

A Brief Study on Toxic Combustion Products of the Polymers Used in High-Pressure Oxygen Systems

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SUMMARY

One likely cause of polymer ignition in a high-pressure oxygen system is the adiabatic-compression heating of polymers caused by pneumatic impact. Oxidative pyrolysis or combustion of polymers in a high-pressure oxygen system could generate toxic gases. This paper investigates the feasibility of using the NASA pneumatic-impact system to conduct adiabatic-compression combustion tests and determines the toxic combustion products produced from the burning of five selected polymers.

Five polymers commonly used in high-pressure oxygen systems, Zytel[®] 42 (Nylon 6/6), Buna N (nitrile rubber), Viton[®] A (copolymer of vinylidene fluoride and hexafluoropropylene), Neoflon[®] (polychlorotrifluoroethylene), and Teflon[®] (polytetrafluoroethylene), were tested in the NASA pneumatic-impact test system at 17.2-MPa oxygen pressure. The polymers were ignited and burned; combustion products were collected in a stainless-steel sample bottle and analyzed using various methods.

The results show that the NASA pneumatic-impact system is an appropriate test system to conduct adiabatic-compression combustion tests and to collect combustion products for further chemical analysis. The composition of the combustion product gas generated from burning the five selected polymers are presented and discussed.

KEY WORDS: polymer combustion; toxic combustion products; adiabatic compression; pneumatic impact; high-pressure oxygen systems

1. INTRODUCTION

Organic polymers have been widely used in oxygen systems; their applications include O-rings, seals, diaphragms, manifold gaskets, flexible hoses, valve seats, and endotracheal tubes. Some organic polymers are frequently used in high-pressure oxygen environments.

It is well-known that polymers are more flammable in oxygen-enriched environments than in air, especially in high-pressure oxygen environments. Ignition of organic polymers in a high-pressure oxygen system may be due to mechanical impact, rapid compression, friction, high-speed particle impact, electrical arcs, or high-operating temperatures¹. When the temperature exceeds the ignition temperature of a polymer, a fire may occur.

Toxic gases could be generated by the oxidative pyrolysis or combustion of polymers in a high-pressure oxygen system. If toxic combustion gases are generated in the oxygen equipment used in medicine, direct inhalation of toxic gases could seriously injure the patient. The ISO document, *Anesthetic and Respiratory Equipment – Compatibility with Oxygen (ISO/DIS 15001.3)*,² recommends methods for the combustion testing and quantitative analysis of combustion products from non-metallic materials. In addition, the ASTM G04 Plastics Toxicity Task Force has begun researching: (1) the development and validation of a reliable methodology for the presence and quantity of combustion products produced by plastics and elastomers used in oxygen systems; and (2) the extension of the reliable methodology to the measurement of combustion products produced by medical cylinder valves, regulators, and flexible tubing.

Because the most probable mechanism for the ignition of organic polymers in a high-pressure oxygen system is adiabatic compression, ISO/DIS 15001.3² recommends an adiabatic-compression test for toxic combustion products. To date, only limited experimental data have been published for the toxic combustion products produced via an adiabatic-compression mechanism. NASA Johnson Space Center (JSC) White Sands Test Facility (WSTF) conducted some tests in an oxygen bomb calorimeter with a test pressure of 3.1 MPa and a thin hot-wire ignition source.³ The main purposes of the present study were to investigate the feasibility of using the NASA pneumatic impact system to conduct adiabatic-compression combustion tests and to determine the toxic combustion products produced from the burning of five selected polymers in a high-pressure oxygen system.

2. MATERIALS AND TEST METHODS

2.1 Materials

Materials tested in the adiabatic-compression combustion tests were Zytel[®] 42 (Nylon 6/6), Buna N (nitrile rubber), Viton[®] A (copolymer of vinylidene fluoride and hexafluoropropylene), Neoflon[®] (polychlorotrifluoroethylene), and Teflon[®] (polytetrafluoroethylene). The aforementioned materials are commonly used polymers for softgoods in regulators and valves. The sample used in this study was a round disk with a 4.8-mm diameter and 1.5-mm thickness. The sample weight ranged from 0.029 to 0.060 g, which is roughly consistent with the typical weight range for most oxygen regulator seats or cylinder valve seats. The use of trade names in this paper does not constitute an endorsement of these materials but is used only to simplify their description and identification.

