INVESTIGATIONS IN CHEMICAL ROCKET PROPULSION

Final Report

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Jet Propulsion Center

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Investigations in Chemical Rocket Propulsion

The research accomplished during the period of this contract from 1 July 1964 through 31 December 1967 is covered under the following general headings.

I. Fundamental Research in Jet Propulsion

II. Liquid Propellant Rocket Research

III. Solid Propellant Rocket Research

IV. Research in Combustion Processes

V. Conclusion

Several of the investigations discussed in this report have been continued under the sponsorship of NASA and other agencies. Under each project the current status of the program is indicated.

I. Fundamental Research in Jet Propulsion

A. Transpiration and Liquid-Film Cooling

Introduction

The development of high performance liquid propellant rocket motors places severe demands upon conventional cooling techniques. It is well known that, with increasing chamber pressure, the capabilities of regenerative cooling are limited. Mass transfer cooling, such as transpiration or film cooling, is one cooling method capable of providing adequate thermal protection for rocket motor chambers and nozzles. In order to enhance the understanding of mass transfer cooling techniques, two programs were initiated to study

a. transpiration cooling
b. liquid-film cooling

1. Transpiration Cooling

In view of the large amount of literature related to the topic of transpiration cooling, a study was undertaken to establish the state-of-the-art of existing theoretical analyses and their agreement with experimental data.

A report of the study has been published as Jet Propulsion Center Report 422, TM-66-5, "Transpiration Cooling-Its Theory and Application" by J.R. Kelley and M.R. L'Ecuyer, June 1966.

Mr. J.B. Kelley received the MSME degree in June 1966 and is presently employed in the heat transfer research department of Esso Oil Company, New Jersey.

Currently no research is being conducted in transpiration cooling.

2. Liquid-film Cooling

An experimental investigation was initiated, employing existing research facilities, to study the heat and mass transfer phenomena characteristic of the process of liquid-film cooling. The overall objectives of the study were: (a) to improve the basic understanding of the fluid dynamic interaction between a high velocity gas stream and a thin liquid film, and (b) to obtain accurate heat and mass transfer data for a liquid film under conditions typical of film cooling applications. The program was designed to provide meaningful correlations for the total rate of mass transfer from a liquid film accounting for the influence of the film surface roughness and mechanical entrainment of liquid by the gas stream.

Initially, an exploratory investigation was conducted under "cold flow" conditions in order to minimize the effects of heat transfer and to concentrate on the fluid dynamic phenomena of film stability and liquid entrainment. Experiments were conducted in a test section of rectangular cross-section by passing air (500 R, 5-10 atm, 65-230 ft/sec) over a thin liquid film (water) formed on the lower (flat) surface by injection through a slot. High magnification photographs were taken for the study of film surface characteristics and film stability. Measurements of the amount of liquid entrained were obtained by terminating the liquid film (10 in. long x 1 in. wide) by means of a withdrawal slot employing a knife-edge.

The exploratory investigation enabled the development of the necessary experimental techniques and demonstrated the relationship between the appearance of large scale surface instabilities on the liquid film and the onset of significant liquid entrainment. Furthermore, for the range of pressures investigated, the amount of liquid entrained was found to be dependent upon $\rho_\infty U_\infty^2$, a parameter indicative of the interfacial shear stress.

A complete report of the exploratory investigation is presented in the thesis, "Liquid-film Cooling: A Cold Flow Study of Film Instability and Entrainment," by K.W. Tate, MSME Thesis, Purdue University, June 1967. Mr. Tate is presently employed in the heat transfer research department, Rocketdyne Division, Canoga Park, California.

Based upon the findings of the exploratory investigation and the experimental techniques developed therein, a detailed program was outlined for a fundamental investigation of the fluid dynamic, heat transfer, and mass transfer phenomena characteristic of the liquid-film cooling process. The objectives of this research program were:

a. To determine the effectiveness of liquid-film cooling as a function of the gas and liquid flow parameters and the properties of the liquid coolant by obtaining considerable experimental data corresponding to a significantly wide range of parameters so that realistic heat and mass transfer correlations could be developed. Moreover, attention was focused on the evaluation of the influence of a streamwise pressure gradient on the film cooling process.

b. To determine the contributions that the phenomena of entrainment and film surface roughness make to the total rate of mass transfer, and to determine the parameters that characterize each of these contributions.

c. To obtain information regarding the hydrodynamics of the flow of a liquid film when substantial liquid is being evaporated from that film.

The investigation is currently being conducted with nominal values and ranges of the pertinent flow parameters as follows:

Gas Stream: T_∞ = 40F, 400F, 600F

P_∞ = 5, 10 atm

U_∞ = 25 - 430 ft/sec

Re_∞ = $10^6 - 10^7$ ft^{-1}

Liquid film: water, methanol, butanol, RP-1

To date all experiments for determining the film mass transfer rate have been completed for water, methanol, and butanol for the constant pressure case. The experiments for RP-1 are in progress and those involving a gas stream pressure gradient will follow.

