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EFFECT OF OZONE ADDITION ON COMBUSTION EFFICIENCY OF HYDROGEN - LIQUID-OXYGEN PROPELLANT IN SMALL ROCKETS

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SUMMARY

An experimental study shows that 2 percent by weight ozone in oxygen has little effect on over-all reactivity for a range of oxidant-fuel weight ratios from 1 to 6. This conclusion is based on characteristic-velocity measurements in 200-pound-thrust chambers at a pressure of 300 pounds per square inch absolute with low-efficiency injectors. The presence of 9 percent ozone in oxygen also did not affect performance in an efficient chamber.

Explosions were encountered when equipment or procedure permitted ozone to concentrate locally. These experiments indicate that even small amounts of ozone in oxygen can cause operational problems.

INTRODUCTION

Although liquid ozone has several potential advantages as a rocket oxidant, its use has been discouraged because of a strong tendency for it to propagate very destructive detonations. However, recent experiments (ref. 1) show that liquid mixtures containing 35 percent or less ozone in oxygen will not propagate strongly initiated detonations in 1/2-inch tubes. Low concentrations of ozone, therefore, may be safe in a properly designed rocket.

Rocket experiments with low concentrations of ozone cannot be expected to show thermodynamic effects of increased chemical enthalpy, but may show effects of ozone on over-all combustion efficiency if such effects are present. Since hydrogen and ozone is a theoretically attractive combination, an early experimental study in a rocket is desirable to determine the existence of any effects on over-all efficiency and to indicate possible operational problems. Work with ozone can be started at low concentrations, and if warranted, continued to higher concentrations.

The results of a study with low concentrations of ozone are presented herein. The effects of small amounts of added ozone on the overall efficiencies of hydrogen-oxygen combustion were determined in several 200-pound-thrust combustor configurations. Characteristic velocities were measured at chamber pressures near 300 pounds per square inch absolute for a range of oxidant-fuel weight ratios from 1 to 6.

EXPERIMENTS

Apparatus and Procedure

Two operations were required for each set of experiments: first the preparation of the desired liquid ozone-oxygen mixture, and then the running of the rocket.

Preparation of ozone-oxygen mixture. - A flow diagram of the oxidant processing equipment is shown in figure 1. Liquid oxygen was forced from a vacuum-insulated tank by helium at a pressure of 50 pounds per square inch to a thermostatically heated evaporator. The oxygen gas was preheated to 1500° F in a coiled length of Inconel tubing resistance-heated by high-intensity current. The hot gas then passed through a bed of copper oxide kept at 1500° F by electric heaters. This was to oxidize possible impurities in the oxygen. The hot gas was then cooled in a water-cooled heat exchanger and passed in turn through towers of activated alumina and sodium hydroxide on asbestos to remove water and carbon dioxide, respectively. The oxygen gas at about 10 pounds per square inch gage then passed through a dust filter and a rotameter, and into a commercial 51-tube water-cooled ozonator. The gas from the ozonator, about 2 percent ozone, was piped to the rocket apparatus shown in figure 2(a). The ozone and some or all of the oxygen were condensed in the oxidant tank of the rocket, which was refrigerated with either liquid nitrogen or oxygen. If 2 percent liquid ozone in oxygen was desired, all the gas was condensed in the tank. When stronger concentrations were desired, the top of the tank was vented and not all the oxygen condensed. Most of the ozone, however, condensed from the oxygen as it bubbled through the liquid in the tank.

Final concentration was made with the ozonator shut off, by removal of gaseous oxygen at reduced pressure with a large water aspirator pump in the tank vent line. (The precautions needed for the safe removal of oxygen are discussed in the section Operational Experience.) The quantity of liquid in the tank was measured by a field-calibrated capacitance level indicator. The ozone concentration in the liquid was determined from the concentration and flow rate into the tank and from the amount of liquid in the tank after concentration. The ozone in the gas was determined by chemical analysis, and the gas flow was measured in a rotameter. The ozone concentration in the tank before final concentration was also checked by a capacitance measurement.

Rocket experiments. - As shown in figure 2(a), all equipment which would contact liquid ozone mixtures was refrigerated with liquid oxygen or nitrogen during the rocket runs. This was to keep ozone from concentrating beyond safe limits by evaporation of oxygen. All valves in contact with liquid-ozone mixtures were remotely operated. The physical arrangement of the rocket apparatus is shown in the photograph in figure 2(b). Personnel were not permitted in the rocket cell when liquid ozone at any concentration was present.

