B-A-1	6.0	0.99980
B-A51-1	40.0	0.99999
B-A51-Pd-1	36.0	0.99995
B-A35-1	32.4	0.99997

Catalyst integration into burner media substrates

Testing of burner performance required coating of the catalyst support onto various types of media substrate forms. Planar burner media substrates, both ceramic and metallic, were coated with catalyst supports through solution phase impregnation near incipient wetness followed by drying prior to calcination in air at elevated temperatures. Using this method, uniform coatings were obtained (based on color uniformity of the treated fabrics) upon which palladium catalyst was subsequently deposited.

4.3.2 Substrate development

The experimental approach for substrate development has been to (1) modify existing burner mesh materials to incorporate a catalyst material and (2) introduce novel media constructions that overcome limitations that are present with existing fiber mesh designs. Initially, it was assumed that commercially available fiber mesh burners would be adequate substrates for the catalyst and that development efforts would focus on the activity and thermal stability of the catalyst through engineering of the support chemistries (see Section 4.3.1). While modest improvements in the NO_x reduction capabilities were achieved by catalyzing a variety of fiber mesh materials, a combination of the mesh construction and catalyst deposition technique limited the ultimate effectiveness of the catalyst. This discovery shifted the focus of the development to the substrate. Results given below highlight the progress through the grant period.

4.3.2.1 Woven mesh substrates

Two woven mesh substrates were used in initial open-air burner testing (see Section 4.2.2) as screening tools for catalyst-support chemistries. These included a woven FeCrAl mesh and a woven ceramic fabric from 3M (Nextel 312 AF-62-XN). Figure 20 - Figure 22 give the radiant efficiency and NO_x emissions for both of these substrates with three different catalyst chemistries (labeled catalyst #5-7). All three catalyst systems on Nextel substrates show modest increases in radiant efficiency (1-4%) at 2.0 and 4.0 slm of methane. In terms of NO_x emissions, catalysts #5 and #6 show decreases in emissions of up to 6 ppm. On the FeCrAl

fiber mesh substrates, catalyst #5 shows a 2-7% increase in radiant efficiency in all conditions except 1.0 slm methane and a 13-21% decrease in NO_x emissions at all firing conditions. Catalyst #7 shows a 3-10% increase in radiant efficiency for all conditions. However, it also shows increased NO_x emissions at two of the five conditions relative to the uncoated FeCrAl fiber mesh. Based on these results, subsequent development focused on catalyst #5 and #7.

Figure 20. Radiant efficiencies for catalysts #5-7 on Nextel substrates at a constant equivalency. Radiant efficiencies for catalyst #5 (red), #6 (green), and #7 (orange) on a Nextel substrate at an equivalence ratio of 0.8. Results for a bare (uncoated) Nextel substrate are given as a reference (blue).

Figure 21. NO_x emissions for catalysts #5-7 on Nextel substrates at a constant equivalency. NO_x emissions for catalyst #5 (red), #6 (green), and #7 (orange) on a Nextel substrate at an equivalence ratio of 0.8. Results for a bare (uncoated) Nextel substrate are given as a reference (blue).

Figure 22. Radiant efficiencies for catalysts #5-7 on uncoated FeCrAl fiber mesh substrates at a constant equivalency. Radiant efficiencies for catalyst #5 (red), #6 (green), and #7 (orange) on a FeCrAl fiber mesh substrate at an equivalence ratio of 0.8. Results for an uncoated FeCrAl fiber mesh substrate are given as a reference (blue).

Figure 23. NO_x emissions for catalysts #5-7 on uncoated FeCrAl fiber mesh substrates at a constant equivalency. NO_x emissions for catalyst #5 (red), #6 (green), and #7 (orange) on a FeCrAl fiber mesh substrate at an equivalence ratio of 0.8. Results for an uncoated FeCrAl fiber mesh substrate are given as a reference (blue).