A preliminary correlation of the existing data for mass transfer under both hot flow and cold flow conditions has been successful in isolating the effects of film surface roughness and liquid entrainment over a considerable range of flow conditions, liquid viscosity and surface tension. A comparison of previous liquid-film cooling data (Kinney, Abramson, Sloop, NACA Report 1087, 1952) with predictions from this preliminary correlation shows good agreement.

The current research program is being conducted by Mr. R.A. Gater a candidate for the Ph.D. degree, with partial support of the National Science Foundation. A report of the research is expected to be published in August 1968.

B. Nozzle Design and Optimization

1. A General Method for Determining Optimum Thrust Nozzle Contours for Chemically Reacting Gas Flows.

The objective of this investigation was to develop an analytical technique for the design of a nozzle contour which develops maximum thrust when the working fluid is a chemically reacting gas. The results of this study are presented in references 1, 2, and 3.

An optimization analysis was developed for the design of axisymmetric rocket motor nozzles with chemically reacting gas flows. The analysis was based upon the usual assumptions for reacting flows. An arbitrary number of chemical species and chemical reactions are included in the analysis. The problem was formulated to maximize the pressure thrust integral along the supersonic nozzle wall contour for a general isoperimetric constraint, such as constant nozzle length or constant nozzle surface area. The governing partial differential equations for reacting flows were incorporated into the analysis by means of Lagrange multipliers. The results of the optimization analysis are a set of partial differential equations for determining the Lagrange multipliers in the region of interest and a set of algebraic equations for determining initial conditions for these Lagrange multipliers on the boundaries of the region. It was shown that the complete set of equations for the gas-dynamic properties and the Lagrange multipliers constitutes a system of first-order, quasi-linear, nonhomogeneous partial differential equations of the hyperbolic type, which can be treated by the method of characteristics. The characteristic and compatibility equations for the system were derived. A technique for employing the results to determine whether or not a given contour is an optimum contour was developed. No method for the direct application of the results of this analysis for the determination of optimum contours was presented. However, it should be possible to develop a relaxation technique based on these results with which optimum nozzle contours can be determined.

2. A General Method for Determining Optimum Thrust Nozzle Contours for Gas-Particle Flows

The objective of this investigation was to develop an analytical technique for designing maximum thrust nozzles for gas-particle flows. This work was cooperatively funded by NASA and the Aerojet-General Corporation under grant NsG 592 and contracts PO 802353 and PO 802357. The results of this study are presented in references 4, 5, and 6.

An optimization analysis was developed for the design of axisymmetric rocket motor nozzles with gas-particle flows. The analysis was based on the usual assumptions for gas-particle flows. Only one particle size was considered, although the results can be extended to any number of different particle sizes or species. The problem was formulated to maximize the pressure thrust integral along the supersonic nozzle wall contour for a general isoperimetric constraint, such as constant nozzle length or constant nozzle surface area. The gas-particle flow governing differential equations were incorporated into the analysis by means of Lagrange multipliers. The results are a set of partial differential equations for determining the Lagrange multipliers in the region of interest, and a set of algebraic equations relating the problem variables on the boundaries. It was shown that the complete set of equations for the gasdynamic properties and the Lagrange multipliers constitutes a system of first order, quasi-linear, non-homogeneous partial differential equations of the hyperbolic type which can be treated by the method of characteristics. The characteristic and compatibility equations for the system were derived. A technique for employing the results to design optimum nozzle contours was developed.

3. Optimization of Conical Thrust Nozzles

The objective of this investigation was to develop a design criterion for maximizing the thrust of conical nozzles. The results of this study are presented in references 7 and 8.

The optimization of the conical thrust nozzle was re-examined. It was found that a more meaningful approach to the optimization problem is obtained by specifying the length of the nozzle and varying the cone angle until the point of maximum thrust is obtained. This approach leads to a new condition that must be satisfied if a conical nozzle of specified length is to develop maximum thrust. This condition remains applicable even when the nozzle exhausts into a vacuum. A comparison of optimum and adapted conical nozzles showed that the thrust of an optimum nozzle is always greater than that of an adapted nozzle having the same length, and that the length and the cone angle of an optimum nozzle are always less than those of an adapted nozzle having the same thrust. A parametric study was performed to compare the optimum conical nozzle with other types of thrust nozzles and to illustrate how the design variables affect the performance and the geometry of the optimum conical nozzle.

The research in nozzle optimization techniques is being continued under Air Force and Aerojet-General sponsorship.

4. References

1. Hoffman, J.D., "Optimum thrust nozzle contours for chemically reacting gas flows," Jet Propulsion Center, Purdue University, Report TM-66-3 (April 1966).

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3. Hoffman, Joe D., "A general method for determining optimum thrust nozzle contours for chemically reacting flows," AIAA J., 5, 670-676 (April 1967).

