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**Variability in Natural Gas Fuel Composition and Its Effects on the
Performance of Catalytic Combustion Systems**

Final Report

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I. Abstract

Natural gas is composed primarily of methane with small amounts of higher hydrocarbons and diluents, which vary by region and over time. Compositions of natural gas from domestic and worldwide sources were surveyed with respect to content of higher hydrocarbons and diluents. The survey showed slight compositional variability between most of the gases, with a small fraction of them containing significantly larger contents of higher hydrocarbons than the mean. As gas-fired turbines will be used for power generation all over the world, they will need to tolerate operation with fuels with a wide variety of compositions, particularly with respect to the concentration of higher hydrocarbons and diluents. Subscale catalytic combustion modules typical of those used in gas turbine power generation with ultra low emissions of pollutants were tested in a subscale test system with natural gas alone and with added known levels of hydrocarbon compounds and diluents. The range of compositions tested contained the range observed in the survey. Test results were used to calculate the effect of composition on catalyst performance. The compositional variability is of little consequence to the catalyst for most of the gases in the survey, including nearly all of the gases delivered in the U.S. To accommodate the remaining gases, the catalyst inlet temperature must be lowered to maintain combustor durability. These results support commercial acceptance of catalytic combustion systems for use in natural gas fired turbines in distributed power generation with ultra low NO_x emissions.

II. Executive Summary

Catalytic combustion in natural gas fired turbines has been demonstrated as an effective and economical technology for the abatement of the emission of NO_x pollutants in electric power generation. Ultra low emissions are needed for permitting of power generation projects in non-attainment areas. Catalytic combustors provide an economically attractive alternative, as compared to exhaust gas clean-up technologies, for the full range of turbine sizes. This is especially true for small turbines, which are expected to provide a considerable amount of electrical power in the distributed generation market. Before commercial acceptance, however, catalytic combustion systems need to demonstrate tolerance to the variability of fuel composition in pipeline natural gases.

The present study surveyed the compositions of natural gas produced and delivered in the United States and throughout the world. Subscale catalytic combustion modules were then tested with controlled addition of higher hydrocarbons and inert gases to simulate the range of gas compositions in the survey. To accomplish this, the fuel delivery capabilities at the test facility were upgraded to deliver precise flows of liquids and of gases other than pipeline natural gas. Testing was done at conditions typical of a gas turbine operating at a pressure ratio of 10 and at 20 to cover the spectrum of industrial and utility gas turbine combustor conditions.

Testing showed that the addition of inert gases had practically no effect on the performance of catalytic combustion modules at 10 and 20 atm pressure, while addition of higher hydrocarbons led to lowering of the required catalyst inlet temperature. The optimal range for the required catalyst inlet temperature is termed the "Operating Window" and specifies the desired operating conditions for the catalyst system. Long chain hydrocarbon molecules such as lubricating and diesel oil components caused the most significant decrease in the operating window, with observed window shifts of up to 110 °C without damage to the catalyst. From the test results, a correlation was derived for determining the window shift with quantity and carbon number of each higher hydrocarbon in the gases listed in the survey. The correlation was then used to calculate the operating window shifts for each of the surveyed gases. The majority of the gases, particularly in the United States, had calculated shifts of less than 20°C, which is within the tolerance of catalytic combustors. Gases with shifts greater than this can be accommodated in catalytic combustion systems by providing for lowering the catalyst inlet temperature to maintain combustor durability.

These results confirm the ability of catalytic combustion systems to run on natural gas with a wide range of fuel compositions. For most gases, the variability is of no consequence in combustor durability. For the rest of the gases, one can easily compensate for the effect of composition to maintain optimum operation of the catalyst and to preserve catalyst durability. We believe the results of this program are valuable in realizing the commercial acceptance of catalytic combustion systems.

III. Introduction

Catalytica Energy Systems, Inc. (CESI) has been developing catalytic combustion for gas turbines since 1988 (until December 2000, under earlier corporate names of Catalytica Combustion Systems, Inc. and Catalytica, Inc.). Over this period, CESI has developed the basic technology for a radically innovative approach to the combustion of hydrocarbon fuels to achieve ultra low levels of oxides of nitrogen (NO_x). This technology had been developed through the stages of 1) rig testing at low and high pressure, 2) demonstration in full-scale combustion systems in development test systems, and very recently 3) engine demonstration tests using a Kawasaki Heavy Industries (KHI) M1A-13A 1.5-MW gas turbine. This system operated over the full load range of the gas turbine and demonstrated emissions levels of less than 2.5 parts-per-million-volume (ppmv) NO_x and less than 5 ppmv of both carbon monoxide (CO) and unburned hydrocarbons (UHC) at the full load condition. The turbine with the catalytic combustion system has been used to generate electric power for the public for more than 8000 hours. The engine demonstration work was done using pipeline natural gas with typical concentrations of heavy hydrocarbon components. However, to be commercially acceptable, a catalytic combustion system will have to demonstrate the durability and tolerance to fuel variations that existing conventional combustion systems provide. The program described in this report addresses the critical issue of fuel variability tolerance of catalytic combustion systems.

The success of catalytic combustion systems, in the sense of being able to provide ultra-low emissions of pollutant species such as NO_x , CO and UHC, allows the development of distributed power systems in urban and suburban areas. Today most of these areas in the U.S. have emission regulations sufficiently severe that gas turbines using conventional combustion systems cannot be used without the use of exhaust gas clean-up systems. The exhaust clean-up system of choice, today, is the selective catalytic reduction system or SCR. This system is mounted in the exhaust of a gas turbine and catalytically reduces NO_x with ammonia gas that is injected into the exhaust stream ahead of the SCR catalyst. The economies of scale are such that SCR systems for small gas turbines, typical of those that would be used in distributed power scenarios, are a much larger percentage of the total cost than for large gas turbines. This economic penalty has largely eliminated the use of small gas turbine power generation in areas with severely restrictive emission regulations.

Catalytic combustion systems can break this paradigm by providing NO_x levels as low or lower than those provided by SCR, and at a cost that is significantly lower for all sizes of gas turbine generation units. This breakthrough is important in that it will allow the distributed power concept to become reality in areas such as California, New York and Chicago. However, approval for use as an alternative BACT system will require demonstration of the practicality (*i.e.*, durability and fuel flexibility) of the catalytic combustion system. Catalytica has developed enabling technologies that will allow gas turbines to penetrate this emerging and very important power generating market segment.

Program success will lead to the use of small gas turbines in a distributed power generation scenario that locates generating systems at or near the point of end use. Power generation in this manner will provide, by minimizing the costs of transmission and distribution, lower electricity prices to the consumer. Voltage droops can be reduced

significantly and transmission losses will be substantially reduced. Also, locating the generation at the "end-of-line" in industrial or institutional facilities accommodates cogeneration, or the use of the exhaust heat from the turbine to replace heat that would otherwise be obtained from a separate burner. Cogeneration is a much more efficient method of fuel conversion, and not only consumes less fuel, but produces lower emissions. Distributed power generation will also improve the reliability of the power supply network, lessening the chances of "brown-outs" or a full "black-out."

Other less tangible benefits of distributed power generation include "environmental justice." Because each community will have its own locally sited power generation system, no single area will be penalized by air polluting emissions. Such emission penalties typically occur when large central power stations that export the bulk of their power are built in a particular community (which is often the poorest) within a larger metropolitan area.