The next series of experiments looked at optimizing the chemistry of the support structure and loading level of the catalyst. Note that changes to the system configuration limit direct comparison of the quantitative results with the previous series of figures. Figure 24 compares the radiant efficiency and NO_x emissions for variations of catalyst #5 on Nextel. The first variation (shown in red) looks at the effect of the metal oxide support without any Pd catalyst. The second variation (shown in green) looks at the effect of loading level of metal oxide support. In this case, the sample has twice the weight of metal oxide and the same loading level of Pd. For both variations, there is up to 3% improvement in radiant efficiency at low firing and negligible change at high firing. In terms of NO_x emissions, when there is no Pd catalyst (only a metal oxide support), the emissions are increased in all but one firing condition. For the sample with greater amounts of metal oxide support, there is up to a 3 ppm decrease in NO_x emissions at low through mid firing conditions relative to the bare Nextel sample. However, at the highest firing condition, the NO_x levels are more than 15 ppm higher. These results suggest that metal oxide by itself is ineffective at reducing NO_x, but that it increases the radiant output when running at low fire (i.e., in radiant mode).

Figure 24. Radiant efficiency and NO_x emissions for variations of catalyst #5 on Nextel. Radiant efficiency and NO_x emissions for bare Nextel (blue), catalyst #5 on Nextel without any Pd (red), and catalyst #5 on FeCrAl with twice the weight of metal oxide support (green).

A second set of optimization experiments considered the loading level of the Pd catalyst. Figure 25 compares the loading level of Pd used in the previously discussed data (labeled 1x), along with 2x, 4x, and 10x loadings. With the exception of low fire, the higher Pd loadings consistently show higher radiant output than both the bare Nextel and the 1x loading. At the higher firing rates, the 2x performance decreases to match the 1x output while 4x and 10x show a 1-2% boost in efficiency all the way through the high firing condition. In terms of NO_x, emissions are consistently higher for all of the Pd coated samples relative to the bare Nextel. Comparing the loading levels, 1x and 2x show higher emissions than both 4x and 10x at all firing conditions, with the differences being the largest at the high firing conditions. These results, when

compared to the samples with metal oxide and no Pd (as shown in Figure 24), demonstrate the importance of the interaction between the catalyst and metal oxide in determining a material's efficacy towards NO_x reduction. It is only with the sample that has both the increased Pd loading and the metal oxide support that there is a reduction in NO_x.

The results from the catalyst chemistry optimization experiments on Nextel (Figure 24 - Figure 25) were used to select a catalyst for the FeCrAl metal fiber mesh coatings. The metal oxide was left unchanged from what was previously used in catalyst #5 and #7 since there was similar radiant output and higher NO_x production in all of the hybrids tested. However, the Pd level was increased to 10x based on the improvements seen on Nextel. Figure 26 shows the radiant efficiency and NO_x emissions for catalyst #5 and #7 with 10x Pd on FeCrAl metal fiber mesh substrates. As was found with the Nextel data in Figure 25, there is an increase in radiant efficiency at every firing condition with the 10x loading of Pd on FeCrAl. However, unlike the Nextel samples without any metal oxide support, there is significant NO_x reduction with the 10x Pd loadings. Catalyst #5 shows 2-9 ppm decreases at all but one firing condition while catalyst #7 shows 20-30 ppm decreases at high fire conditions.

Figure 25. Radiant efficiency and NO_x emissions for varying Pd loading on Nextel. Radiant efficiency and NO_x emissions for bare Nextel (dark-blue) and variations in the Pd loading: 1x (red), 2x (green), 4x (orange), and 10x (light-blue), all on Nextel.

Figure 26. Radiant efficiency and NOx emissions FeCrAl fiber mesh substrates with 10x Pd loading. Radiant efficiency and NOx emissions from half-can burner head testing for an uncatalyzed sample (blue curve) and two catalyst chemistries (catalyst #5: green and catalyst #7: red) with 10x Pd loading.

Both the improvement in radiant efficiency and decrease in NOx can be explained by increased flame stabilization at the burner surface relative to the uncoated FeCrAl fiber mesh substrates. Figure 27 shows the substrate temperature for both the catalyzed and uncatalyzed systems. As the amount of methane fed to the burner is increased, all three systems initially increase in surface temperature and then plateau. This high surface temperature is indicative of the burner running in radiant mode, with most of the combustion occurring at the burner surface. The decrease in surface temperature marks the transition to blue-flame mode, with the combustion moving away from the surface. This transition occurs at nearly twice the firing rate for the catalyzed system, making the surface combustion regime twice as large. By holding the flame at the surface, a lower overall combustion temperature is achieved and less thermal NOx generated. In addition, by keeping the combustion at the burner surface, a larger percentage of the heat is radiated from the surface rather than transferred to the flowing gas.

