QUARTERLY PROGRESS REPORT

PROJECT SQUID

A PROGRAM OF FUNDAMENTAL RESEARCH

ON LIQUID ROCKET AND PULSE JET PROPULSION

FOR THE

BUREAU OF AERONAUTICS AND THE OFFICE OF NAVAL RESEARCH

OF THE

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PURDUE RESEARCH FOUNDATION
and
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

1 APRIL 1947

PHASE NO. 1

STATEMENT OF PROBLEM

Development of a method of measuring instantaneous gas temperatures fluctuating at frequencies from 50 to 100 cycles per second in a range of temperatures from room temperature to 3,000° F. (pulse-jet gases).

SUMMARY

The major part of a survey of the literature available at Purdue University has been completed. Theoretical and experimental studies dealing with factors affecting lag are in progress as well as the design and construction of special thermocouples.

PROGRESS

Because of the following circumstances, it was decided to limit the study to the measurement of gas temperatures by means of thermocouples:

(a) Impossibility of expanding the staff as rapidly as had been expected, because of the difficulties of hiring engineers. At present 1 full-time engineer, one three-quarter time engineer, and several part-time senior engineering students are employed on the project.

(b) Early limitation placed upon the budgeted funds for the purchase of special equipment.

(c) Suggestions received from outstanding authorities, concerning the use of thermocouples as a means of temperature determination.

(d) Important facts acquired during the literature survey.

It is recognized, without question, by the investigators at Purdue University that the problems involved in the use of thermocouples for measuring the temperatures of gases under transient conditions are many and may be unsolvable. However, from the point of view of engineering use, the many advantages of a system based on the thermocouple are obvious. It may be possible to devise a satisfactory system employing thermoelements which may not measure the actual temperature but, by use of suitable correction terms, may be used to determine the temperature within ten percent plus or minus. This type of apparatus would find wide use from the standpoint of engineering design. The investigators have, therefore, elected to proceed along this avenue of development work. The scope of the program and the progress made are presented in the following discussions:

(1) Survey of the literature available to the research staff at Purdue University.

The major part of the survey of the literature has been completed. Methods and apparatus used for measuring the temperatures of gases flowing at subsonic and supersonic velocities have been studied. It is hoped that restricted information dealing with the subject will at an early date, be released by the Navy to the engineering staff working on the project.

(2) Experimental and theoretical studies of bare, shielded, and suction types of thermocouples.

Theoretical studies covering the various factors that influence the time lag of the measuring element are in progress.

(3) Design of suitable apparatus for detecting, amplifying, observing, and recording the electrical impulses from thermocouples.

Apparatus has been constructed and is being tested and calibrated. The time lag of the instruments has been reduced to values far below the minimum time lag of the measuring element.

PLANS

In the course of the next several months, experimental as well as theoretical studies will be made of actual thermocouple installations.

PHASE NO. 2

STATEMENT OF PROBLEM

To study continuous process combustion, defining effects of combustion-chamber size and shape, fuel and oxidizer distribution, and turbulence with available fuels and oxidizers.

SUMMARY

Reasonably satisfactory combustion was obtained with propane and air mixtures. Quantitative values of flame speed were not obtained. Combustion of fuel-oil and air was unsatisfactory

and thus indicated the necessity of improving fuel dispersion and vaporization.

PROGRESS

Preliminary operation of the small-scale combustion set-up disclosed numerous faults which created fire hazards due to leakage of liquid fuel and discharge of flame in the vicinity of buildings. Modifications, which included a heavier combustion chamber with leak-proof connections and a heat-resistant Vycor cylinder for observation of flames, were incorporated. With these modifications it was possible to discharge flames and gases vertically. A flame-quenching water spray is quickly available for emergency use. Provisions were made to prevent fuel from running back through the inclined air-supply duct within the building, a condition that might have created a hazard in case of flash-back.