The specific goals of the project involved two primary tasks: 1) Surveying the range of natural gas compositions that are encountered in the United States and worldwide. 2) Taking a catalyst system with proven performance with domestic pipeline natural gas and testing it over the composition range obtained in the survey to observe the effects of varying natural gas composition, specifically higher hydrocarbons and inert gases, on the performance of the system. The information obtained in this program has been used to adapt catalytic combustion systems to accommodate the observed range of compositions.

IV. Background

To be commercially viable, gas turbine combustion technologies must be able to utilize natural gas fuel from a large variety of locations in the United States and throughout the world. While the composition of these fuels does not differ markedly today, and most are near to pure methane, small differences do exist and these might deleteriously affect the performance of gas turbine catalytic combustion systems. These variations are expected to increase in severity in the future as higher quality reserves are depleted and the demand for non-methane hydrocarbons changes.

- *Higher Hydrocarbon Contamination*

The compositions of natural gas fuels throughout the United States have been summarized in reports from the Gas Research Institute (GRI). In a report published in 1992, GRI reviewed over 6800 gas analyses covering 26 cities in 19 states and assembled a picture of the composition variation for the U.S.¹ One part of this study described the variations in composition as delivered to gas turbine power generation sites. This study identified two generic problems that are both connected to the presence of higher molecular weight hydrocarbons. These hydrocarbons are often found in natural gas obtained from wells associated with petroleum deposits. These two problems are:

- 1. Very small vapor concentrations of higher hydrocarbons having eight through fourteen carbon atoms in the molecule are often present in natural gas and these can condense at low temperatures and appear as droplets in the fuel supply.*
- 2. Higher hydrocarbon vapors can also combine with water vapor to produce*

“hydrates” that will result in condensation of the higher hydrocarbons at higher temperatures or at low concentrations of these higher hydrocarbon species.

Because higher molecular weight hydrocarbons have substantially lower autoignition temperatures, they potentially can autoignite in the fuel–air-mixing section of a lean premix combustor or catalytic system. In addition, liquid droplets, if present, can create, locally, high vapor concentrations of higher hydrocarbons thus increasing the tendency for autoignition.

A second implication of having some level of higher hydrocarbons in natural gas is that they potentially can affect the flame position and combustion stability. With higher hydrocarbons in the natural gas the oxidation kinetics (reaction rate) are substantially higher than that of pure methane and this results in augmentation of the flame speed and in changes in flame location or position within the combustion system. This issue is under current intense study for lean premix systems,^{2,3} and is important for catalytic combustion systems as well. To summarize in the case of catalytic combustion systems, the possible issues are:

- 1. Higher hydrocarbon liquid or hydrate droplets could represent an auto-ignition threat in the fuel-air premixer system.*
- 2. The varying composition of the fuel stream can result in varying reactivity on the catalyst and varying ignition delay time in the post-catalyst homogeneous gas phase combustion zone.*

The first potential problem area is essentially identical to that faced by all lean premix combustion systems. The work being undertaken in this area to predict when the high molecular weight hydrocarbon concentrations in natural gas become “hazardous” to the integrity and performance of lean premix combustion systems will be directly applicable to catalytic combustion systems. Similarly, the solutions to this problem, which will probably require the use of some combination of fuel conditioning and “drying” to eliminate the questionable hydrocarbons, will also apply to catalytic combustion systems.

The second issue is unique to the area of catalytic combustion and is addressed by the work summarized in this report. The trace components in natural gas exhibit different reactivities over the catalyst when compared to methane. The diffusivities within the catalyst structure are also different, and can change the fuel conversion within the catalyst and the temperature of the catalyst.

- *Diluents*

Some natural gas compositions contain inert species such as carbon dioxide (CO₂), which, because of its higher heat capacity, could change the overall thermal balance at the catalyst surface. For this reason, it will be important to study both reactive higher hydrocarbons as well as non-reactive diluents.

- *Sulfur Compounds as Trace Species*

The U.S. Department of Energy (DOE) has also expressed interest in the changing composition of natural gases and, in particular, has been concerned with the increasing levels of sulfur compounds in such gases. There are large reserves of natural gas in the U.S.; however, the "sweet" gases are rapidly being depleted, leaving increasingly "sour" gases for future use. Today, the sour natural gases, those containing hydrogen sulfide or other organo-sulfur compounds, are being extracted and diluted with sweet or sulfur-free gases to maintain the desired low levels of sulfur in the gas. In the near future, sulfur removal will become necessary, and this will mean that all natural gases will tend toward having the maximum allowable sulfur levels.

- *Unconventional Natural Gas*

In addition to the changing composition of natural gases from conventional sources, there is increasing use of natural gas obtained from what can be termed "non-conventional sources." The largest contributor to the national natural gas system today is the gas obtained from coal seams. This "coalbed methane" can be obtained as virtually pure methane by pre-draining coal seams before mining occurs. This removal of methane before mining starts is considered to be an essential part of mine safety because it reduces the amount of methane released during the mining operations.

Methane can also be extracted (often diluted with air) from "gobs" or collections of collapsed roof rubble found in mined-out areas. Similar methane-air mixtures can be extracted from coal seams during mining operations. In this type of extraction, the gas is removed via boreholes drilled horizontally into the coal seam just ahead of the active working face. These latter two gas types usually consist of methane and air mixed. The concentration of methane in these gas streams can be controlled, if desired, to levels close to 90%. Such gases often meet the minimum heating values for pipeline quality natural gas. These gases, however, add air to the natural mixtures in the pipelines, and this can result in the formation of sulfur-based acid gases (from the sulfur compounds) or condensed phase (liquid) acids.

V. Literature Study Overview (Task 1)

The literature study includes reviews of government and industry institute publications, and reviews of industry data. Data available from the literature and from sources such as GRI and DOE and also industrial manufacturers were reviewed, and a fuel composition range was defined for use in the experimental evaluation of catalytic combustion systems. Particular emphasis was placed on selecting compositions that have trace species that potentially could prove deleterious to catalytic combustion systems. Since the primary market of interest is associated with dispersed power generation, fuels such as refinery off gas and process waste gas streams were not included. In summary, the work included in this task was:

1. *Gather best available literature on the fuel composition throughout the United States and the world.*

2. Identify a target market segment for gas turbines equipped with catalytic combustion systems and identify and analyze the natural gases this market would likely use.
3. From the above, determine a natural gas composition range to be studied in Task 3.

VI. Modify Existing Catalytica High Pressure Test Facility (Task 2)

The current high-pressure test facility is described and shown schematically in Figure 6.1. This system takes natural gas from the Pacific Gas and Electric distribution pipeline and compresses this gas to pressures as high as 500 psig for metering to the catalyst test system. At the start of the project, no provision was available to feed hydrocarbon mixtures or to inject low concentrations of liquid fuels. This task included design and installation of a fuel feed and mixing system to permit the doping of the current natural gas fuel with low levels of higher hydrocarbons. It was necessary to feed propane and higher hydrocarbons up to dodecane (C_{12} - kerosene used as a surrogate) and mix these with the natural gas fuel. Concentration levels were up to 8 vol% for propane. Typical concentrations of the minor fuel constituents for natural gas sources in the United States are also shown in Table 6.1, and include values for regions that mix in propane during periods of high demand, or peakshaving.