Figure 27. Burner surface temperature for FeCrAl fiber mesh substrates. Burner surface temperature from half-can burner head testing for an uncatalyzed sample (blue curve) and two catalyst chemistries (catalyst #5: green and catalyst #7: red) with 10x Pd loading.

Based on the promising performance for catalysts #5 and #7 in open air testing on cylindrical head burners, testing on the FeCrAl fiber mesh substrates moved to in-boiler testing. The NTI Trinity Ti150 boiler was selected as a representative boiler system with a burner head size (150 kBTU/hr maximum) that is within the current processing capabilities of the lab. While the test protocol was originally designed to screen the best performing catalysts from open-air testing and also look at new catalyst modifications, it evolved into an iterative series of tests trying to replicate the performance observed in open-air testing due to unforeseen challenges with boiler system constraints.

Initial testing of the catalyst coated fiber meshes showed little differentiation between the catalyst and the bare FeCrAl substrate. Figure 28 shows the NO_x emissions for catalysts #5 and #7 at two excess air (EA) conditions (10, 30%). At 10% EA, the emissions are nearly identical while at 30% EA there is a slight decrease (~10 ppm) with the catalyzed material. This result differs significantly from the ~75% reduction in NO_x emissions observed previously at high fire conditions.

Figure 28. In-boiler NOx emissions for catalysts #5 and #7. NOx emissions for catalysts (a) #5 and (b) #7. Green and purple data is from uncoated FeCrAl (control) while blue and red data is the catalyst coated samples. Green and blue data is at 10% excess air while red and purple data is at 30% excess air.

Figure 29 shows the (a) NOx emissions and (b) CO emissions for catalyst #7 after correcting the processing conditions and achieving the high surface area catalyst structure. The NOx results continue to show little differentiation between the catalyzed and bare samples at either of the excess air conditions. The CO emissions illustrate a second problem associated with operating in a boiler versus open-air burner testing. CO emissions can be used as an indicator of the combustion quality, with higher levels suggesting inadequate gas mixing and incomplete combustion. Figure 29b shows that at 10% EA, there is a rapid increase in CO levels as the firing rate is increased. This is in contrast to the results from the open air testing, where CO levels were typically well below 100 ppm at ~23% EA for all firing conditions. The inadequate mixing in the boiler is a result of the compact gas train design that is common among most boilers. This problem is typically overcome by running at higher excess air levels. However, this reduces the thermal efficiency of the boiler and is counter to the project objective of a low NOx, high efficiency burner. In an attempt to run at lower excess air levels, a perforated plate was inserted between the burner and the combustion chamber to act as a pressure drop. Ideally, this would help minimize any pressure gradients within the gas train and improve the gas mixing. This proved ineffective, as CO emissions continued to be in excess of 700 ppm at high firing conditions.

Figure 29. In-boiler NOx and CO emissions for catalyst #7. (a) NOx emissions and (b) CO emissions for catalyst #7. Green and purple data is from bare FeCrAl (control) while blue and red data is the catalyst coated samples. Green and blue data is at 10% excess air while red and purple data is at 30% excess air.

In addition to decreasing the thermal efficiency, higher excess air levels also reduce the surface temperature of the burner. Figure 30 gives the burner temperature during in-boiler testing that was measured with a surface thermocouple. At 30% EA, there is a 50-100°C decrease in the surface temperature. However, even at 10% EA, the surface temperature is >400°C cooler than temperatures measured in open-air burner testing. This is problematic for the catalyst, as it is too cool to expect significant catalytic activity. This result was counterintuitive, since one would expect the confinement of the heat exchanger to increase the burner surface temperature relative to the open-air testing. To increase the temperature, half of the burner surface was covered, as shown in Figure 31a. This increased the input power density from 0.3-3.3 kBTu/hr/in² to 2.2-6.7 kBTu/hr/in². The surface temperature, however, did not increase and the NOx emissions remained undifferentiated from the bare FeCrAl (see Figure 31b).