Modifications of the fuel system were made to include a liquid-fuel supply with a controllable pressure range up to 1000 p.s.i. and sufficient power for more than 2000 pounds of fuel per hour, a supply which is ample for combustion with the 20,000-pounds air capacity per hour available from one supercharger. Also, a multi-unit propane fuel system with provisions for measuring flow was set up. Several designs of fuel-discharge nozzles and tubes were prepared to obtain maximum dispersion with a minimum of restriction to flow and also to permit selective use of propane and liquid fuels in any ratio.

A high-voltage ignition system with various types and locations of sparkgaps was constructed to obtain the satisfactory spark necessitated by use of low volatility fuel and low air-supply temperature.

To permit the attaining and controlling of higher air temperatures and to eliminate supercharger surging, a by-pass has been incorporated around the centrifugal supercharger. Thus it will be possible to evaluate the effects of air temperature on combustion efficiency, flame speed, etc.

Several runs were made to determine the degree of flame stability with fuel oil and propane gas as fuels and with variation of mass-mixture flow through the perforated burner plate covering the discharge end of the contracting-air nozzle to be used for later experiments. Reasonable stability of flame appeared with maximum calculated mixture velocities of sixty feet per second and with propane used as a fuel. Sufficient vaporization and dispersion of the fuel oil was not obtained, a fact resulting in greatly delayed burning so that the liquid fuel coated the surfaces of the duct system downstream from the initial point of burning. However, combustion was obtained and flame held at certain areas of the burner plate mass when mixture-velocities approached one hundred and eighty feet per second.

Explosion of gases resulted in failure of the Vycor glass cylinder, which prevented continuation of these studies until suitable replacements are obtained. The procurement of pyrex as well as Vycor cylinders and the fabrication of a steel cylinder with suitable window inserts had been initiated before the failure, so that a minimum of delay will occur before the resumption of experimentation.

The mock-up of the various systems required for the operation of the engine and superchargers to be used as a source of air supply for combustion has proceeded to the point where the fabrication of identical equipment for all six engines and twelve superchargers can be started.

Numerous contacts were made with various offices of the U. S. Navy to obtain approval of the structure to house the project. The final approval has not yet been obtained. The hazards and noise associated with the research prevents desired experimentation on the campus with the small-scale facilities constructed for temporary use.

PLANS

It is anticipated that both quantitative and qualitative study of continuous process combustion can be initiated in the next quarterly period with the use of more volatile fuels, such as propane. A study of the effect of possibly one variable, such as mixture temperature, on combustion rate is projected.

PHASE NO. 3

STATEMENT OF PROBLEM

This phase undertakes the study of corrosion in connection with jet propulsion. The purpose of the research is to identify the corrosion products, to investigate the process of corrosion as affected by the chemical and physical properties of the materials, and the conditions of exposure.

SUMMARY

The oxide layers formed on high chrome-steel alloys at high temperatures have been investigated by x-ray and electron diffraction methods. Under certain conditions a rough scale is formed which is found to contain FeO, Fe_3O_4 or $FeO{\cdot}Cr_2O_3$, small amounts of the mixed ferric-chromic oxides, and larger amounts of the pure (ic) oxides.

Under other conditions a protective layer is formed which is too thin for x-ray diffraction analysis. By an x-ray absorption analysis the chromium content is found to decrease from 26% to 21% after increasing the oxidation from ten to twenty hours. The thickness corresponds to approximately 0.4 and 0.7 milligram of oxide/cm^2.

PROGRESS

The protective oxides formed on chromium-steel samples when heated to 775-800° C. in air or oxygen are being investigated by x-ray, electron diffraction, and electron-microscope methods in order to understand the mechanism of self-protection of heat-resistant alloys.

The identification of the various oxides present, from their x-ray or electron diffraction patterns, is complicated by the many crystalline forms that may occur and the very close similarity of many of the patterns.

In regard to 18 Cr-Fe steel which, when oxidized in air at 800° C., gave a rough but adherent blue-grey scale, the following conclusions may be drawn:

1. FeO constitutes less than 10% of the scale.
2. There is strong evidence that $FeO{\cdot}Fe_2O_3$ and/or $FeO{\cdot}Cr_2O_3$ are present only in small amounts.
3. One or more of the oxides, $3Fe_2O_3{\cdot}Cr_2O_3$, $Fe_2O_3{\cdot}Cr_2O_3$, and $3Cr_2O_3{\cdot}Fe_2O_3$ are present in greater proportions than those mentioned in item two.
4. Fe_2O_3, and either Cr_2O_3 or $3Cr_2O_3{\cdot}Fe_2O_3$, are the most prevalent oxides.