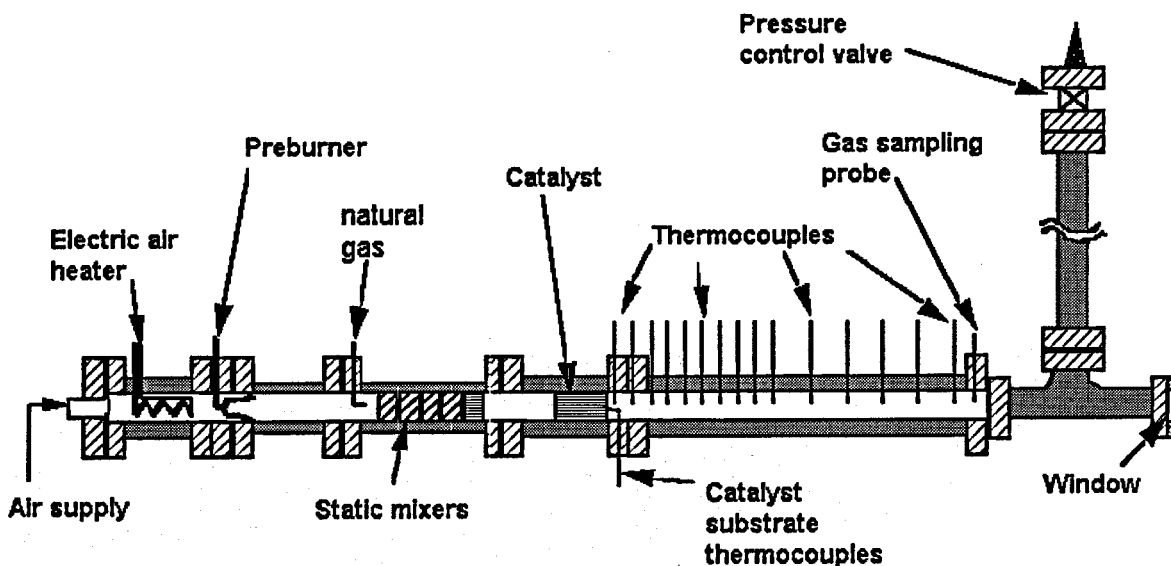


Figure 6.1 -- Catalytic combustion test facility schematic design.

Two such high-pressure rigs are available at CESI's Mountain View facility.

Concentration mole %	Methane	Ethane	Propane	Propane +C3 *	Hexanes
Mean	93.9	3.2	0.7	0.7	0.1
Minimum	74.5	0.5	0	0	0
Maximum	98.1	13.3	2.6	23.7	0.4

*C3 refers to additional propane injected by supplier typical of propane peak shaving processes

Table 6.1 -- Composition Variability of Natural Gases in the United States

Specific work in this task included:

1. *Design modifications were developed for the High Pressure Catalyst Test Facility at CESI to accommodate the levels of dopants and diluents that were added to the natural gas fuel.*
2. *The test facility modifications as developed above were implemented.*
3. *Shakedown testing was performed to establish that the facility modifications provided the required fuel compositions to the catalyst and met the fuel/air ratio, uniformity criteria specified for the catalyst system.*

VII. Natural Gas Variability Parametric Tests (Tasks 3, 4, and 5)

The form of the experimental evaluation of the effects of natural gas trace species on both the catalytic combustion system and the catalyst proper was largely determined by the results of Task 1 to establish fuel composition limits. Work was performed to ascertain the effects of higher hydrocarbons in natural gas on catalytic combustion systems.

7.1 Test Rig Approach Overview

There are two main approaches that can be taken to provide controlled "doped" natural gas. Methane could be procured in bottle form and a tank farm created to supply the test rigs. This pure methane could then be doped with the desired trace species, also procured in bottle form, by injecting them into the methane stream ahead of a static mixer section. Initial analysis suggests that this approach will be too costly and is probably not necessary.

The less costly alternative, which was used in this study, is to use pipeline natural gas and dope this relatively clean natural gas as needed for the parametric tests. In addition, this pipeline natural gas can be "cleaned-up" using activated carbon adsorption beds to produce a relatively pure methane for selected tests and for tests at relatively low levels of additive species. To minimize the complexity of the doping system, multiple species could be procured in a single bottle using either methane as the carrier or some large concentration dopant such as carbon dioxide. In this manner, a group of higher hydrocarbon compounds can be added at one time. The work reported here, however, tested dopants one at a time.

7.2 Parametric Study of Natural Gas & Higher Hydrocarbon Mixtures (Task 3)

This task evaluated the effects of higher hydrocarbons on the performance of the catalyst. Compositions were defined in Task 1. The tests utilized a catalyst design based on the standard design ("Xonon 1") tested on the KHI M1A-13A engine combustor in Tulsa,

OK in 1997. A typical test sequence was to measure the "operating window" of the catalyst at full load for the pipeline natural gas. (The operating window is defined as the area bounded on one side by catalyst inlet temperatures and on the other by a range of fuel/air ratios within which the catalytic combustor will operate and give the required low emissions and durability). Then, the higher hydrocarbon components would be added and the operating window measured again. Comparison of these results establishes the effect of the trace components. If the operating windows for fuel gases of varying compositions are similar, then the performance of the catalyst will be essentially constant.

Specific work included:

1. *Measure operating window at full load of the catalyst system in terms of fuel / air ratios for natural gas.*
2. *For each higher hydrocarbon concentration, again measure the catalyst operating window over the appropriate fuel / air ratio range.*

The exact compositions to be studied were defined in Task 1, but a test with 99.99% methane was also included in the program. Hydrocarbon dopants tested were:

Propane up to 8%

Hexanes up to 4%

Dodecane (kerosene as surrogate) up to 1%

7.3 Parametric Study of Diluent Components (Task 4)

As noted above, some natural gas streams contain CO₂ or other inert (e.g., nitrogen) and this component could affect the catalyst behavior. This task will look at the effects of inert gases in a manner similar to that described in Task 3.

The work accomplished included:

1. *Measure operating range at full load of the catalyst system.*
2. *For each CO₂ concentration, measure the catalyst operating range. The exact compositions to be studied will be defined in Task 1.*

7.4 Parametric Study of Trace Liquids (Task 5)

As discussed above, the presence of higher hydrocarbons in the natural gas fuel can result in the presence of droplets in the gaseous fuel stream as it is injected into the gas turbine combustor, either by condensation or by hydrate formation. This subtask was to have addressed the question as to whether the impingement of these droplets on the catalyst will have a detrimental effect. It should be noted that we did not study the impact of these droplets on potential autoignition since it was not part of the original work scope and work currently in progress at several OEMs and at DOE Morgantown is addressing this issue.

The work to be accomplished was to include:

1. *Develop the existing liquid injection hardware to inject higher hydrocarbon droplets into the gas stream just upstream of the catalyst. Insure that liquid droplets are impacting the inlet catalyst face.*

2. *Study the effect of liquid droplets on the catalyst performance. This could include short term testing to assess any changes in catalyst operating window or longer-term tests to assess whether any new degradation phenomena have developed.*

Testing for this task was considered implicit in the testing in Task 3, which included testing with vaporized kerosene at up to 1 vol% as C₁₂. The maximum expected droplet concentration is ~0.05% (as C₁₂, from Task 1), which is well within the range tested. Also in industrial practice, filtering of the incoming gas streams is common and highly effective in removing droplets to low ppm levels.

VIII. Discussion

8.1 Catalyst Design

The catalyst system consisted of two stages, an inlet stage that converts roughly 20% of the natural gas, and an outlet stage that converts enough of the remaining natural gas to achieve ignition of the fuel-air mixture downstream of the catalyst. The catalyst was aged for 10 h prior to testing. This break-in period is needed to provide a stable catalyst such that variations in performance are due to the fuel composition and not the catalyst condition. Each series of runs with a particular dopant included a baseline with natural gas alone. Runs were performed with increasing amounts of dopant until the operating window shifted by more than 20 °C. Runs were performed at 10 and 20 atm pressure, typical of the pressures in gas turbines that are targeted for the distributed power generation market. Catalyst inlet temperatures were varied between 350 °C and 550 °C, within the range of temperatures that can be achieved with a low-NO_x generating preburner upstream of a catalyst in a gas turbine combustor. The catalyst inlet face velocity (13 m/s at 450 °C) reflects current practice.