4. Hoffman, Joe D. and Thompson, H. Doyle, "Optimum thrust nozzle contours for gas-particle flows," Jet Propulsion Center, Purdue University, Report TM-66-2 (May 1966).

5. Hoffman, J.D. and Thompson, H.D., "A general method for determining optimum thrust nozzle contours for gas-particle flows," AIAA Paper 66-538 (June 1966).

6. Hoffman, Joe D. and Thompson, H. Doyle, "Optimum thrust nozzle contours for gas-particle flows," AIAA J., 5, 1886-1887 (October 1967).

7. Scofield, M.P. and Hoffman, J.D., "An analysis of optimized conical thrust nozzles," Jet Propulsion Center, Purdue University, TM-66-6 (July 1966).

8. Scofield, M. Peter and Hoffman, Joe D., "Optimization of conical thrust nozzles," J. Spacecraft and Rockets, 4, 1547-1549 (November 1967).

C. Secondary Injection of a Gas into a Supersonic Stream

The overall objective of this research program is to obtain an understanding of the physical phenomena resulting from secondary gas injection into a supersonic nozzle so that a mathematical model may be formulated. The program was designed and conducted to fulfill that objective within the limitations of available finances and existing research equipment. The research was initiated at Purdue in 1962 by funding from Aerojet General Corporation and has since been jointly sponsored by NASA and Aerojet General Corporation. During the period of the joint support References 1 through 9 were written. They include the details of the experimental and analytical investigation to date.

The research is currently being funded by Aerojet General Corporation. It is anticipated that the program will be terminated April 1968 for lack of support.

Research Assistants who have worked on the project are:

R.D. Guhse	Ph.D. candidate	(expected degree June 1969)
G.L. Niksch	M.S. candidate	(completed work August 1967; degree January 1968)

References:

1. 1964 Review of Research, Purdue University, JPC 396, Report No. TM-65-1, pp. 331-354.

2. Guhse, R.D., An Experimental Investigation of Thrust Vector Control by Secondary Injection, Purdue University, JPC 401, TM-65-3 (March 1965).

3. Guhse, R.D., An Experimental Investigation of Thrust Vector Control by Secondary Injection, NASA CR-297 (1965).

4. 1966 Review of Research, Purdue University, JPC 428, TM-66-8, pp. 71-91.

5. 1967 Review of Research, Purdue University, JPC 435, TM-67-3, pp. 47-51.

6. Guhse, R.D., "On Secondary Gas Injection in Supersonic Nozzles", J. Spacecraft Rockets, Vol. 3, No. 1, Jan. 1966, pp. 147-149.

7. Niksch, G.L., Parameters Influencing Thrust Vector Control by Secondary Injection, MS Thesis, Purdue University, August 1967.

8. Niksch, G.L. and Guhse, R.D., Parameters Influencing Thrust Vector Control by Secondary Injection, Purdue University, JPC 437, TM-67-6 (August 1967).

II. Liquid Rocket Research

A. Investigation of High Pressure Combustion Phenomena

1. Influence of High Combustion Pressure Upon Performance, Heat Flux, and Combustion Stability

Theoretical calculations indicate that an increase in the combustion pressure from 1000 to 5000 psia, for the propellant combustion N_2O_4 and Aerozine-50 causes an increase of approximately 10 percent in specific impulse at sea level operating conditions. Experimental and theoretical studies conducted by Priem of NASA indicate that combustion pressure has a marked influence upon combustion stability over the pressure range from 100 to 500 psia. It is of interest, therefore, to investigate the influence of pressure upon combustion stability at higher pressures. It is also of interest to determine the general effects of operating a rocket motor at combustion pressures above the critical pressures of the propellants.

The preliminary phases of the high pressure liquid rocket research program including literature review, preliminary rocket motor design, and injector design were conducted by Mr. Thomas Carpenter, candidate for PhD degree, under Grant NsG 592. The required experimental rocket motors were designed and fabricated and the instrumentation system was designed.

A research program for the continuation of the study was submitted to NASA and is being continued under Grant NGR-15-005-058.

Two master's degree candidates, Mr. Dale Carstens and Mr. Glen Buchan assisted in the high combustion pressure program. Both have received the M.S. degree.

B. Study of Staged Combustion Phenomena at High Combustion Pressures

During the first seven months of the time period Mr. Robert Strickler, candidate for PhD Degree, was employed on the subject program he did the major portion of the design of the propellant supply system, including the inert gas propellant pressurization system, for the Combustion Research Laboratory constructed under Grant NsG (f) 21. The details of the design and the progress made in the fabrication and installation of the system are reported in the quarterly Progress Reports for NsG(f) 21. The work of Mr. Strickler represents a major contribution to the Combustion Research Laboratory project.