Figure 30. In-boiler burner surface temperature. Surface temperature for catalyst #7 as a function of firing rate at 10% (blue) and 30% (red) excess air.

Figure 31. Increased burner heat flux. (a) Image of the burner running in the open-air with half of the surface area obstructed. (b) In-boiler NO_x emissions for the burner shown in (a) at 10% EA with the bare FeCrAl (blue) and catalyst #7 (green). The red data is from the bare FeCrAl with no surface blocked.

This series of experiments highlights the engineering constraints with operating in a boiler system. During open-air burner testing, a set of optimal operating conditions were identified, including burner surface temperature (600-900°C), excess air (10-23%), and input power density (3-7 kBtu/hr/in²). In moving to in-boiler testing, there was an added constraint of the system design, including the burner, gas train, and heat exchanger enclosure. This aspect of the project is essentially fixed, as a redesign of the boiler is beyond the scope of the project. Based on the results shown above, we were unable to find an operating condition for in-boiler testing that achieved the desired temperature or excess air level and thus were unable to reproduce the NO_x reductions measured in open-air testing.

An alternative to redesigning the boiler is to modify the existing fiber mesh material. The major problem with the fiber mesh substrates is that they are relatively thin and densely packed. As a result, the catalyst coating is concentrated at the exposed surface of the mesh and has minimal contact with the reactive gases as they pass through the burner. The goal with modifying the substrate is to increase the gas-catalyst contact time while maintaining or reducing the pressure drop across the burner material. One approach is to increase the thickness of existing fiber mesh substrates.

The FeCrAl metal fiber meshes tested in an open air burner and boiler testing with catalyst #5 and showed slight improvements in NO_x emissions over a limited firing region. These materials had an aerial density of ~1,400 g/m² and thickness of 1.4 mm. Thicker meshes are also available commercially, which are twice as thick and twice as dense. Figure 32 shows the NO_x emissions data from open-air burner testing for 1.4 mm and 2.8 mm thick FeCrAl fiber mesh. The thicker mesh (red data) shows a small reduction in NO_x emissions when compared to the thinner (blue data). When coated with catalyst #5, both show slight decreases in NO_x at low fire

conditions relative to the bare meshes and increased NO_x at high fire (>200kBTU/hr/ft²). While this thicker substrate helps increase the contact time between the gas and the substrate, the dense weave limits the coverage of catalyst to the outer most surface of the mesh. Therefore, the catalyst-gas contact time remains relatively constant compared to the thinner meshes and shows negligible improvements in the NO_x emissions.

Figure 32. 2x FeCrAl fiber mesh thickness. NO_x emissions for 1.4 mm (blue) and 2.8 mm (red) thick FeCrAl fiber mesh. The plot on the right includes the same data, along with catalyzed (catalyst #5) fiber meshes for 1.4 mm (green) and 2.8 mm (purple) thick FeCrAl fiber mesh.

4.3.2.2 Novel media constructions

Novel catalyzed media constructions were developed to overcome the limitations of the fiber mesh substrates. This novel media effectively increases the thickness of the substrate and increases the gas-catalyst contact. The construction of the novel media also gives much greater control over the temperature profile that the catalyst experiences by adjusting the amount of surface area coated with the catalyst. This is advantageous, both in terms of preventing exposure to excessively high temperatures and in maintaining sufficient temperatures for catalytic activity.

In an initial set of experiments, the ratio of catalyzed (catalyst #5 with 10x Pd) to uncatalyzed surface area was varied such that <50% of the available surface area was uncoated. This sample was tested from low to high fire in the burner system and was found to have significant improvements over the bare substrate. An increase in the radiant power density was observed (Figure 33a), which corresponds to a 3-13% increase in radiant efficiency over the entire test range. The highest increase in the radiant output was observed in the radiant region of 29-

175kBTU/hr/ft², where the highest upstream and downstream temperatures are measured (Figure 33b). It is in this region that we would expect to see media damage due to the high temperature. These high temperatures are destructive not only to the media but also to the stainless steel burner-can and will need to be addressed to achieve adequate lifetime results.