8.2 Testing Procedures

Ambient air and pipeline natural gas are compressed separately to 500 psig. Flow of each stream and the reactor pressure are automatically controlled. The catalyst inlet temperature is controlled with an electric resistance heater. In line static mixers are used to provide uniform temperature and fuel concentration profiles at the catalyst inlet. The feed stream is sampled and analyzed to confirm the fuel concentration. Catalyst wall, interstage, and downstream temperatures are monitored with S-type thermocouples. The effluent is sampled 25 ms downstream of the catalyst exit face and analyzed for CO, unburned hydrocarbons, oxygen, and NO_x.

Tests were run at constant adiabatic temperature. When the catalyst inlet temperature was changed, the fuel flow was adjusted to keep the temperature in the postcatalytic zone constant. Other tests were run at constant catalyst inlet temperature, while varying the adiabatic temperature by adjusting the fuel flow. Typically, inlet temperature or fuel flow was increased until the durability limit was reached, then decreased until the emissions limit was reached.

Propane, hexane, and kerosene were delivered with a syringe pump. Carbon dioxide was delivered from cylinders via the alternate gas delivery system. Dopant flows were adjusted in each run to maintain a constant percentage in the fuel.

8.3 Results

The addition of higher hydrocarbons increases the gas phase reactivity of the fuel mixture, bringing the homogeneous combustion front closer to the catalyst outlet face for a given outlet gas temperature and T_{ad} (see Fig. 8.3.1). Therefore, the emissions limit is reached at lower catalyst inlet temperature, and the operating window bottom is lowered. At a fixed catalyst inlet temperature, addition of higher hydrocarbons to the fuel increases the reactivity on the catalyst, increasing the outlet stage wall temperature (see Fig. 8.3.2). Therefore, the durability limit is also reached at lower catalyst inlet temperature, lowering the operating window top. An example of the operating window shift is shown in Figure 8.3.3 for 2 vol% hexane doping. The effect of 8 vol% propane doping was similar to 2 vol% hexane doping (Fig 8.3.4), but represents twice the heat content, so propane has less of an effect on both a volume percent and heat content basis. The shift with 1 vol% dodecane doping (kerosene as surrogate) had a greater effect than 2 vol% hexane doping (Fig 8.3.5), even though the heating content was the same, so kerosene has a greater effect than hexane on both a volume percent and heating value basis.

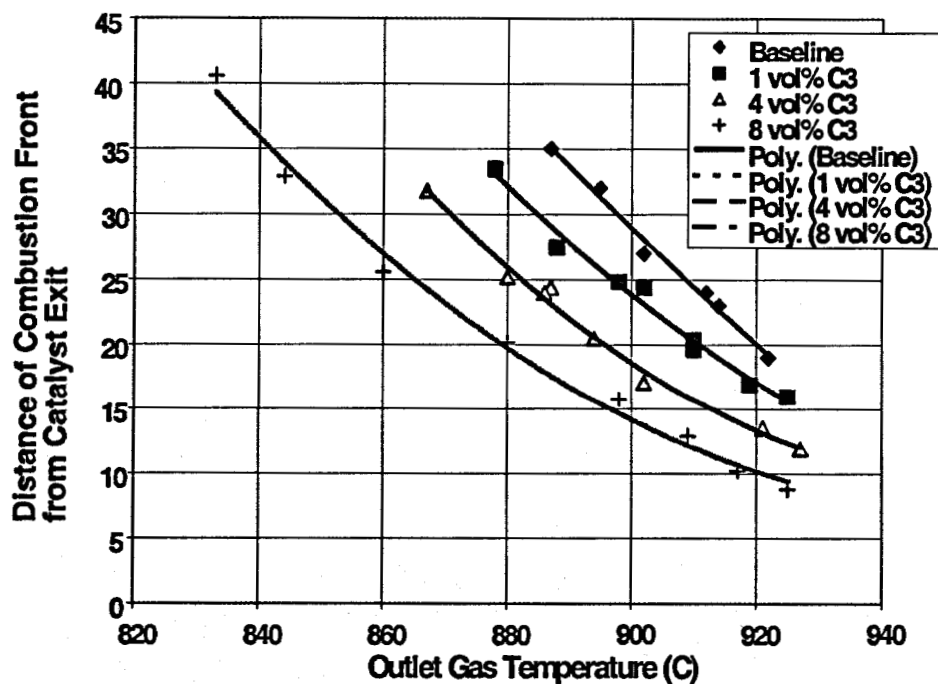


Figure 8.3.1 -- Combustion Front Locations - Propane Addition

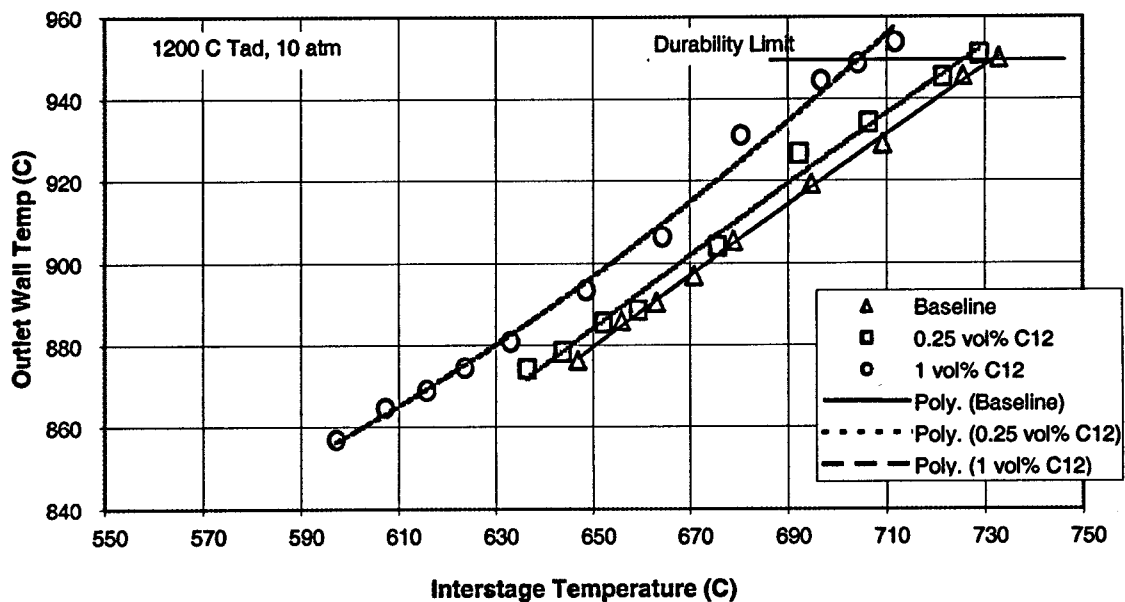


Figure 8.3.2 -- Outlet Wall Temperatures - Kerosene Addition (C12)