During the final eight months of employment under Grant NsG 592, Mr. Strickler was engaged in the initial phase of a high chamber pressure liquid propellant rocket program. Mission analysis conducted by several of the large liquid engine manufacturers and by government agencies have indicated that there is considerable performance increase potential in the staged combustion cycle at high combustion pressures. In that cycle all of the oxidizer is reacted with a portion of the fuel in a primary chamber at high pressure (1500 to 5000 psia) to yield oxidizer rich gases (at approximately 1200 F for N_2O_5 - Aerozine-50 propellants). After expansion through the turbine driving the propellant pumps, the oxidizer rich gases, with the remaining portion of the fuel, are injected into the secondary combustion chamber operating at between 1000 and 3500 psia combustion pressure. The products of combustion from the secondary combustion chamber are then expanded through an altitude compensating nozzle. The staged combustion cycle effectively utilizes all of the turbine exhaust gases to produce thrust.

The postulated increase in performance, associated with the utilization of high combustion pressure is accompanied by a marked increase in heat flux from the combustion gases to the walls of the secondary combustion chamber and thrust nozzle. Should the actual heat fluxes attain the magnitude predicted from theory, liquid film cooling or transpiration cooling would be required to insure the integrity of the rocket motor. Either of those methods of cooling results in a decrease in performance. It is possible that the postulated increase in performance resulting from operation at increased combustion pressure may be offset by a loss in performance resulting from the required use of film or transpiration cooling.

From an experimental investigation of the staged combustion cycle one can evaluate liquid-gaseous phase reactions, high chamber pressure heat transfer characteristics, the effect of cooling techniques on performance and the influence of chamber pressure on combustion stability over a range of combustion pressures.

Since the amount of fuel added in the thrust chamber can be varied over a wide range, one can study cooling techniques over a wide range of thrust chamber temperatures.

All of the experimental rocket motors including both the gas generator or primary chambers and the thrust or secondary combustion chambers were designed and fabricated under the direction of Mr. Strickler while he was employed under Grant NsG 592.

Details of the high staged combustion research program and descriptions of the experimental rocket motors are published in Jet Propulsion Center 1966 Research Review, Report TM-66-8, April 1966, and 1967 Review of Research, Report TM-67-3.

The Staged Combustion research program as conceived on Grant NsG 592 has since been approved by the Office of Naval Research, Power Branch and is continuing under Navy sponsorship as Nonr 1100 (21).

Mr. Strickler was assisted by one masters degree candidate, Mr. Ibrahim Keskin, who was employed on Grant NsG 592 to design and supervise the construction of a static firing test stand. The test stand facilitates the static testing of a variety of rocket motor configurations developing thrusts from 1000 to 20,000 pounds.

The stand is currently being employed in the staged combustion rocket motor project being sponsored by the Office of Naval Research.

C. Laboratory Data Acquisition

The data reduction computer program used initially in support of work being undertaken in High Combustion Pressure Research was developed by Mr. M.J. Barsic, a candidate for a Master's Degree and is described in his report "Computer Programming for a Digital Computer", Jet Propulsion Center Report No. TM-66-7, August 1966. This program was written for the Digital Data System located in the Combustion Research Laboratory at Purdue University, Jet Propulsion Center.

As the research progressed, it became apparent that the initial program as written by Mr. Barsic was inadequate to handle the desired variety of instrumentation. Mr. M.C. Byrd and Mr. T. O'Hara, candidates for Masters degrees initiated a second programming effort and expanded the program's capabilities so that one program could be used for calibration and/or experimental runs with little or no modifications. Heretofore, the programs required alterations before they could be used to process data for a particular experiment. The program was adapted to accommodate most experiments using the analog-to-digital system by the use of the appropriate introductory identification data.

The introductory identification data was manually inserted on the computer tape by means of thumbwheel switches on the EECO Computer Format Control Buffer. By effective utilization of this means of manually inserting data, the program controls were set up to process the data, program and channel identification information entered directly on the tape. The program identification information can now include the test operator's name, date of test, type of test, while the channel identification data may include the type of transducer, its serial number, and the maximum and minimum operating limits of the transducer.

The computer program has also been altered so that it will accept calibration data directly from the computer tape for linear response transducers and reduce it; instead of requiring a card input for calibration data. This can be done for either a calibration only or a calibration and experimental test where both the calibration data and experimental data are on the same tape. The program will also accept non-linear calibration data to reduce experimental data by a third order curve interpolation.

Provisions were made so that particular channels designated in the introductory identification data may be rescanned or repeated before a new cycle of the multiplexer is initiated. This feature allows the test operator to examine critical functions at a higher sampling rate; thus providing a more efficient mode of recording data.

An additional programming change provided the automatic generation of a library tape for storage of test data. This feature was of considerable significance because it allowed the test operator to store all of his experimental and/or calibration tests on one library tape for future reference.