The functions of the rocket components are summarized in figure 2(a). The flows of the liquid ozone-oxygen mixture were measured by two turbine-type flowmeters in series. The hydrogen gas was at ambient temperature, and the flow was measured with a flat-plate orifice system. The total and differential pressures at the hydrogen orifice and the rocket chamber pressure were sensed by strain-gage transducers. Signals from the pressure transducers and turbine flowmeters were recorded by strip-chart potentiometers and by a multichannel optical-galvanometer oscilloscope. The primary measurement of rocket chamber pressure was by a Bourdon strip-chart recorder. Oxidant tank pressure was noted from an indicating Bourdon gage.

A cross section of the rocket chamber is shown in figure 3. The chamber body was mild steel, 2 inches in inside diameter and either 4 or 8 inches long. It had a spark plug 1 inch from the injector face. The exhaust nozzle, made of copper, was of the simple convergent type and was water cooled. Two injectors, one inefficient and the other efficient, were used. The inefficient one is shown, and is of the single-element concentric-tube type. In operation an axial stream of liquid oxygen is surrounded by an annular blast of gaseous hydrogen. The efficient injector has a repetitive pattern with nine smaller concentric elements. Both injectors are the identical ones used in an earlier study (ref. 2).

Each experimental series of runs consisted of two sets, one with liquid ozone in the oxygen, the other without ozone. The latter runs were for reference purposes and were intended to duplicate as nearly as possible the runs with ozone addition.

After a desired liquid ozone-oxygen mixture had been prepared in the propellant tank, the refrigerant trough containing the valves and lines was filled with either liquid nitrogen or oxygen, and the oxidant tank was pressurized. The equipment was then operated by an automatic sequence timer. Oxidant injection overlapped hydrogen injection before and after the run; ignition was by a 5000-volt continuous induction spark. Both the oxidant and the hydrogen lines beyond the propellant control valves were flushed with helium immediately after the control valves closed. The oxidant-fuel ratio was varied by changing pressures in the oxidant tank and of the hydrogen gas between runs. The runs were about 3 seconds long.

After the ozone-oxygen mixture in the propellant tank was exhausted, the propellant tank was refilled with liquid oxygen, and another set of runs at similar conditions was made.

Materials. - Before final assembly all parts of the oxidant processing system and the rocket were completely disassembled and washed in turn with 1-1-1-trichloroethane, a trisodium phosphate solution, and distilled water, and then dried in air. Parts were handled with freshly laundered cotton gloves or specially cleaned tools. Materials of construction in contact with ozone or oxygen were stainless steel, Pyrex glass, and Teflon. The ozonator was built to NASA specifications intended to eliminate all sources of oxidizable material and to facilitate intensive cleaning.

Later in the program the system could have been inadvertently contaminated by some recompressed helium. Some of the helium in use elsewhere at this center was found to contain traces of oil.

Operational Experience

Except for an explosion discussed later, few unexpected problems were encountered. It was found that the oxidant inlet valve (number 7, fig. 2(a)) should not be refrigerated when ozone-oxygen gas is being passed through it. When the valve was refrigerated small amounts of ozone condensed in it and detonated when it was operated. These explosions broke up the Teflon packing; a leak and Teflon fragments in the system resulted.

The components causing the most consistent trouble were the turbine-type flowmeters. The rotors were frequently put out of alinement. In a few cases this was attributed to Teflon fragments, probably from the oxidant inlet valve. In one instance very fine steel particles were found on the rotor hub. In several cases the turbines may have overspeeded because of inadvertent passage of high-velocity helium through the line. Another reason for failure of flowmeters could have been that small amounts of concentrated ozone collected and remained in the refrigerated part of the line below valve 7 (fig. 2(a)) during collection in the tank. If concentrated ozone was in the line, it would be part of the first liquid to contact the flowmeters. Very small explosions may have misalined the rotors.

The program terminated when an explosion destroyed the liquid-oxidant flow system of the rocket. This explosion, however, is thought not to have been caused by any unknown property of ozone. The explosion occurred at the start of an attempted series of runs with 20 percent by weight ozone. In order to speed up concentration of the mixture, the refrigerant had been drained from around the oxidant propellant tank, and

the oxygen was being removed at a pressure of about 2/3 atmosphere absolute. At this pressure it is possible that the liquid ozone-oxygen mixture in the tank would have been cooled to a temperature low enough to cause a concentrated liquid phase (refs. 3 and 4) containing about 80 percent ozone to settle to the bottom of the tank. The tank was later warmed to -183° C, but the separated phase, if present, may have remained at the bottom because of its higher density.