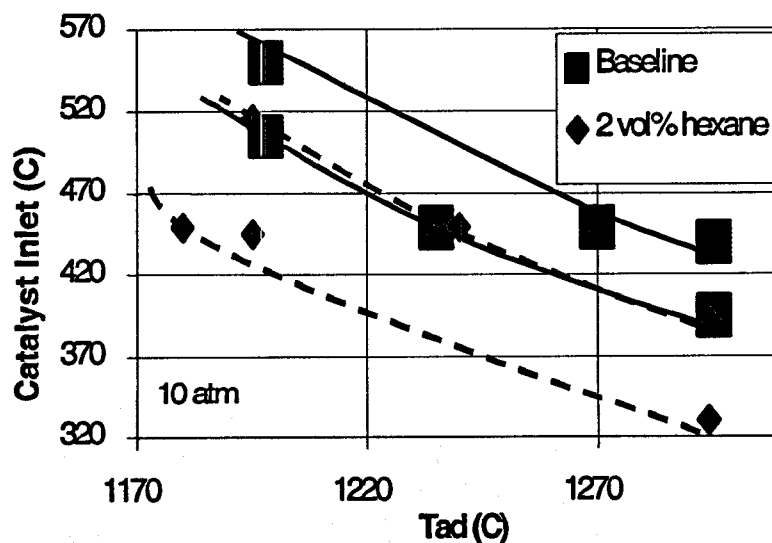


Figure 8.3.3 -- Operating Window Shift - Hexane Addition

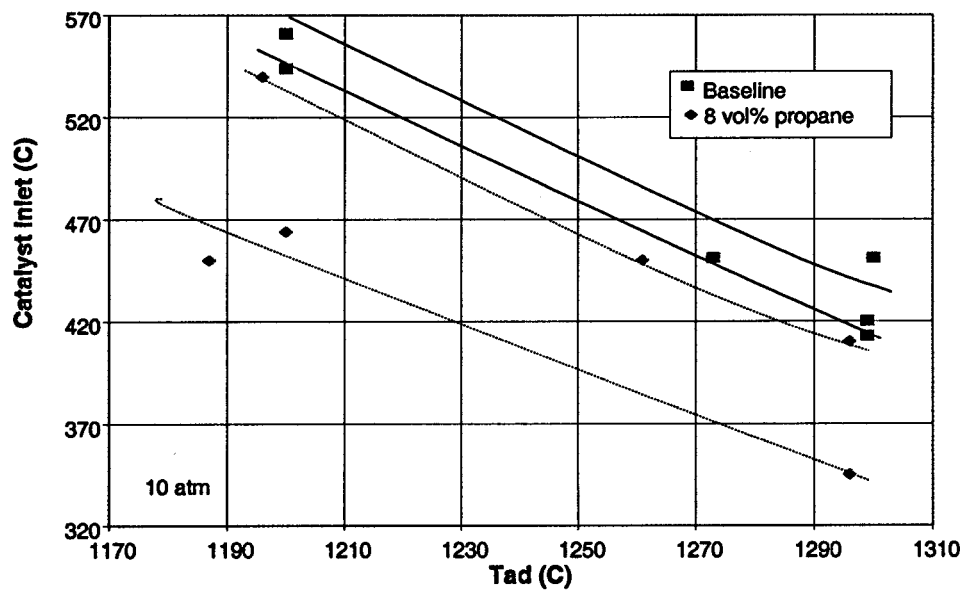


Figure 8.3.4 -- Operating Window Shift - Propane Addition

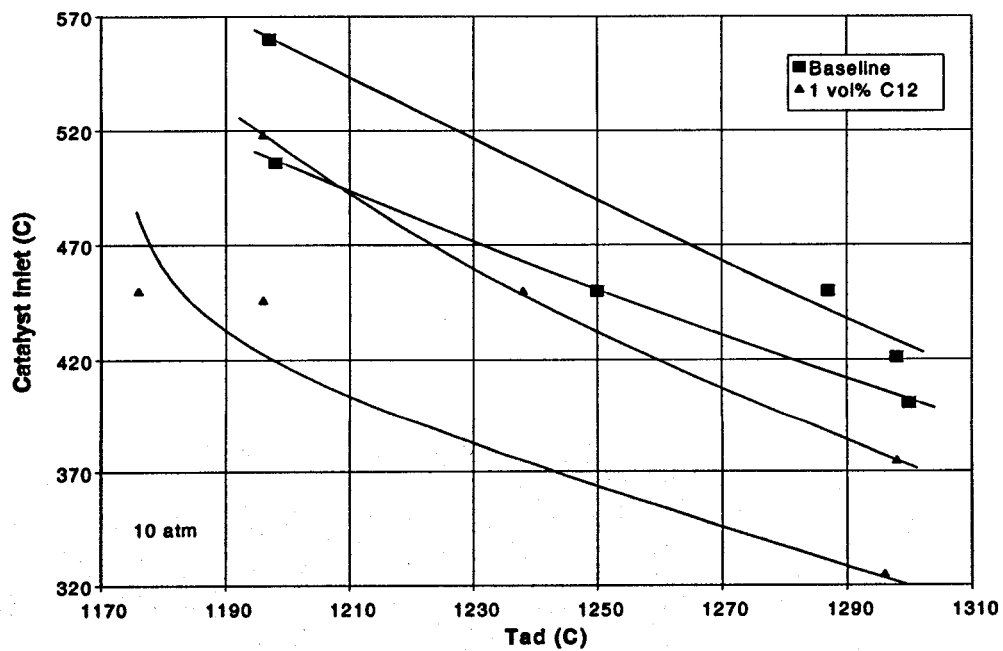


Figure 8.3.5 -- Operating Window Shift - Kerosene (C12) Addition

CO₂ had no effect on burnout, and practically no effect on catalyst reactivity, so there was less than a 20 °C shift in operating window at all percentages tested, up to 25 vol% (Figure 8.3.6).

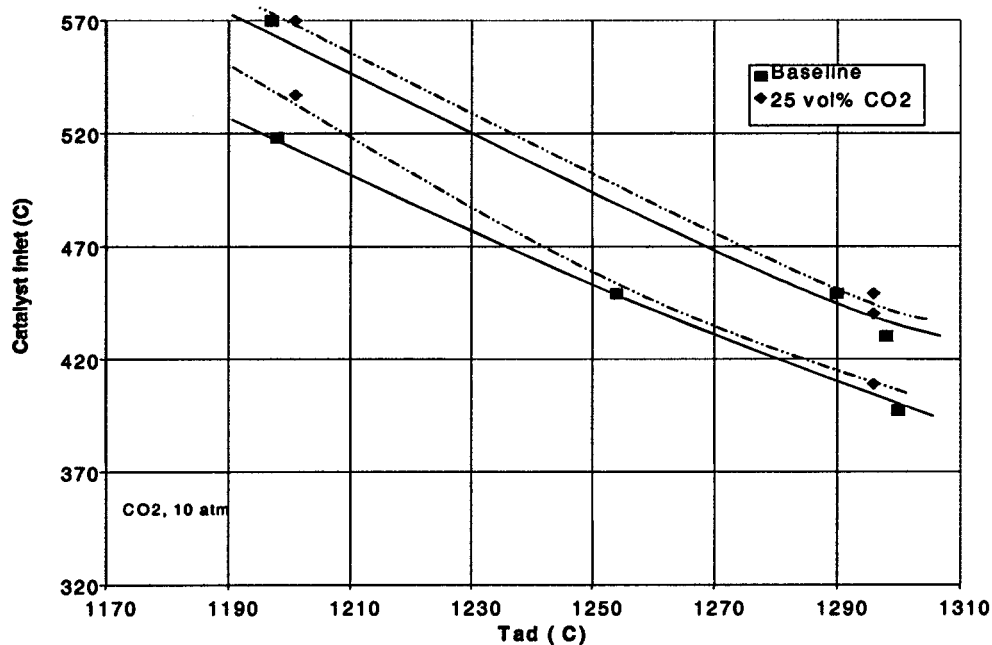


Figure 8.3.6 -- Operating Windows - CO₂ Addition

Table 8.3.1 summarizes the limits at which the 20 °C shift was observed in all of the experiments, and the average of 3 experiments for each pressure and dopant. When the 20 °C shift limit is not obtained, the highest tested value is listed (designated by a + symbol). It is evident that the limits are tighter with increasing carbon number and at higher pressures.