Throughout the entire programming effort emphasis has been placed on simplicity and flexibility to permit insertion or removal of program elements as the character of the experimental programs change at the Purdue University Jet Propulsion Center.

III. Solid Propellant Rocket Research

A. An Experimental Investigation of the Gaseous Phase Reaction Zone in a Composite Solid Propellant.

The object of this investigation was to experimentally measure the temperature profile above the burning surface of a composite solid propellant. This Research was conducted by Mr. R.L. Derr, a candidate for the PhD. Knowledge of the temperature profile above the burning surface is important because it can be related to the role the gaseous reaction zone plays in the overall combustion process of a composite solid propellant. In the past, a number of attempts have been made to measure this temperature profile for a composite propellant. Unfortunately, the results have exhibited little agreement. One possible cause for the lack of agreement is the dependence of each of the previous investigations on a single scan temperature measurement technique. In that technique, the temperature measurement zone is fixed in space and the propellant surface burns past the measurement zone. Quite obviously, the single scan technique will yield invalid results unless the temperature profile remains constant with time.

The single scan limitation was suspected in the inceptive stages of this program as the cause for the poor agreement between previous temperature profile measurements in composite solid propellant flames. As a result, a temperature measurement system was developed which measured the temperature over a fixed region in the flame for a controlled length of time. The system consisted of a modified line reversal pyrometer and a servo-controlled propellant feedshaft. The servomechanism served two purposes. The first was to drive the propellant strand toward the temperature measurement region at a rate equal to the propellant burning rate, enabling the examination of a zone in the flame for a controlled length of time. The second was to locate the burning surface with respect to the temperature measurement zone at any given time.

The burning surface was detected with a visible light beam position detection system. In that system, a tungsten lamp was used to supply a beam of light over the surface of the propellant strand. The fraction of light passing by the strand was detected by a photomultiplier tube. As a result of the optical design, the output from the photomultiplier tube was proportional to the propellant position with respect to the temperature measurement region. To permit discrimination between the radiation from the tungsten lamp and the luminosity of the combustion zone, the light beam emanating from the lamp was chopped at a low audio frequency (450 cps) before passing over the burning surface.

The temperature measurement was accomplished by a modified line reversal pyrometer which was capable of a temperature measurement once every two milliseconds. The D lines of sodium were used as the reversing lines and a calibrated tungsten strip lamp was employed as the comparison source. A complete description of the overall temperature measurement system is presented.

The propellant examined in the program was a nonmetalized polysulfide-ammonium perchlorate propellant. Two unimodal oxidizer grinds were used in the propellant, a fine grind of mean diameter equal to six microns and a coarse grind of mean diameter equal to 50 microns. Each propellant was salted with 0.5% by weight of NaCl powder (mean diameter less than 5 microns).

Motion pictures were taken of the burning surface of a propellant sample to determine the ability of the servomechanism to position the surface for the temperature measurement. Also, the films supplied a means of establishing the asperities of the burning surface as it was positioned for the temperature measurement. The results of the films showed that the servomechanism operated in a satisfactory manner and that the degree of surface roughness was insignificant in comparison to the region over which the temperatures were measured.

Temperature measurements were made over a pressure range of atmospheric to 200 psi. The results showed that the gaseous reaction zone is very inhomogeneous. In particular, the temperature measurements showed that for any given distance above the burning surface less than 1000 microns, the temperature in the gas phase ranged from a lower limit of 1800°K to an upper limit of 2200°K which represents the lower limit of the temperature measurement technique and the approximate adiabatic flame temperature of the propellant. Variation in propellant strand thickness and temperature measurement zone height were introduced in the experiment for the purpose of averaging a temperature profile above the surface; however, no profile was noted in any of these tests. As a result, it is concluded that one-dimensional theoretical and experimental approaches to the steady state combustion of a composite solid propellant will never supply the information needed to formulate accurate analytical models of the gaseous reaction zone. In particular, it appears that future studies in the gaseous phase must now be directed towards understanding reactions that occur in a zone which is at least 1000 microns thick and contains inhomogeneities of the order of several hundred microns.

B. Experimental Investigation of Chemical Processes Leading to the Ignition of a Composite Solid Propellant

This investigation was concerned with the chemical processes which occur prior to the ignition of a composite solid propellant. Research on this program was conducted by Mr. S.D. Kershner, a candidate for a PhD degree. Attention was directed principally to the polymer pyrolysis and reactions of the polymer with the products of decomposition of the propellant oxidizer. The experimental investigation consists of three phases: 1) a study of the pyrolysis products of the heated polymer, 2) ignition characteristics of the heated polymer when rapidly exposed to an oxidizing environment, and 3) ignition characteristics of the heated propellant when rapidly exposed to an oxidizing environment. The propellant employed in this investigation was a PBAA-AP formulation containing 2% aluminum. The polymer utilized in phases one and two had the identical formulation as the propellant binder and was prepared from the same lot of constituents.