At the start of the run a shattering or "brisant" detonation occurred in the line between the oxidant control valve (number 5, fig. 2(a)) and the oxidant tank. The tubing and flowmeters were fragmented, and the heavy forged bodies of valves 5, 6, and 7 were split and expanded. The refrigerant trough was torn into several pieces, which were thrown with considerable velocity. The propellant tank showed evidence of high internal pressure but no brisant detonation. The detonation was probably arrested by the sudden diameter increase from the tube to the tank. Evidence of high pressure but no brisant detonation was found in the line between valve 5 and the chamber injector. It is important to note that the brisant detonation initiated somewhere in the line or valves away from the rocket combustor, probably from a low-energy source. A contributing factor in the initiation may have been contamination from the helium.

In spite of this misadventure, detonation data (ref. 1) indicate that 30 percent by weight ozone in liquid oxygen if properly handled can be run safely in a rocket. The important lesson here is to avoid procedures which will cause the temperature of the liquid to fall to the two-phase-separation temperature. An absolute pressure of at least 1.5 atmospheres should eliminate this possibility for all mixtures (refs. 3 and 4). Although the program terminated earlier than planned, enough data were obtained to show effects of ozone addition on over-all reactivity.

RESULTS AND DISCUSSION

Low-Efficiency Injector

A low-efficiency injector was used with the idea that changes in over-all rate could be sensed more readily with it than with an efficient one. The single-element concentric-tube injector (ref. 2) was selected because, in addition to being inefficient, it gives steady combustion which does not deteriorate rocket chamber parts. This injector was run with 2 percent by weight ozone in chambers 8 and 4 inches long. The measured characteristic velocities c^* are shown in table I and figure 4. The percent of theoretical c^* is also shown for each experiment (table I). These values are based on theoretical values for liquid oxygen and gaseous hydrogen (table II) computed at this center by an automatic

system using the method of reference 5. These theoretical values are satisfactory for comparison of over-all kinetic effects of 2 percent ozone in oxygen, since the chemical enthalpy would contribute a theoretical increase in c^* not exceeding 0.2 percent.

The experimental data in the 8-inch chamber with oxygen (fig. 4(a)) agree reasonably well with data obtained with an identical chamber on another stand operated by other personnel (ref. 2). When the data of the shaded symbols of figure 4(a) are compared, it can be seen that the presence of 2 percent ozone had no noticeable effect on performance. The data of the shaded points are all from one series of runs and represent the best available comparison with this chamber configuration.

Some of the early data with neat oxygen (series A (fig. 4(a)) show abnormal scatter near an oxidant-fuel weight ratio O/F of 3. This may have resulted from hydrodynamic effects in the equipment. No data for 2 percent ozone were obtained exactly at the same conditions, and hence an appraisal of the effect of ozone addition on this type of erratic operation is not possible.

Data from the inefficient injector with a 4-inch-long chamber are shown in figure 4(b) and are all from one series of runs. At low O/F the c^* values are about the same as in the 8-inch chamber, but as O/F increased toward stoichiometric, the efficiency decreased more rapidly than it did in the 8-inch chamber. There is no decisive difference between the results with 2 percent ozone and neat oxygen.

In general the data with the inefficient injector show that when the O/F is greater than 3 the efficiency falls off with increasing O/F in a nearly linear fashion, and this decline in efficiency is greater with smaller chamber length. Similar results are shown in reference 2 for longer chambers. The longer chambers, however, gave ceilings of efficiency which were higher. These trends are reasonable. Efficiency would be expected to increase with decreasing O/F because of the greater atomizing action on the liquid-oxygen jet by the increased hydrogen gas flow. Efficiency should also increase with chamber length because of increased stay-time.

High-Efficiency Injector

The nine-element concentric-tube injector in earlier studies (ref. 2) has given steady combustion which does not deteriorate any of the chamber components. It was used with an 8-inch-long chamber in this work. The primary purpose of this configuration was to measure the effect of chemical-enthalpy increase as the concentration of ozone in oxygen was increased toward 30 percent by weight. The project terminated before higher concentrations could be studied, but data were obtained for 9 percent

ozone. These results are shown in table III and figure 5. The oxidant flowmeter apparently changed its calibration during the flow of the liquid ozone-oxygen mixture in the first set of runs in series D (table III); therefore, the flowmeter was recalibrated using a correlation between previously obtained flow rates and tank pressure. The flow rates of neat oxygen in this series may therefore be less accurate than previous ones.