2.2 Test Methods

2.2.1 Adiabatic-compression (Pneumatic-impact) Combustion Test

The adiabatic-compression (pneumatic-impact) combustion tests were conducted according to NASA-STD-6001 Test 14.⁴ This test method is similar to that of ASTM G74, *Standard Test Method for Ignition Sensitivity of Materials to Gaseous Fluid Impact*.⁵ Figure 1 shows a partial schematic diagram of the pneumatic-impact system and Figure 2 presents the detailed diagram of the test assembly. A sample was placed in the test chamber, and an upstream accumulator (4.2 L) was pressurized with the desired pressure of oxygen. The test chamber was then purged with oxygen, and the sample was impacted with high-pressure oxygen by opening a high-speed valve between the accumulator and test chamber. The test pressure was 17.2 MPa for all the materials tested. The test chamber was pressurized from ambient pressure to 17.2 MPa in 50 ms. In this study, the sample was impacted only one time by 12-mL oxygen at 17.2 MPa instead of a sequence of five times as specified by NASA and ASTM test standards. A reaction was evidenced by a sudden rise of test chamber temperature. If a reaction occurred, the combustion product gas was collected using a 300-mL stainless steel sample bottle and analyzed using various methods. Prior to testing, a blank pneumatic-impact test without the sample was performed and the background gas was collected and analyzed to ensure the sampling line and sample bottle were free of contaminants. The stainless steel sample bottle was a newly added component and was not present in the original NASA pneumatic-impact system. The impact pressure of this pneumatic-impact system can be up to 68.9 MPa and the oxygen concentration of the impact gas can also be varied.

2.2.2 Analytical Methods for Determining the Composition of Combustion Product Gas

Table I lists target toxic compounds which might be present in the combustion product gas from the burning of the selected polymers. The LC₅₀ and TLV of those compounds are also included in Table I. Carbon monoxide (CO) was analyzed using a gas chromatography (GC) with a 10-meter column packed with 80/60 mesh molecular sieve; the detectors were a methanizer and a flame ionization detector. Carbon dioxide (CO₂), ammonia (NH₃), nitrous oxide (N₂O), and carbon tetrafluoride (CF₄) were analyzed using a GC with a 30-meter column packed with a 5- μ m 100 percent polymethyldisiloxane phase; the detector was a HP 5965 Fourier transform infrared detector. Hydrogen cyanide (HCN), carbonyl fluoride (COF₂), carbonyl chloride (COCl₂), carbonyl chloride fluoride (COCIF), chlorine oxide (Cl₂O), chlorine dioxide (ClO₂), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), sulfuryl fluoride (SO₂F₂), and thionyl fluoride (SOF₂) were analyzed using a GC with a 30-m column packed with a 5- μ m 100 percent polymethyldisiloxane phase; the detector was a HP 5970 mass selective detector. Fluorine (F₂) was analyzed by a Dräger[®] tube. Chlorine (Cl₂) was analyzed using the NIOSH 6011 method.⁶ Hydrogen fluoride (HF) and hydrogen chloride (HCl) were analyzed using the NIOSH 7903 method.⁷ Nitric oxide (NO) and nitrogen dioxide (NO₂) were analyzed using the NIOSH 6014 method.⁸ HF, HCl, Cl₂, NO, and NO₂ were measured as milligrams (mg) and converted to parts per million (ppm). For all GC analytical methods, triplicate gaseous samples were analyzed; and for Dräger tube and NIOSH methods, duplicate gaseous samples were analyzed. The average standard deviation for the analyses was within 15 percent.

3. RESULTS AND DISCUSSION

3.1 Investigating the Feasibility of Using NASA Pneumatic Impact System to Conduct Adiabatic-compression Combustion Tests

In this study, the NASA pneumatic-impact test system uses the accumulator (4.2 L) to simulate a medical cylinder, the test chamber (12 mL) to simulate a compartment of the softgoods in a regulator, and the sample bottle (300 mL) to simulate a human lung (Figure 1). For adults, the tidal volume of the human lung is about 0.5 L,⁹ but the lungs can hold about ten times this volume if they are filled to full capacity. Over 1000 pneumatic-impact tests have been performed in this study at various levels of impact pressures on different polymers. The results show that most polymers can be ignited successfully in the NASA pneumatic-impact test system under certain conditions. With a proper system design (Figure 1) and safe operation procedures, the high-pressure combustion product gas can be safely transferred to the sample bottle for chemical analysis. It should be noted that not every polymer tested can be successfully ignited at each pneumatic impact. Zytel 42 exhibited the highest ignition probability (100 percent) at 17.2 MPa impact pressure. However, the ignition probability was low for Neoflon (30 percent) and Teflon (4 percent). Here, the ignition probability was defined as the number of ignitions per one hundred tests. To obtain the combustion product gas of some polymers, multiple pneumatic-impact tests may be necessary. If the sample did not ignite at the first impact, it is suggested to replace the sample and impact it again. The previous study¹⁰ showed that pneumatic-impact ignitions of some polymers, (e.g. Teflon and Neoflon) are predominately sample-dependent. Replacing the sample and impacting the replaced sample may provide a better chance of ignition than repeatedly impacting the same sample. The sample size in the NASA pneumatic-impact test system is restricted by the size of the sample holder. The sample holder holds a standard size sample (4.8-mm diameter and 1.5-mm thickness). A larger sample holder and test chamber will be needed if one attempts testing larger samples.