In phase one a minute sample of polymer (less than one milligram) was subjected to pyrolysis in the direct inlet probe of a Bendix Time-of-Flight mass spectrometer at temperatures up to 290 C. Nine different mass spectra were recorded over the temperature interval 30 C to 290 C at pressures less than $2X10^{-6}$ torr. At temperatures above 200 C the mass spectra exhibited peaks at almost every mass number from mass 27 to mass 230. Predominant series of peaks were recorded at masses 41, 55, 67, 79, 93 and 107 indicating loss of CH_2.

To determine the equilibrium concentration of fuel vapor adjacent to the surface of the polymer, a small sample of polymer (about 1 cm in diameter and 4 mm thick) was heated to 260^{o}C in a 100% nitrogen environment. This experiment was conducted at 1 atmosphere pressure and in a closed volume of 8 cc. A 0.1 cc sample of equilibrium gas mixture was analyzed both qualitatively and quantitatively with a gas chromatograph column in series with the TOF mass spectrometer. Although the nitrogen analysis was as expected, no species attributable to the fuel vapor could be identified. This result suggests that the partial pressure of the fuel vapor is very low, probably less than 10 torr and that the small quantity of fuel vapor present may have been trapped in the chromatography column. Observation after this experiment revealed that the polymer sample is molten at 260 C, but it is enveloped by a thin solid "skin", apparently caused by the surface pyrolysis or possibly by reaction with the nitrogen environment. This "skin" was not present in the case of the sample subjected to vacuum pyrolysis in the mass spectrometer.

For phases two and three, the experimental procedure may be described as follows. A small sample of the polymer or propellant was initially heated in a nitrogen environment and then rapidly exposed (within 5 milliseconds) to a hot oxidizing gas. The ignition delay (operationally determined as the time from first exposure to the oxidizing gas until first light emission from the reaction zone) was measured as a function of sample temperature, oxidizing gas temperature, oxidizing gas pressure, oxidizing gas species, oxidizing gas concentration, exposed surface area of the sample and surface preparation of the sample. Pressures were varied over the range one to twenty atmospheres and temperatures of the nitrogen and oxidizing environments were independently varied over the range 90^{o}C to 260^{o}C. Oxygen and chlorine, both decomposition products of ammonium perchlorate, were utilized as oxidizing species. The sample exposed to the oxidizing gas had either a freshly cut surface, devoid of pyrolysis products and inert adsorbed molecules, or the surface conditioned in the inert environment. Provisions were made in the experimental apparatus for obtaining a gas sample from an 8 cc closed volume enclosing the surface of the polymer or propellant sample. The gas samples were obtained during the ignition delay period, and were normally taken within a twenty millisecond time interval, and transferred in a heated sample valve to the gas chromotograph-mass spectrometer apparatus for analysis.

Polymer samples failed to ignite in a reasonable time interval (within 10 sec.) when exposed to a 100% oxygen environment at temperatures up to 260 C and pressure up to 20 atmospheres. The results were the same regardless of surface preparation. These results were not unexpected when compared with those of McAlevy, et. al, and Pearson and Sutton. However, the failure to ignite even with a freshly cut polymer surface indicates that the oxygen-polymer reaction rate is too low to contribute significantly to the ignition process.

Propellant samples also failed to ignite when exposed to a 100% oxygen environment at temperatures up to 240 C and pressures up to 20 atmospheres. Higher temperatures were not investigated since the auto-ignition temperature of the propellant is about 250 C.

Polymer samples exposed to chlorine gas at 200 C and 5 atmospheres ignited in less than 500 milliseconds. The ignition delay decreased with increasing pressure and for samples with freshly cut surfaces. Analysis of gas samples taken prior to ignition have failed to identify any fuel species in the sample. Propellant samples exposed to chlorine gas have essentially the same ignition delays as the polymer samples for like conditions.

These results for chlorine strongly suggest a hetegeneous reaction mechanism. However, the data are insufficient to identify the chlorine-polymer reaction as the critical one leading to ignition. The perchloric acid-polymer reaction is also known to occur rapidly even at 1 atmosphere pressure.

Currently this research is being supported by the Thiokol Chemical Corporation.

C. Measurement of the Surface Temperature of Burning Ammonium Perchlorate

The measurement of the surface temperature burning AP (ammonium perchlorate) as a function of the burning rate was undertaken by Mr. N.E. James, a candidate for a M.S. degree. An infrared emission technique was employed to circumvent most of the criticisms of previous experimental methods.

These experiments were stimulated by a suggestion in an early paper by Wilfong, Penner, and Daniels (1) that the linear burning rate of a solid propellant may be controlled by the kinetics of the solid phase gasification process. If the surface gasification process is a kinetic one and can be represented by an Arrhenius type expression, then the linear regression rate of the propellant components is directly controlled by its surface temperature. Thus, there has been great interest in obtaining the kinetic parameters of the AP decomposition process, especially since the burning rate of propellants containing AP is apparently largely controlled by the AP.