		1300C T_{ad}	1200C T_{ad}	450C T_{ph}	Average
10 atm	Hexane	1.7	1	1.3	1.3 v% C6
	Kerosene	0.6	0.5	0.5	0.5 v% C12
	Propane	8.0+	8	5.4	7.1 v% C3
	CO ₂	25+	25+	25+	25+ v% CO ₂
20 atm	Hexane	1.2	1.4	0.6	1.1 v% C6
	Kerosene	0.2	0.5	0.2	0.3 v% C12
	Propane	6	8.0+	5.3	6.4 v% C3
	CO ₂	15+	15+	15+	15+ v% CO ₂

Table 8.3.1 -- Maximum Allowable Dopant Levels

IX. Conclusions and Recommendations

9.1 Project Technical Goals

These were the technical objectives from the work statement

1. Understand the range of fuel properties likely to be encountered in commercial gas turbine applications using catalytic combustion.
2. Evaluate the effects of higher hydrocarbons and other potential fuel components on catalyst performance, and
3. Develop a catalyst system that delivers low emissions and meets turbine operational requirements for both variable gaseous and liquid hydrocarbon fuels.

Natural gas composition data was obtained from several reports and from sampling data in Tulsa, OK and Milpitas, CA.^{1,4,5,6,7,8} The listings contained the concentrations of methane, ethane, propane, butanes, pentanes, hexanes+, CO₂ and nitrogen in the gas. Heating values and specific gravities were calculated from the gas composition. Figure 9.1.1 summarizes the overall data in a plot of cumulative distribution functions of maximum and mean higher heating values (HHV) of natural gas delivered to U.S. cities, in U.S. pipelines, and in pipelines outside the U.S. Each point represents the fraction of cities/pipelines that have gas with a lower HHV.

Most of the available gas has an HHV between 1010 and 1060 Btu/scf, consisting of primarily methane with small amounts of higher hydrocarbons (mostly ethane and propane) and inert gases. Gas with HHV lower than 1010 Btu/scf generally has higher inert content, and gas with HHV higher than 1060 Btu/scf has larger amounts of higher hydrocarbons. From the figure, it is evident that natural gas delivered to U.S. cities is

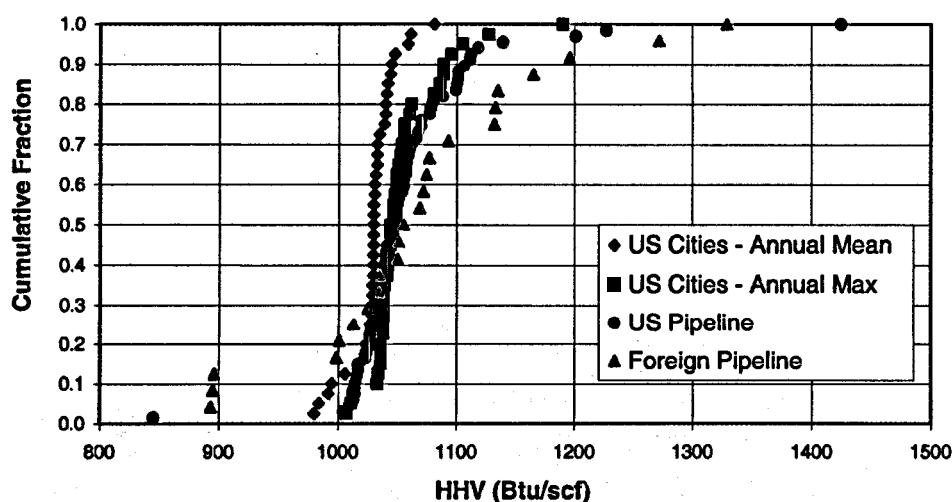


Figure 9.1.1 -- Heating Value Distributions

more uniform than the gas flowing in pipelines. Foreign pipeline gas generally tends toward higher HHV than U.S. pipeline gas.

Gas turbines are used in all parts of the world, so the target market segment should include as many of the areas that have gases that do not stress the catalyst as possible. With that in mind, the testing protocol was to find the maximum amount of dopant (propane, hexane, kerosene, or CO₂) that the catalyst could tolerate while shifting the operating window less than 20 °C from the undoped case. The effects of ethane, butanes,

and pentanes were interpolated from the effects of the three hydrocarbons tested. Each gas composition in the survey was then evaluated by summing the contributions of the individual components, weighted accordingly, and comparing the sum to the 20 °C limit.

Prior to this program, the high-pressure combustion test facility only had equipment for compressing and metering the flow of air and natural gas into the test rigs. The rig itself contained equipment for heating the air and mixing it with the natural gas to obtain uniform temperature and fuel concentration profiles at the catalyst inlet. Equipment was needed to meter the flow of gases other than natural gas into the rig, and to pump precise quantities of liquids into the rigs. For metering the non-NG gases, a manifold was acquired (Scott Gases) and installed for the use of up to 6 gas cylinders. The pressure in the manifold was regulated down to between 200 and 500 psig. Mass flow controllers (Brooks) were then used for metering the gas flow. This gas was then injected into the rig together with the natural gas. For pumping the liquids, a pair of syringe pumps (Isco) was acquired with the capability of continuously pumping liquids at up to 200 cm³/min into the rigs. Wiring (for power, instrumentation, and control) and process piping were installed according to local safety codes by local contractors. A coriolis meter (Micromotion) was used to measure the liquid mass flow rate. An external mix, air assist spray nozzle (Bete) was mounted in a water-cooled jacket for dispersing the liquid in the airstream inside the pressurized rig immediately upstream of the natural gas injector and static mixers. When the system was tested, the temperature and concentration uniformity at the catalyst inlet was within $\pm 2\%$ of the mean value according to horizontal and vertical traces measured by physically scanning a thermocouple and a gas sampling probe across both axes at the catalyst inlet face.

Operating windows were measured at 10 and 20 atm pressure. The pressures were chosen to cover the expected range of compression ratios of turbines that will serve the distributed generation market. The air flow rate was chosen to deliver 13 m/s velocity calculated at a catalyst inlet face temperature of 450°C. This velocity was chosen to be typical of Xonon applications. Windows were measured at two adiabatic combustion temperatures (T_{ad}), 1200°C and 1300°C, varying the inlet temperature to find the emissions and durability limits. A window measurement was also done at a fixed inlet temperature, varying T_{ad} by adjusting the fuel/air ratio. These measurements were done for natural gas alone, for each concentration of dopant, and for 99.97% pure methane.

An example of a natural gas-only operating window is shown in Figure 9.1.2, showing the emissions (lower) limit and durability (upper) limit of the catalyst operating window.