Figure 33. Radiant efficiency and burner surface temperatures. Radiant efficiency and burner surface temperature data of two novel media samples tested in the half-can burner system. The blue sample has no catalyst coating; the red sample has 70-80% of the available surface area coated with catalyst #5 with 10xPd.

One of the other significant improvements with this sample is the large reduction in NO_x (see Figure 34a) for both low and high fire. An average NO_x reduction of 64% is measured for firing conditions higher than 175kBTU/hr/ft² (blue flame region) as compared to the bare media and a 69% NO_x reduction when compared to a bare FeCrAl mesh substrate. The radiant region shows a 13% increase in radiant output and an average NO_x reduction of 83% when compared to both the uncatalyzed media and bare FeCrAl mesh substrate. In addition, the radiant region also has an increase in the adjusted CO levels (see Figure 34b), indicating less efficient combustion than in blue flame. This decrease in combustion efficiency is not that significant, as greater than 97.9% of the methane is combusted for all tested conditions (see Figure 35).

Figure 34. NO_x and CO Emissions. NO_x and CO emissions data of two novel media samples tested in the half-can burner system. The blue sample is uncoated while a majority of the surface of the red sample (>50%) has been coated with catalyst #5 with 10xPd loading.

Figure 35. Unburned hydrocarbons. Unburned hydrocarbons data of two novel media construction samples tested in the half-can burner system. The blue data is uncatalyzed while the red data has been coated with catalyst #5 and 10x Pd.

Based on the encouraging results shown in Figure 33 and Figure 34, a set of experiments was designed to systematically vary the ratio of uncoated to coated surface area in a sample. By lowering the concentration of catalyzed surface area, the overall media temperature should decrease and increase the lifetime of the media. Four ratios were tested with catalyzed media content of 0-100% (by volume) with catalyst #5 with 10x Pd and labeled as samples A-D.

Radiant efficiency and NO_x emissions results are shown in Figure 36. For sample A, there is minimal change in the NO_x emissions relative to the bare media. Samples B and D initially look quite similar and lower the NO_x emissions to sub 5 ppm at low fire. However, with increasing firing rate, sample B jumps up to NO_x levels close to the bare media while sample D stays around 30 ppm. This is due to the fewer catalytic surfaces relative to sample B, which helps to reduce the media temperature to approximately 800°C. This expands the operating range where the catalyst is active ($T > T_{50}$) yet thermally stable ($T < 800\text{--}1000^\circ\text{C}$) and lowers the NO_x emissions over the entire fire range. This performance has been shown to be consistent over 13 hours of testing, with a constant media temperature and NO_x emissions throughout. This included seven cycling tests (1-16 slm) and four hours of continuous testing at a single condition (see Figure 37).

Figure 36. Radiant efficiency and NO_x emissions values. Radiant efficiency and NO_x emissions from half-can burner head testing with mixtures novel media coated with catalyst #5 with 10xPd or uncoated media. The four samples tested are sample A (red), B (orange), C (blue), and D (green).

Figure 37. Extended operation NO_x emissions for sample D. Time dependent NO_x emissions (red), media temperature (blue), and outer burner surface temperature (green) for extended burner operation with sample D in open air conditions with 4.0 slm CH₄ and 23% EA.

Based on the improvements seen in NO_x with the novel media, adaptations of this design concept were developed that reduce the pressure drop as well as increase the heat transfer through the media. This construction (hence forth referred to as novel media NM2) has a lower pressure drop when compared to the novel media discussed earlier, referred to here as novel media NM1 (see Figure 38). This reduction in pressure drop is a result of the increased open space in novel media NM2.

Figure 38. Pressure drop through burner media. Pressure drop through samples of three different burner media in their typical configuration. Novel media NM1 (blue) is the construction used in the initial testing (see Figure 36) and novel media NM2 (green) is the construction with greater open space. FeCrAl metal fiber mesh (red) is also shown as a reference material.