Early experiments were performed with isothermal bulk samples decomposing in vacuum. Many features of the AP decomposition process were revealed but the kinetic parameters obtained were not accepted as representative of the conditions in a rocket motor.

In an attempt to represent the intense surface heating environment of a burning propellant, the Linear Pyrolysis method was developed. In this method, a strand of AP is pressed against a heated plate and the surface temperature and regression rate are measured. By plotting the linear regression rate, r, on a log scale versus the reciprocal of the surface temperature, the parameters of the Arrehenius expression are obtained directly. The activation energy, E, is the slope of the line and the frequency factor, A, is the intercept. If it is assumed that these data are representative of the conditions in propellant combustion, the surface temperature is established at any given burning rate. Or, the Arrehenius expression obtained may be employed as a boundary condition in quantitative burning rate theories.

However, the Linear Pyrolysis method is subject to at least two criticisms. First, the true surface temperature, usually measured with a thermocouple at the plate surface, is difficult to obtain because of the temperature drop across the film of gaseous decomposition products, and second, there is the probable absence of energetic reactions in the film covering the surface and thus the effects of pressure, which would be present under actual operating conditions.

Other experiments have been performed to directly measure the surface temperature of burning AP and fuel mixtures. Summerfield and associates (2) employed thermocouples embedded in strands of AP and conventional polymer binders to obtain the surface temperature as the surface burned past the thermocouple. Powling and Smith (3,4) employed an infrared emission technique to find the surface temperatures of mixtures of AP and the solid fuel paraformaldehyde. In this case, the fuel was added only to sustain combustion since AP will burn as a monopropellant only above approximately 20 atmospheres pressure.

In both of the above experiments the steep subsurface temperature gradient present in a burning material places a severe limitation on the accuracy of the measurement. In the case of the thermocouple measurement, even the smallest thermocouples are large relative to the temperature gradient. The limitation in the infrared emission technique arises because AP is a semitransparent material and the emission coming from beneath the surface is not representative of the surface temperature.

It was the objective of this study to account for the effects of the subsurface temperature gradient and to thereby obtain the true surface temperature from measurements of the surface emission.

The apparatus which was constructed consists of three subsystems; (1) the combustion bomb and pressure control system, (2) the propellant positioning servomechanism, and (3) the infrared measurement system.

On one axis of the bomb are windows for passing the light beam of the position detecting system. An infrared transmitting window was mounted at the front of the bomb. All of the windows were kept free of exhaust products by nitrogen purges.

The propellant positioning feedshaft mechanism was mounted to drive the propellant strand toward the front of the bomb and the focal point of the infrared detector optics. The propellant was fed through a tube which has a dual purpose of supporting the strand and directing purge or fuel gas along the strand. The feedshaft mechanism was portable and could also be mounted below the bomb to drive the strand out of the plane of the figure to permit measurement of the gas phase emission only in the profile of the flame.

The infrared detection system included a Perkin-Elmer Model 99 prism monochromator, a reference blackbody, and exterior optics for focusing emission from the strand or the blackbody onto the monochromator entrance slit.

The experimental apparatus was completed and checked out. The servomechanism has been operated satisfactorily and the infrared detection system has been aligned and calibrated.

Experiments were conducted to find satisfactory burning conditions for the fuel samples. The fuel samples were pressed strands of pure AP one-half inch square in five inch lengths. In addition, similar strands of pure AP plus 10% paraformaldehyde (PF) were available for studies below the low pressure combustion limit of pure AP. Ignition tests were run for the following conditions.

1. AP/10% PF at pressures from atmospheric to 100 psi in nitrogen atmosphere.

2. AP.10% PF at atmospheric pressure with gaseous hydrogen or ammonia added.

3. Pure AP at 200 - 600 psi in nitrogen atmosphere.

4. Pure AP at atmospheric pressure with gaseous hydrogen added.

In all tests, the ignition device employed was a retractable hot wire grid which covered the entire surface. The purge flow velocities were varied from one to seven ft/sec and the gaseous fuels were added to either the strand support tube or face window purges.

The purpose in adding the fuel gases was to increase the energy feedback to the surface and thereby maintain a stable burning surface. In ignition tests of the AP/PF strands, there was erratic or unstable surface burning at each of the test pressures. No improvement was found by adding ammonia fuel gas but a stable burning surface could be maintained with mixtures of nitrogen and approximately 7% hydrogen. However, the mixture ratio was very critical and different burning characteristics existed at the two different feedshaft positions.

In the ignition tests of pure AP, there was rapid extinction of the burning as soon as the ignition wire was removed at all of the test pressures. The use of hydrogen to support combustion of pure AP at atmospheric pressure was also investigated but it was found that thermal shock from the surface heating caused severe chipping of the sample. There was no problem of sample chipping at the higher pressures.