It has been impossible to determine the physical arrangement of the various oxides in the scale because of the small amount of oxide present.

Electron-diffraction patterns taken by "reflection" from a surface yield the crystalline structure of a very thin layer near the surface, because of the limited penetration by even high-energy electrons. For the sample 18 Cr-Fe steel, Cr_2O_3 is found on the surface. This is in agreement with the experience of Gulbranson, Phelps and Hickman, who have compared the structure found by electron diffraction from the surface with that obtained by transmission after stripping the oxide film from the base. In contrast with this, the earlier work of Pfeil and others with relatively heavy scales indicates that the iron oxides tend to be on the surface and the chromium oxides near the metal. In view of the fundamental importance of this question, apparatus for electrolytically stripping the scale has been set up, so that transmission experiments can be made. After preliminary experiments, this apparatus is being revised to simplify the retrieving of the film after removal.

When other specimens of the sample discussed above are exposed under similar conditions, a very thin, yellow-brown, adherent film is formed. The cause of this different behavior has not been completely determined, but it seems to be associated with the degree and quality of polish of the specimen. The protection offered by the smooth coating is much greater than by the rough scale. After twenty hours of oxidation at 775° C. the diffraction patterns of the oxide are still too weak for satisfactory analysis.

A second x-ray method of investigation has been used. The intensity of a crystal-diffraction line from the base metal may be compared with the weakened intensity found for it when the base metal is covered with the oxide scale. Since the absorption coefficient is not known, because the composition of the oxide layer is uncertain, the thickness of the layer cannot be calculated from this weakening. It has been found, however, that if the weakening is observed with two different radiations of suitable wave length, the approximate percentage of chromium in the layer may be computed. By using Fe Kα radiation, the absorption in chromium is found to be larger than in iron, but with Cu Kα radiation the reverse is true. Because of this differential effect, the percentage of chromium may be found even when the exact state of oxidation is not known.

The rough type of scale formed in two hours at 800° C. is found to be approximately 10% chromium with 1.2 milligrams of oxide/cm^2. The smooth type of layer after 10 hours at 775° C. is approximately 26% chromium, and 0.4 milligram of oxide/cm^2; after 20 hours, it is approximately 21% chromium and 0.7 milligram of oxide/cm^2.

Attempts are being made to develop techniques for the preparation of polished and etched cross-sections through the oxide layer which are suitable for optical and electron-microscope examination. It is difficult to obtain a sufficiently flat and clean surface across the boundary between the hard specimen and the softer mounting material, but some progress has been made.

PLANS

Binary alloys of various compositions of Cr-Fe, Ni-Fe, and Ni-Cr have been ordered. When these materials are available, systematic investigations of them will be made by the methods described. Development of the film stripping technique and cross-section preparation will continue. It is hoped that the latter may be extended to permit the making of sections thin enough for x-ray microradiography. If this can be done, it should be possible to establish the segregation of the metal components in the oxide layer.

PHASE NO. 4

STATEMENT OF PROBLEM

The purpose of this research is to study, by means of bomb or continuous-flow experiments, temperatures, pressures, and concentration of reactants, for various oxidation reactions of materials that may be of value as fuel for a rocket or jet engine.

SUMMARY

Several qualitative experiments were made in a continuous-flow system with mixtures of methane and air burning in a glass combustion chamber. An attempt has been made to find some method for analyzing the gases present in a flame. However, it is doubtful if even a qualitative spectroscopic analysis which would determine all of the constituents present could be made of the flame.

PROGRESS

The original plan for this investigation was to investigate reaction rates by continuous combustion of a fuel in a reaction tube by quenching the reaction during its progress by means of an inert gas. Initial experiments of a qualitative nature were made on the problem of propagating a stationary flame inside a tube. A mixture of methane and air was used as the reacting mixture.