Open air burner testing of both of the uncatalyzed novel media constructions produce similar results (see Figure 39). When each of these samples are catalyzed with Pd, the NO_x emissions for both drop significantly relative to the uncatalyzed samples. However, the media temperature is quite different for the catalyzed novel media samples. When NM1 is catalyzed, there is a spike in the temperature at low fire, followed by temperatures similar to the uncatalyzed samples. For NM2, the temperature spike at low fire is absent and the temperature is >200°C above the uncatalyzed sample over the entire range. These changes can be attributed to the lower pressure drop of NM2 and improved heat transfer.

Figure 39. NO_x emissions and novel media temperature. The above graphs show the NO_x novel media temperature data catalyzed and uncatalyzed novel media. Novel media NM1 uncatalyzed (dark blue), novel media NM1 catalyzed with Pd (orange), novel media NM2 uncatalyzed (green), novel media NM2 catalyzed with Pd (purple) are shown.

Testing of the novel catalyzed media NM1 was also conducted in a residential sized boiler (NTI Trinity Ti150). Figure 40 shows the NO_x results from these tests. The first two sets of data compare the uncatalyzed fiber mesh (blue data) to a catalyzed fiber mesh (purple data). Throughout the firing range, the catalyst sample shows no significant deviation from the uncatalyzed sample. As mentioned earlier, this is due to a combination of the mesh construction and catalyst deposition technique that limit the penetration of the catalyst through the mesh thickness. This surface concentrated coverage provides inadequate contact between the fuel and the catalyst and limits its effectiveness. The second two sets of data are for novel catalyzed media NM1 with catalyst #5. The amount of catalyzed surface area is equivalent to sample B (orange data) and sample D (green data) in Figure 36. The novel media NM1 shows significant decreases in the NO_x emissions at both the low and high firing rates relative to the fiber mesh. The similarity of NM1 with sample B and D coverage suggests that the overheating issues experienced in the open-air testing with sample B might have been mitigated by the close proximity of the condensing heat exchanger.

Figure 40. Boiler NO_x emissions. NO_x emissions from boiler testing (NTI Trinity Ti150) at 30% EA, including uncatalyzed fiber mesh (blue), fiber mesh with catalyst #5 (purple), novel catalyzed media NM1 with catalyst #5, with the amount of catalyzed surface area equivalent to sample B (orange) and sample D (green) in Figure 36.

Based on all the constructions tested, the results for the novel media far exceeded the fiber mesh samples for NO_x emissions in both the open air and boiler testing. Of these, novel media #2 (NM2) showed the added benefit of a stable thermal profile across all firing conditions and will be the focus of continued development. This will include optimization of the percentage of catalyzed material and the pressure drop through the media.

5.0 Benefits Assessment

Catalyzed combustion offers the advantages of increased fuel efficiency and decreased emissions (both NO_x and CO), along with an expanded operating range. These performance improvements are related to the ability of the catalyst to stabilize the flame within the burner media and to combust fuel at a much lower temperature compared to uncatalyzed combustion. The improvement in radiant efficiency with the addition of a catalyst has been previously reported (Cerri, Pavese, Saracco, & Specchia, 2003; Rumminger, Hamlin, & Dibble, 1999; Barnes, 2011).

It is assumed that this catalyst technology will best be applied to boilers ranging in size between 1 and 10 MMBtu/hr. During the course of this program, we have developed a catalyzed novel media that has demonstrated a 5-40% improvement in radiant efficiency in open flame testing compared to commercial uncatalyzed FeCrAl knit fabric. This improvement in radiant efficiency could lead to an improvement in boiler efficiency of 0.5% which would result in an aggregate annual energy savings of up to 8.9 TBtu/yr for industrial and commercial boilers within the target size range. In addition, that same catalyzed novel media has shown to reduce the NO_x emissions by 65% in blue flame mode and 75% in radiant mode, again compared to the emissions levels for uncatalyzed FeCrAl knit fabric in open air testing. When tested in a boiler, the novel catalyzed media demonstrated a reduction in NO_x of almost 50% in radiant mode and 35-40% in blue flame mode compared to NO_x values measured in the same boiler with FeCrAl knit fabric. Using the 40% reduction in NO_x demonstrated in the boiler system, it is anticipated that the annual NO_x emission levels could be reduced by up to 40,000 tpy by adoption of this technology into boiler applications within the targeted size range.

