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for the period October 1, 1990 - January 31, 1994

Submitted to

National Aeronautics and Space Administration Ames Research Center Moffett Field, California 94035

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Abstract

Analytical studies have been conducted to determine the best methods of reducing NO_x emissions from proposed civilian supersonic transports. Modifications to the gas turbine engine combustors and the use of additives were both explored. It was found that combustors which operated very fuel rich or lean appear to be able to meet future emissions standards. Ammonia additives were also effective in removing NO_x , but residual ammonia remained a problem. Studies of a novel combustor which reduces emissions and improves performance were initiated.

In a related topic, a study was begun on the feasibility of using supersonic aircraft to obtain atmospheric samples. The effects of shock heating and compression on sample integrity were modeled. Certain chemical species, including NO_2 , HNO_3 and $ClONO_2$ were found to undergo changes to their composition after they passed through shock waves at Mach 2.

The use of detonation waves to enhance mixing and combustion in supersonic airflows was also investigated. This research is important to the use of airbreathing propulsion to obtain orbital speeds and access to space. Both steady and pulsed detonation waves were shown to improve engine performance.

Introduction

Theoretical studies have been conducted on methods of reducing oxides of nitrogen (NO_x) emissions from aircraft gas turbines as part of the NASA High Speed Research Program (HSRP). These studies are critical to the feasibility of future civilan supersonic aircraft operating in the stratosphere since current gas turbine engine designs, such as those used on the Concorde, are believed to emit levels of NO_x that could be harmful to the stratospheric ozone layer.

In order to predict the amount of NO_x which would be emitted by future jet engines, it was necessary to model gas turbine combustors and exhaust flows. The combustors were modeled by well stirred reactors while the exhaust flows were simulated by plug flow reactors. Chemical reaction mechanisms for NO_x formation and destruction were developed and validated using existing experimental data.

Analytical studies performed during this project had shown that the amount of NO_x emitted by aircraft gas turbine engines could be reduced by substantially redesigning the combustors. These modifications included operating the combustor under fuel rich or lean conditions. However, both of these strategies would appear to create design and operational problems. The rich combustor would be difficult to cool and would require a second combustion zone to oxidize the soot, unburned fuel and carbon monoxide formed in the rich combustion zone. The lean combustor would have mixing, flame stability and flashback problems. A study of a novel method of reducing emissions and improving combustor performance was also initiated. This combustor would operate in a pulsed mode and was the subject of a Director's Discretionary Fund (DDF) proposal.

Since all of the combustor modifications would involve costly and time consuming redesign

and testing programs, the use of additives to reduce emissions in unmodified engines was appealing. Certain chemicals were already known to reduce NO_x when added to the exhaust stream of ground-based turbines. These additives included ammonia gas and cyanuric acid, a solid material at room temperature. Previous studies had shown that the effective use of the cyanuric acid required a long exhaust residence time, about 100 ms compared to the 5 ms time available in an aircraft gas turbine. While long residence times were possible in ground based installations through the use of tall exhaust stacks, this was not possible in an aircraft gas turbine. Therefore, this study focused on the use of ammonia as an NO_x reduction additive.

Another area of research covered by this project was also related to emissions studies for supersonic transports. This involved the investigation of atmospheric sampling by supersonic aircraft. For example, the European aircraft industry had proposed that Concorde aircraft be used to follow one another to obtain samples from their exhaust plumes. Concurrently, in the United States it was proposed that supersonic aircraft such as NASA's SR-71 be employed to obtain atmospheric samples from remote polar regions which are inaccessable to subsonic aircraft. In both cases, when supersonic aircraft are employed, there is shock heating and compression of the sample which may change its chemical composition and give incorrect sampling results.

A third topic of research involved the use of detonation waves to enhance mixing and combustion in supersonic combustors. This subject is important to the use of airbreathing propulsion for aerospace vehicles that can reach earth orbit. Such Trans-Atmospheric Vehicles (TAVs) include the National Aerospace Plane (NASP). At vehicle speeds above about Mach 6, the airflow in the combustor must be supersonic to maintain high propulsive efficiencies. At these high airflow speeds, the time available for mixing and combusting the fuel is very small, on the order of milliseconds. Ordinary diffusive mixing is very slow compared to the flow speed in the combustor. By creating detonation waves, either steady or perodic, the mixing and combustion processes can be accelerated substantially.