The flame consisted essentially of three zones, the first of which was a very thin reaction zone where rapid combustion occurred, a zone of after burning within the tube extending from the flame front to the end of the tube, and a third zone extending from the end of the tube and resembling a weak Bunsen flame. The thin reaction zone was highly luminescent and the heat given off in this zone was so intense that it caused the glass wall adjacent to it to soften in a very short time. This indicates that most of the reaction between the methane and the air occurred in this zone. The thinness of the reacting zone, indicating a fast reaction, suggested difficulties in sampling the reaction products at various time intervals after initial ignition of reactants. Since it is the region of fast reaction that is the subject of this research, some thought was given to the method of analyzing the combustion products during the process of the combustion.

The maximum linear velocity of reactants flowing through the reaction chamber is limited by the burning speed of the reactant mixture. The data of Lewis and Von Elbe (J. Chem. Phys. **2**, 283, 1934), on the decomposition of ozone to form oxygen indicate that the majority of the reaction occurred in the time of the order of 0.0000004 second. These results are not exact; however, the order of their magnitude is significant. These results show that it would be impossible to create a gas velocity which required in the reaction tube to elongate the flame front sufficiently for purposes of analysis.

Spectroscopy was considered as a means of studying the progress of the combustion reaction. Qualitative spectroscopy has already been employed to establish the existence of certain compounds in the flames of hydrocarbon. Quantitative spectroscopy might offer a possible solution to the analysis of combustion products during the combustion, but quantitative spectroscopy has not been completely developed for analyses of this sort.

Another method that may be of value in this study is the use of a constant-volume bomb. Results from this type of equipment may be obtained in the form of pressure rise during reaction, time for the flame front to traverse the gaseous region, and possibly the maximum temperature reached during combustion. Bomb experiments have, in the past, provided the major portion of the present knowledge of the combustion reaction, but can give no indication of actual reaction rates, since the amount of material burned inside a bomb in a given time is more dependent upon the flame speed than upon the reaction rate.

PLANS

In view of the difficulties which would arise in attempting to measure combustion rates, as distinguished from flame velocities, it appears that some modification of the original problem should be made. The present plans should perhaps be directed toward a study of flame velocities for one or more fuels, and toward determination of whether such data would be useful in studies concerned with jet propelled engines.

PHASE NO. 5

STATEMENT OF PROBLEM

The purpose of this research is to determine, for liquid-fuel rockets and pulse-jet engines, the radiation factor and its contribution to heat-transfer coefficients inside a pipe with gas flow at low and also at high temperatures.

SUMMARY

The apparatus required for the successful conclusion of this project is beginning to arrive. Most of the time during the quarter has been spent in building and assembling the various parts of the experimental equipment. The remainder of the period has been utilized to outline the test program and to define and foresee the chief difficulties that may be encountered.

PROGRESS

During the past three months orders have been placed for all the remaining important pieces of equipment. Some of this material has arrived and most of the time has been spent in constructing and assembling apparatus. In particular, the gas-fired furnace for preheating the gas stream has been installed and a Nichrome coil fabricated for insertion in the furnace.

Some thought has been given to establishing the sequence to be followed in the experimental work. To separate the radiation heat-transfer rate from the measured total rate, which is the real objective of the project, will require an accurate knowledge of the convection heat-transfer rate. It is proposed to obtain this information from experimental measurements in the same apparatus on a non-radiating gas such as nitrogen. Therefore, the first experimental work to be undertaken when the equipment is in operation, will be to evaluate the convection heat-transfer rate at high temperatures. These results, while not fulfilling the ultimate objective of the project, should be worth while, because there are so few data on convection coefficients at temperatures of 2000° F. and above.

PLANS

In the next quarter the main objective will be to complete the construction and calibration of the experimental apparatus and to begin the experimental studies as outlined.