5.1 Benefit from decreased NO_x emissions

One by-product of natural gas combustion is NO_x production, which has been shown to have adverse health and environmental effects and is regulated by the EPA and several states. To lower NO_x emissions, the amount of excess air is often increased. While this lowers the NO_x levels, it also cools the combustion products and decreases boiler efficiency. The addition of a catalyst can lower the NO_x levels while maintaining or decreasing the amount of excess oxygen by lowering the temperature of methane oxidation. This achieves a reduction in NO_x emissions without sacrificing energy efficiency.

As reported above, 3M's catalyst novel burner media has demonstrated a 65% reduction in blue flame regime and 75% reduction in radiant mode in open air testing compared to emissions levels measured from the same head with a commercial uncatalyzed FeCrAl knit fabric media. When tested in boiler, the novel catalyzed media demonstrated a reduction in NO_x of almost 50% in radiant mode and 35-40% in blue flame mode. Using these results, it is anticipated that a NO_x reduction of up to 40,000 tpy can be achieved in small boiler systems (1-10 MMBtu/hr) in the US.

The calculations for NO_x reduction were based on data presented in a NESCAUM report (Amar, Senior, & Afonso, 2008). Industrial, commercial, and institutional (ICI) boilers accounted for NO_x emissions of approximately 1,100,000 tpy in the US in 2002. Though natural gas accounts for 70% of the fuel used in these boilers, other fuel sources can also produce NO_x emissions. The potential NO_x reduction was calculated by assuming 25% of the emitted NO_x is associated with natural gas boilers and taking into account that 36% of the boilers are units used for smaller industrial and commercial applications. The potential NO_x reduction is based on the 40% reduction that has been previously demonstrated with the 3M novel catalyst during in-device testing in a commercial boiler. Using these assumptions, it is anticipated that the annual NO_x emission levels could be reduced by up to 40,000 tpy by commercial adoption of this technology.

Table 6. NO_x reduction calculation

Total NO _x emission from ICI boilers (tpy)	1,100,000
Percentage of total NO _x emissions associated with natural gas boilers	25%
Percentage of boiler units in size range applicable for technology	36%
Demonstrated NO _x reduction during program	40%
Estimated total annual NO _x reduction (tpy)	40,000

5.2 Benefit from improved efficiency

As shown in Figure 39 and Figure 40 of this report, the novel catalyzed media showed an improvement of 5-40% in radiant efficiency compared to commercial uncatalyzed FeCrAl knit fabric. This material has not yet been tested in a boiler to translate this radiant efficiency into boiler efficiency, but for the sake of these calculations, we will assume that this improvement translates into a 0.5% improvement in boiler efficiency.

The calculations for potential efficiency improvement are taken from data published by Energy and Environmental Analysis, Inc (Energy and Environmental Analysis, Inc., 2005). In 2005 it was reported that there were 163,000 industrial and commercial boilers in operation in the US, of which 85% were commercial boilers and the remainder being industrial systems. These boilers consumed 8,100 TBtu/yr, accounting for 40% of all energy used in these sectors. In the industrial sector, natural gas makes up 67% of the purchased boiler fuel (2,141 TBtu/yr). Natural gas consumption is dominated by the chemical industry (775 TBtu/yr), the paper industry (379 TBtu/yr), the food industry (approx 300 TBtu/yr), and other manufacturing (approximately 400 TBtu/year). If one assumes all of the boilers less than 10 MMBtu/hr operate on natural gas, by taking into account the average capacity factor and assuming the 0.5%

increase anticipated from the 5-40% improvement in radiant efficiency, a total savings of 2.6 TBtu/year is possible within the industrial sector. See Table 7 for details of the calculation.