It has been reported in the literature (6) that the low pressure combustion limit of pure AP may be as low as 300 psi depending on the method of ignition, type of specimen, and the effect of the local environment on surface heat losses. Similar factors probably affect the AP/PF samples. Therefore, it was planned to investigate the following methods for improving the burning and ignition conditions.

1. Improved ignition. Pyrotechnic paste or strips of conventional propellant will be placed on the strand in an attempt to obtain more even ignition.

2. Reduced purge velocities. Minor modifications to the purge system will be made to permit metering and controlling very small purge velocities.

3. Smaller particle size samples. Pellets will be pressed from micron sized particles of pure AP only.

Currently the program is inactive because of the absence of support.

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IV. Research in Combustion Processes

A. The Effect of Chemical and Thermal Nonequilibrium on Supersonic Combustion Performance

Initial work entailed a survey of existing literature on the subject of supersonic combustion to determine the present state-of-the-art in the field of simulation of flight conditions by ground installations. Existing experimental work in supersonic combustion was found to be concentrated on flight regimes less than Mach 6 or greater than Mach 10. Testing in the lower Mach number range is conducted in blowdown facilities and employing heated air in the higher range, by so-called "hot-shot" tests using shock tube techniques. Conventional, convective means for heating air to be used for the intermediate Mach number range, $6 < M_\infty < 12$, are impractical because of the temperature required. However, the production of a vitiated air to operate within this range may be quite practical provided the effects of vitiation on supersonic burning can be established with a reasonable degree of certainty. Consequently, the subject research program was directed toward establishing a correlation between supersonic combustion with heated air and vitiated air, so that the range of ground simulation can be increased for future propulsion endeavors.

The vitiated air for this program will be produced by a rocket engine using a liquid propellant combination of nitrogen tetroxide and hydrazine. Nitrogen is then added to the hot gases to reach the required fraction of unreacted oxygen. The flight conditions to be simulated and composition of reactants and products of the gas generator are listed below:

A. Simulated Conditions

$M_\infty \sim 7.0$

Altitude $\sim$ 90,000 feet

To = 4000°R

Po = 1000 psia

B. Gas Generator

	Reactants		Products	
	N_2O_4	= 9.2 #/sec	N_2	= 8.2
	N_2H_4	= 2.6	H_2O	= 2.9
	N_2	= 3.2	O_2	= 3.9
Total		15.0 #/sec		15.0 #/sec

The composition of the products given above represents that in the test section prior to injection of the supersonic combustion fuel which in this study is hydrogen. At this point the vitiated air has been expanded to the following conditions:

C. Test Section Conditions

$P_{t.s.} \sim 25$ psia

$M_{t.s.} \sim 2.9$

$T_{t.s} \sim 1800^{o}R$

The design effort during this period was concerned with the test stand, gas generator and test section. Completed drawings were prepared for the test stand and the initial test hardware. The initial hardware will be uncooled with later configurations designed to incorporate an external means for cooling, if required. The present designs are fabricated from stainless steel coated with a thermal barrier of Zirconium Oxide. During the period when the project was under the initial grant the materials for the test stand and gas generator were ordered and fabrication had began.

The project has been continued under NASA sponsorship and the "checkout" of the gas generator system is underway in test cell No. 2 of the Combustion Research Facility. With completion of checkout of the gas generator the supersonic burner section will be installed and the experiments to determine ignition lag and combustor performance with vitiated air will be conducted.

B. Attenuation of Transverse Combustion Pressure Oscillations

The objective of this investigation was to examine the acoustics of injector face baffles for the transverse modes of combustion pressure oscillations which can occur in rocket motor combustion chambers. The results of this investigation are presented in reference 1.

The phenomenon of acoustic wave propagation in rocket combustion chambers with ring-spoke baffles was investigated under the assumption that baffles block these waves near the injector. The eigenfunctions which define the space and time dependence of the standing waves peculiar to various cell geometries were thoroughly investigated, with particular emphasis being placed on the radial eigenfunctions and their eigenvalues. The behavior of transverse standing waves was investigated by means of acoustic pressure contour maps. Superposition of standing waves was considered, and both spinning and aperiodic combinations were studied. The characteristic frequencies of the states were examined, and the possibility of a rational approach to baffle selection was suggested. The appendices of reference 1 include a tabulation of 500 transverse frequency eigenvalues and contour maps of the six lowest states in each of 24 cells. Experiments with a slosh tank which may be used to demonstrate the behavior of transverse states is described in reference 1.

References

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V. Conclusion:

The foregoing report covers, in addition to the primary areas of research included in previous progress reports, many areas of research which were not completely funded on NASA Grant NsG 592. These are included to show that the research initiated on this grant was of sufficient interest to warrant continued support from other sources.

The names of the many students that conducted the research discussed in this report are included to indicate the value of this type of grant in preparing trained researchers for their future careers in the propulsion field, both in government and industry.

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