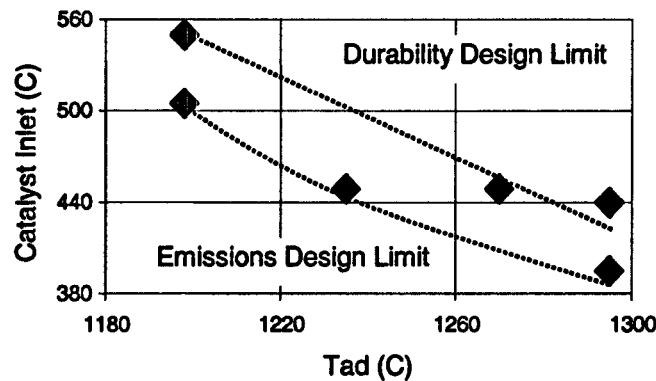


Figure 9.1.2 -- Baseline Operating Window

The plot shows the catalyst inlet temperature vs. burnout or adiabatic combustion temperature (T_{ad}). With any combination of catalyst inlet and burnout temperature at the emissions design limit, the catalyst converts just enough gas to achieve homogeneous combustion downstream of the catalyst such that the emissions targets on CO and unburned hydrocarbons are met at the turbine exhaust. Similarly, at the durability limit, the catalyst is stressed such that its expected life is reduced below the required target. Some factors associated with combustor durability are oxidation of metal parts and catalyst life.

When hydrocarbon dopants are added, the reactivity downstream of the catalyst increases such that the emissions design limit is reached at a lower catalyst inlet temperature than in the undoped case. The reactivity within the catalyst also increases such that the durability design limit is also reached at a lower catalyst inlet temperature than in the undoped case. These effects are shown schematically in Figures 9.1.3 and 9.1.4. Figure 9.1.5 shows the decrease in catalyst inlet temperature at the durability and emissions design limits with increasing hexane content for 10 atm pressure and 1300 °C T_{ad} .

The base composition of the natural gas was presumed to be that of the 1991/92 annual average from PG&E (see Table 9.1.1). The gas used in tests did not vary significantly in composition from this base.

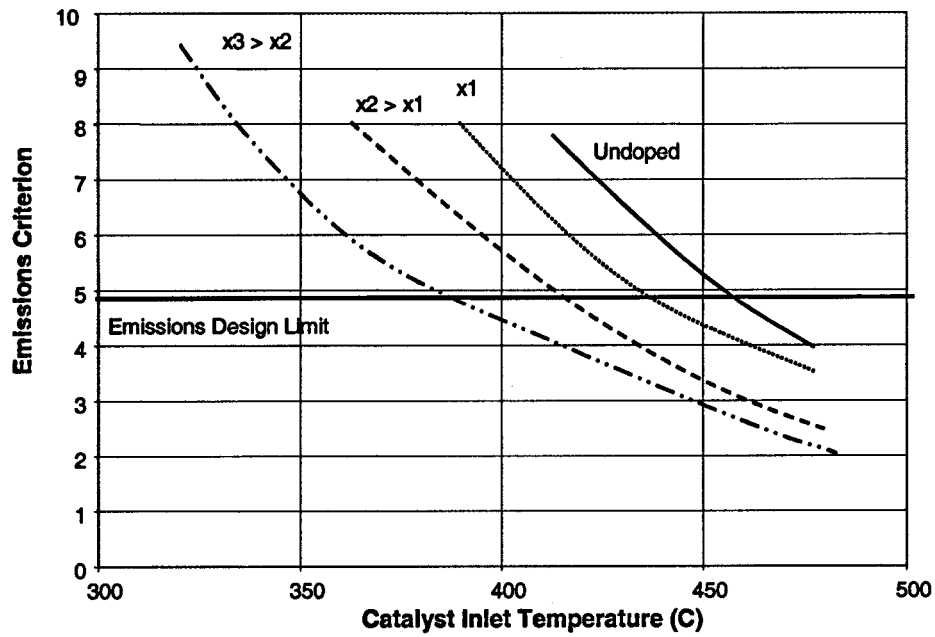


Figure 9.1.3 -- Effect of Hydrocarbon Dopants on Emissions Limit

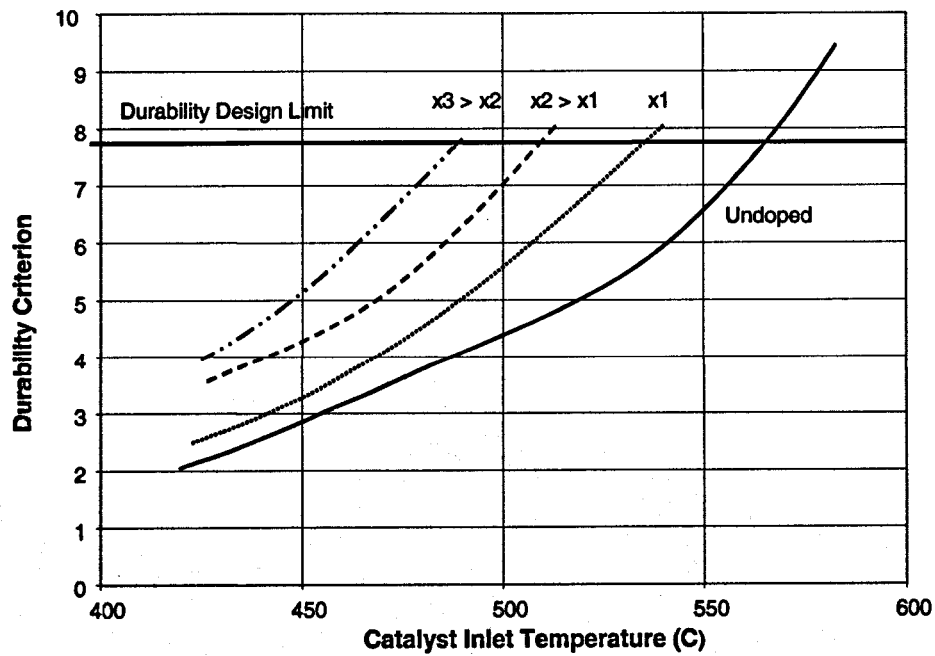


Figure 9.1.4 -- Effect of Hydrocarbon Dopants on Durability Limit

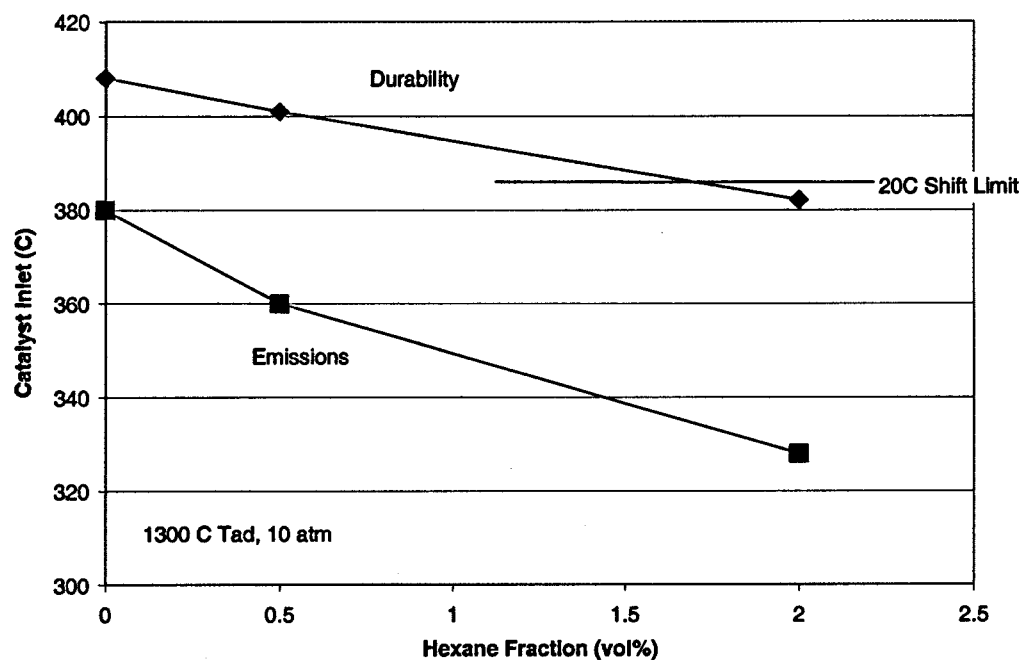


Figure 9.1.5 -- Operating Window Limits - Hexane Addition

Component	Volume %
Methane	95.9
Ethane	2.05
Propane	0.1
i-Butane	0.01
n-Butane	0.02
i-Pentane	0.01
n-Pentane	0
C6+	0.01
HHV (Btu/scf), dry	1013
Specific Gravity	0.57