PHASE NO. 6F

STATEMENT OF PROBLEM

The purpose of this research is to determine experimentally the heat of formation and combustion, the specific heats, and other thermodynamic properties of various fuels and oxidizers used in pulsating jet engines. If possible, a correlation of thermodynamic properties of these fuels may be made, so that calculations may be extended to include new fuels.

SUMMARY

Delays in the delivery of equipment have held up actual experimental work on this project. We have received notification from the manufacturers that the main pieces of equipment will arrive within one or two weeks.

PROGRESS

At the present time this research is being directed toward the determination of heats of formation of compounds which might be useful as fuels in pulsating jet engines. The heats of formation will be determined from standard heats of combustion obtained by use of an adiabatic calorimeter. The experimental work in this research program has not been started as yet because of delays in delivery of equipment. All the minor pieces of equipment have been obtained and assembled, and the only piece of equipment which is lacking is the adiabatic calorimeter. The manufacturers indicated that this calorimeter was to be shipped on 15 March 1947. After all the equipment has been assembled, the calorimeter will be calibrated by use of a standard material such as benzoic acid obtained from the Bureau of Standards, before making any determination on a new fuel.

The planning division of the Office of Naval Research of the Navy Department has suggested a number of compounds whose heats of formation are desired. A number of these compounds can be obtained from commercial sources; a number of them, however, will be prepared in the laboratories of Purdue University. A library survey has indicated that the available data for one of the types of compounds suggested by the Office of Naval Research are very meager. For this reason, the present research at the outset will be directed toward determining the heats of formation for this type of compounds.

PLANS

The experimental work in the immediate future is to be directed toward the determination of the heats of formation of one of the types of compounds suggested by the Office of Naval Research. Heats of formation of all derivatives of this type of compound will be determined, provided samples of the various derivatives can be obtained, and with this information it may be possible to determine the effect of group contribution in estimating the heats of formation of similar compounds.

PHASE NO. 6G

STATEMENT OF PROBLEM

The subject of the research on Phase 6G is the determination of heats of combustion of various chemical compounds suitable as high-energy fuels and oxidizers.

SUMMARY

The apparatus for the determination of heats of combustion has been calibrated. The metal organic compounds to be furnished by Aerojet Engineering Corporation have not arrived; meanwhile the heats of combustion of rocket fuels as developed at Purdue are being determined. The first compound to be studied is the methyl ester of nitroacetic acid.

PROGRESS

During the early months of this project, and preceding the period covered by this report, the apparatus to be used in determining the heats of combustion of the compounds selected for investigation was cleaned and repaired and placed in operating condition. The potentiometer, the analytical balances, the weights, and the volumetric glassware were calibrated, and a routine of operation for the combustion experiments was established. Thus, at the beginning of this quarter only the calibration of the calorimeter required completion before beginning the combustion experiments on those compounds whose heats of combustion are desired.

During this period from 1 January to 31 March, the preliminary calibration experiments were completed and the value of the heat capacity of the calorimeter in calories per microvolt was determined. Also, certain improvements were incorporated in the apparatus which would permit more accurate temperature control, greater precision of time measurement, and greater ease of manipulation of the apparatus.

Arrangements were made with the Aerojet Engineering Corporation for obtaining samples of the metal-organic compounds whose heats of combustion are to be determined. The samples have not as yet been delivered. Several oxidizers of the type used in rocket fuels devised at Purdue have been considered, and work has been started on the determination of the heat of combustion of one of these fuels, the methyl ester of nitroacetic acid.

PLANS

Future work will consist of measuring the heats of combustion of the compounds selected as soon as the compounds are available. In addition, it is intended to conduct further calibration experiments so that any change in the heat capacity of the calorimeter or any variation in the oxygen used may be detected as soon as it occurs and corrective steps taken.

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ABSTRACT:

Apparatus was designed by which gas temperatures could be measured by suction type thermocouple and be observed and recorded. Combustion and fuel studies were made. Combustion was satisfactory with propane and air mixtures but not with fuel-oil and air. High chrome steel was investigated by X-Ray and diffraction methods to analyze oxide scale formed at high temperatures. Several materials were tested to determine their value as fuels for rocket or jet engines.

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