Analytical Studies

In order to investigate methods of NO_x control, reaction rate mechanisms associated with the formation of NO_x in the combustor or its destruction in the exhaust stream by additive injection were developed. The reaction mechanism for the destruction of NO by ammonia, known as Thermal De- NO_x , depends on the formation of an intermediate specie, N_2H . In the past, the lifetime of this specie was predicted to be about 10^{-4} s. However, calculations performed by the Computational Chemistry Branch at NASA-Ames Research Center have shown that N_2H has a much shorter lifetime, on the order of 10^{-9} s. This shorter lifetime required a revision of the commanly accepted Thermal De- NO_x mecahnism. This was accomplished by changing the rates of other reactions involving hydrogen and oxygen. The new reaction mechanism was tested against experimental data and was found to reproduce these results as well as the short lifetime model.

Both prompt and thermal NO_x formation were studied. Thermal NO_x is formed by the combination of oxygen and nitrogen from the air at combustion temperatures. Prompt NO_x is not formed by the normal thermal mechanism. Instead, prompt NO_x is formed by a different mechanism involving air and fuel. Beacuse of the speed of the prompt NO_x reactions, these emissions are harder to minimize by combustion modifications than thermal NO_x and may only be controlled by additive injection.

Both well-stirred reactor and plug flow reacting fluid dynamic codes were used to model the NO_x formation and destruction process. A comprehensive methane reaction set simulated gas turbine fuels. Experimental data on the formation of NO_x was used to validate the

reaction mechanism and rates. Once the mechanism was validated, it was used to study the production of NO_x at conditions typical of HSRP combustors. A sensitivity study was made of the influnce of pressure, temperature and air-fuel ratio on NO_x .

The possibility of atmospheric sampling from supersonic aircraft was also investigated. In the past, all atmospheric sampling has been conducted using subsonic aircraft. In this case, conversion of the kinetic energy of the sample, when it is brought to rest inside the aircraft, results in very little heating or compression. However, if supersonic aircraft are used, the sample must pass through shock waves generated by the aircraft and/or the probe. In this case, the heating and compression are severe and the sample could react and change composition. Since there have been no studies of the supersonic sampling process, this investigation is unique.

The use of detonation waves to enhance mixing and combustion was studied through through the use of computer models of the fluid flow and chemical reaction process in the supersonic combustion chamber. In addition, a vehicle synthesis code was employed to design a Transatmospheric Vehicle in order to predict the integrated performance of the conceptual engine design. One-dimensional engne cycle codes were used to provide engine data as a function of vehicle speed and altitude.

Results

It was found that up to 80% of the NO_x in gas turbine exhaust could be removed by ammonia in the available time, about 3-5 ms. The temperature window for NO_x removal was narrow and centered about 1200 K. It was possible to shift the window to lower temperatures with the addition of hydrogen peroxide. Unfortunately, there was considerable unreacted ammonia left in the exhaust, sometimes exceeding the original amount of NO_x . Since the effects of ammonmia on stratospheric ozone are unknown, and may be detrimental, this approach was not considered feasible at this time. The results of these studies were presented at the AIAA/ASME/SAE/ASEE Joint Propulsion Conference¹.

The investigation of prompt NO_x was continuing with the establishment of a data base of relevent chemical reactions and rates. This information had been incorporated into the 1-D reacting fluid models which were used in the past.

The second area of research concerned the problems of obtaining accurate atmospheric samples using supersonic aircraft. Initial studies of the sampling process examined the fate of oxides of nitrogen (NO_x) samples taken at high speeds.

A Director's discretionary Fund (DDF) proposal was sumbitted on this topic in early 1993 and has been awarded funding for FY 1994 and FY 1995. In addition, a paper co-authored with Dr. Stephen Langhoff was presented at the annual High Speed Research Program Conference on The Atmospheric Effects of Stratospheric Aircraft². This study showed that the concentrations of certain key atmospheric compounds such as NO_2 , HNO_3 and $CINO_3$ change substantially after they pass through shock waves. This result indicated that these compounds cannot be accurately measured by intrusive sampling from supersonic aircraft

The detonation wave studies showed that a TAV powered by an Oblique Detonation Wave Engine outperformed a conventional scramjet vehicle. These results were presented at a NASA-Langley Workshop³ and published in an archive journal⁴. Another method of using detonation waves in the pulsed mode was also investigated. Here the periodic detonation waves were created inside a conventional scramjet engine. These theoretical studies showed that the detonation waves enhanced mixing and increased thrust⁵.

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