Table 7. Proposed efficiency improvement calculations – Industrial Sector

Industry	Boiler Capacity units <10MM Btu/hr (MMBtu/hr)	Capacity Factor	Natural Gas Consumption (Tbtu/yr)	Energy Savings with 0.5% efficiency gain (TBtu/yr)
Food	31070	75%	204	1.02
Paper	4105	66%	24	0.12
Chemicals	28660	50%	126	0.63
Refining	1255	25%	3	0.01
Metals	7505	47%	31	0.16
Other	29710	50%	130	0.65
TOTAL				2.6

Notes: 1) For the food industry, a capacity factor of 75% is assumed instead of the reported value of 31% as it was reported that the low capacity factor was due to the seasonal nature in the large boiler applications. 2) A capacity factor of 50% was assumed for other manufacturing since no factor was reported.

The commercial sector is dominated by boilers between 1 and 10 MMBtu/hr (78% or 93,650 units). Natural gas is the primary fuel source for commercial boilers, accounting for 85% of the units and 87% of the capacity, with a total natural gas capacity of almost 1,000,000 MMBtu/hr. When calculating potential savings, the healthcare sector is removed since it is dominated by very large boilers. For the other sectors, the average boiler size 9.6 MMBtu/hr and therefore within the target size range for this technology. A low capacity factor (20%) is assumed since commercial boilers are often used for space heating or hot water and therefore are seasonal. Using calculations similar to those in the industrial sector, a potential savings of 6.3 TBtu/yr is possible, as shown in Table 8.

Table 8. Potential radiant efficiency improvements – Commercial Sector

Total Capacity (MMBtu/hr)	1,147,610
Total Capacity minus healthcare (MMBtu/hr)	830,500
Total Annual Capacity (TBtu/yr)	7,275
Capacity associated with Natural Gas (87%)	6,329
Average Capacity Factor	20%
Efficiency Improvement	0.5%
Total Potential Savings (TBtu/yr)	6.3

6.0 Commercialization

This program entered the stage gate new product introduction system in Oct 2011. The scope of the program is the commercialization of catalyzed coatings for commercially available burners, in addition to catalyst coating of novel 3M ceramic media for burners.

7.0 Accomplishments

Patents

No patents have been awarded.

Publications / Presentations

No publications and presentations were made for industry or government groups.

8.0 Conclusions

The primary objective of this project was to develop a cost-effective burner based on a high-activity, low-loading catalyst technology that dramatically exceeds industry standards for boiler performance. From a materials development perspective, this can be divided into three parts: catalyst, support, and substrate development. Considerable progress has been made over the course of the grant period in accomplishing each of these objectives.

In the area of Pd-based methane oxidation catalysts, highly active catalysts were developed with relatively low loadings of Pd metal using proprietary coating methods. The thermal stability testing demonstrated that certain catalyst supports offer enhanced stability toward both PdO decomposition and/or thermal sintering/growth of Pd particles. When applied to commercially available fiber mesh substrates (both metallic and ceramic) and tested in an open-air burner, these catalyst-support chemistries showed modest improvements in the NO_x emissions and radiant output compared to uncatalyzed substrates. However, these results did not translate to the boiler testing, due to operating constraints inherent to boilers. These experiments demonstrated the importance of the time-temperature profile for the contact of the gas with the catalyst and the limitations with fiber mesh substrate designs.

Novel catalyzed media constructions were developed to overcome the limitations of the fiber mesh substrates. The novel media increases the gas-catalyst contact, in addition to providing greater control over the temperature profile that the catalyst experiences. By adjusting the amount of surface area coated with the catalyst, this profile can be tuned to prevent exposure to excessively high temperatures while maintaining sufficient temperatures for catalytic activity. When the amount of catalyzed surface area is optimized, these substrates demonstrated a 65-75% reduction in NO_x emissions across the firing range when tested in an open air burner. In testing in a residential boiler, this translated into NO_x emissions of <15 ppm over the 15-150 kBtu/hr firing range.

9.0 Recommendations

Future work should continue to focus on increased activity and/or stability of Pd-based catalysts by identifying both thermally stable and active catalyst supports. In addition, catalyst lifetime should be challenged under more stringent accelerated aging conditions. Based on the significant benefits achieved with the novel media, these materials should be subject to additional boiler testing and accelerated towards commercialization. Continued development of the substrate should explore modifications to the novel media design to further enhance the effectiveness of the catalyst.

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