Table 9.1.1 -- Milpitas Mixer Annual Average Gas Composition (1991-1992)

For higher hydrocarbon (C2+) contents in excess of that in the base gas, the catalyst inlet temperature at the durability limit was observed to shift downward. The greater the carbon number in the component, the larger the shift. Using this correlation, shifts in the durability limit were calculated for the gases in the surveys reviewed in Task 1. The cumulative distribution functions of these shifts are shown in Figure 9.1.6. Natural gas compositions to the left of the limit line would operate without difficulty. Natural gas compositions on the right side of the limit line would require a lower catalyst inlet temperature.

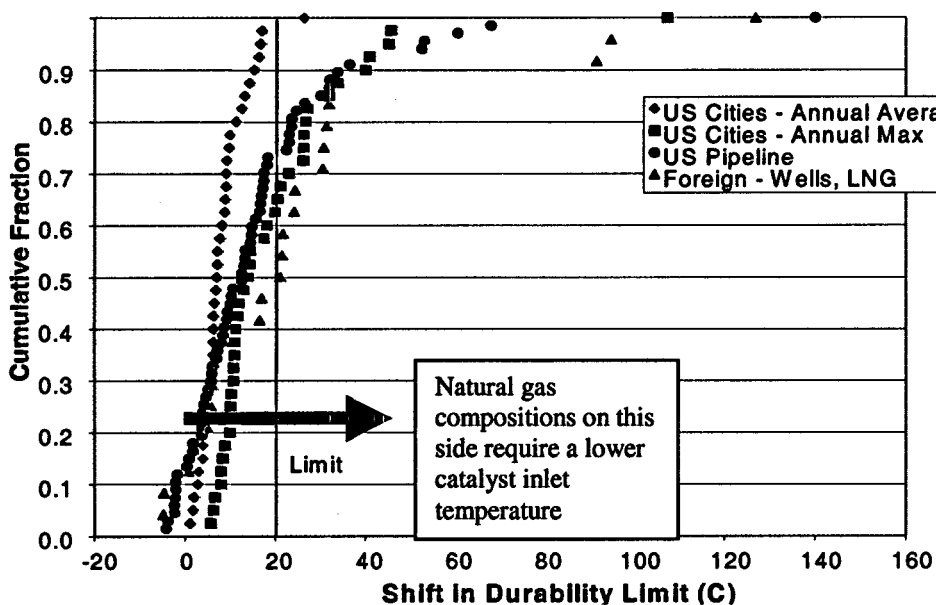


Figure 9.1.6 -- Durability Limit Shift Distribution of Surveyed Gases

Negative (upward) shifts relative to the base gas are calculated for the gases that are essentially pure methane, but the shift is less than 5 degrees. The methane-only rig test also showed such a minor upward shift. The majority of the gases surveyed, particularly in the U.S. (97% of the annual averages sampled), had higher hydrocarbon contents low enough to yield shifts that were within the 20 °C limit. However, a number of gases in the survey had sufficient content of higher hydrocarbons to yield shifts greater than 20 °C. For these gases, the catalyst can and does convert the gas without driving the catalyst outside of its preferred operating window. Provisions must be made, however, for lowering the catalyst inlet temperature with increasing content of higher hydrocarbons, thus maintaining the durability of the catalytic combustor without sacrificing emissions performance. Catalytica is currently addressing this issue.

Testing with CO₂ showed no appreciable shift in operating window at concentrations up to 25 vol% in the fuel (Wobbe number of 750). This shows that the catalyst itself is insensitive to the presence of inerts up to 25 vol% in the fuel.

9.2 Project Economic Goals

The economic goals of the project were tied to the technical goals. Key observations include: a) The catalyst can operate on gases with compositions covering the entire survey range without suffering damage. And b) for the minority of gases with compositions that can affect combustor durability, economically feasible provisions can be incorporated into the catalytic combustion system (such as lowering the catalyst inlet temperature).

9.3 Commercialization Potential

The results of this project support the commercialization of catalytic combustion systems for gas turbine power generation. Demonstration that the catalyst is insensitive to inerts in the fuel at concentrations up to 25 vol% is important in areas where natural gas is extracted with large contents of nitrogen and/or carbon dioxide. The observation that large amounts of higher hydrocarbons do not damage the catalyst short term, and can be accommodated to recover long term durability by operating at lower catalyst inlet temperatures, is also important. In areas where the higher hydrocarbons are not routinely condensed out of the gas, or in cases where condensation is inefficient (such as during periods of excessive gas consumption), the gas will certainly contain more of these components.

These results can be incorporated into the commercial combustor package in one of two ways. If used to designate a fuel specification, indicating the maximum amount of higher hydrocarbons in the natural gas at a project site, no cost would be added to the package. If the fuel specification cannot be met, accommodations are necessary for adjusting the catalyst inlet temperature to maximize the durability.

9.4 Benefits to the Environment

Catalytic combustion systems provide ultra-low emissions levels of pollutant species such as NO_x, CO and UHC. This allows the development of distributed power systems in urban and suburban areas throughout much of world. Today most of these areas have emission regulations sufficiently severe that gas turbines using conventional combustion systems cannot be used without the use of exhaust gas clean-up systems. One such system is selective catalytic reduction or SCR, which catalytically reduces NO_x with ammonia gas that is injected into the exhaust stream ahead of the SCR catalyst. The economies of scale of SCR systems impede its use on small gas turbines, typical of the size turbine that would be used in distributed power scenarios, as the much larger percentage of added cost (capital and operating) from SCR render power generation with small engines uneconomical. This economic penalty has largely eliminated the use of small gas turbine power generation in areas with severely restrictive emission regulations.

Catalytic combustion systems can break this paradigm by providing NO_x levels as low or lower than those provided by SCR at a cost that is significantly lower for all sizes of gas turbine generation units. This breakthrough allows the distributed power concept to become a reality. The approval for use as an alternative BACT system (in progress), requires demonstration of the practicality (*i.e.*, durability and fuel flexibility) of the catalytic combustion system. The results of this project demonstrate the ability to operate on natural gas with the range of compositions delivered to California cities.

Program success will lead to the economic viability of small gas turbines in distributed power generation that locates generating systems at or near the point of end use. Power generation in this manner will provide, by minimizing the costs of transmission and distribution, lower electricity prices to the consumer. Also, locating the generation at the "end-of-line" in industrial or institutional facilities accommodates cogeneration, or the use of the exhaust heat from the turbine to replace heat that would otherwise be obtained from a separate burner. Cogeneration is a much more efficient method of fuel conversion,

and not only consumes less fuel, but produces lower emissions. Distributed power generation will also improve the reliability of the power supply network, thus avoiding and widespread planned or unplanned interruptions in power delivery.

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