Some of the characteristic velocities measured with both 9-percent ozone and neat oxygen at lower oxidant-fuel ratios were higher than theoretical. The theoretical calculations do not account for the compressive energy in the hydrogen gas above 300 pounds per square inch absolute. At O/F values below 2 this energy can raise measured characteristic velocity a detectable amount. The data show little effect ascribable to 9 percent ozone in the oxygen.

CONCLUSIONS

Small amounts of ozone have little effect on the over-all reaction efficiency of liquid oxygen with gaseous hydrogen in a small rocket.

Explosions were encountered when equipment or procedure permitted ozone to concentrate locally. These experiments indicate that even small amounts of ozone in oxygen can cause operational problems.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, March 11, 1959

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TABLE I. - PERFORMANCE OF LIQUID OZONE-OXYGEN MIXTURES WITH HYDROGEN USING AN INEFFICIENT INJECTOR (SINGLE-ELEMENT CONCENTRIC-TUBE)

(a) 8-Inch chamber.

Oxidant-fuel weight ratio, O/F	Chamber pressure, lb/sq in. abs	Characteristic velocity, c^*		Series
		Experimental	Percent of theoretical	
Neat liquid oxygen.				
2.72	224	6020	73.0	A
2.79	284	6000	72.8	
3.40	314	7750	95.4	
3.24	334	6590	80.7	
5.68	304	5700	76.6	
4.56	314	6400	82.1	
5.27	324	5970	78.9	
5.05	314	6080	79.6	
2.11	304	7320	88.7	B
2.60	309	7350	89.1	
4.30	304	6850	87.0	
4.85	324	6160	80.0	
6.06	321	5500	75.0	
5.70	324	5630	75.7	
5.96	344	5440	73.9	
1.49	259	7270	89.8	
.84	244	6980	92.0	
1.25	314	7350	92.6	
1.13	289	6860	87.4	
4.00	344	6720	84.4	
2.2±0.2 Percent by weight ozone in liquid oxygen				
1.35	257	7100	88.6	B
1.94	279	7200	87.4	
2.42	332	7400	89.6	
3.48	354	7230	89.2	
3.57	330	7120	88.1	
4.30	317	6500	82.6	
5.45	314	5720	76.1	
5.53	323	5800	77.5	
5.37	341	5840	77.5	
5.97	382	5650	76.8	

(b) 4-Inch chamber.

Neat liquid oxygen				
1.67	279	7450	91.2	C
1.51	274	7040	86.9	
1.23	279	7060	89.1	
1.83	312	7120	86.7	
2.17	297	7180	87.0	
3.09	292	6740	82.3	
4.74	285	5470	70.7	
5.43	282	5000	66.5	
6.10	274	4410	60.2	
5.99	272	4550	61.9	
6.32	289	4410	60.8	
6.09	294	4460	60.9	
5.48	284	4900	65.3	
6.10	277	4450	60.8	
2±0.2 Percent by weight ozone in liquid oxygen				
1.64	249	7090	86.9	C
1.41	284	7450	92.6	
1.68	294	7180	87.8	
3.29	289	6670	81.8	
4.69	292	5530	71.4	
5.17	274	5020	66.1	
5.90	279	4710	61.3	
6.09	284	4620	63.1	
6.53	304	4450	61.8	
3.39	291	6950	85.5	
2.08	287	7250	87.9	
1.69	312	7400	90.5	

TABLE II. - THEORETICAL CHARACTERISTIC VELOCITIES OF LIQUID OXYGEN AND GASEOUS HYDROGEN

[Temperature, 500° R; chamber pressure, 21.4 atm; gas composition frozen during expansion.]

Oxidant-fuel weight ratio, O/F	Equivalence ratio	Fuel in mixture, percent by weight	Characteristic velocity, c^*
0.794	0.1000	55.75	7532
1.587	.2000	38.65	8131
2.381	.3000	29.57	8265
3.174	.4000	23.95	8180
3.968	.5000	20.13	7976
4.761	.6000	17.36	7732
5.556	.7000	15.25	7485
6.349	.8000	13.6[illegible]	7250
7.143	.9000	12.23	7030
7.936	1.0000	11.1[illegible]	6825