3.2 Determining the Composition of Combustion Product Gas

The composition of combustion product gas is strongly dependent on the polymer composition and burning conditions. The five polymers evaluated include two nitrogen-containing polymers (Zytel 42 and Buna N) and three halogenated polymers (Viton A, Neoflon, and Teflon). Zytel 42 contains carbon, hydrogen, oxygen, and nitrogen. Buna N contains carbon, hydrogen, nitrogen, and sulfur. Viton A contains carbon, hydrogen, fluorine, and sulfur. Neoflon contains carbon, fluorine, and chlorine. And lastly, Teflon contains carbon and fluorine. The detailed composition of Zytel 42, Buna N, and Viton A are not known because each of them contains unknown quantities of additives and fillers.

3.2.1 Burning of Nitrogen-containing Polymers: Zytel 42 and Buna N

Table II shows the combustion product gas analysis of Zytel 42, and Table III shows the analysis of Buna N. The results indicate that the combustion of nitrogen-containing polymers in a high-pressure oxygen system was very complete. Almost all the carbon atoms were converted to CO₂; only 1 or 2 ppm of CO was found in the combustion product gas. The results also show that most nitrogen atoms in polymers were converted to gaseous nitrogen. HCN, NO, N₂O, and NH₃ were not detected. Only 15 ppm NO₂ from Zytel 42 and 24 ppm NO₂ from Buna N were detected in their combustion product gas. The LC₅₀ of NO₂ was 115 ppm and the TLV was 5 ppm (Table I). The burning of Buna N also produced a trace amount of SO₂ (6 ppm). The source of sulfur was

presumably from the vulcanizing agent in the elastomer. The LC_{50} of SO_2 was 2520 ppm and the TLV was 5 ppm (Table I).

3.2.2 Burning of Halogenated Polymers: Viton A, Neoflon, and Teflon

Previous studies reported the burning of fluorinated polymers produce CO, CO_2 , CF_4 , and COF_2 .^{3,18} If the fluorinated polymers contain hydrogen (e.g. Viton A) or there is some moisture in the sample or around the burning environment, significant amounts of HF can be generated.¹⁹ CF_4 is generally not considered a toxicant; its LC_{50} has not yet been established. However, inhalation of high concentrations of this vapor may cause heart irregularities and unconsciousness.²⁰ COF_2 is a normal-toxic compound;¹⁸ its LC_{50} (360 ppm) is about one tenth that of CO (3760 ppm).

The results shown in Table IV indicate that the burning of Viton A produced significant amounts of CO_2 , CF_4 , and HF; moderate amounts of COF_2 and SO_2F_2 ; and trace amounts of CO, SOF_2 (6 ppm), and F_2 (4 ppm). The LC_{50} of SOF_2 (260 ppm) was comparable to that of the COF_2 .

The burning of Neoflon produced a complex gas mixture (Table V). The gas mixture contained significant amounts of CO_2 , COF_2 , CF_4 , and HF; moderate amounts of F_2 and HCl; and trace amounts of CO, Cl_2 , ClO_2 , $COClF$, and $COCl_2$ (1 ppm). The generation of HCl and HF was due to the presence of moisture in the sample. $COCl_2$, known as phosgene, is a very toxic compound; its LC_{50} is 5 ppm and the toxicity is about 28 times that of HCN.

Table VI shows the combustion product gas analysis of Teflon. Unlike Neoflon, the product gas was simple. It contained significant amounts of CO_2 , COF_2 , CF_4 , and HF with trace amounts of CO and F_2 .

Table VII compares the major toxic combustion products produced by burning Viton-A, Neoflon, and Teflon in 17.2 MPa oxygen. The concentrations of toxic compounds presented in this table were calculated based on a 0.10 g sample weight. In general, the combustion toxicity of Neoflon was higher than Teflon and that of Teflon was higher than Viton A. Besides the production of HCl and Cl_2 , Neoflon also produced considerably more F_2 than Teflon. It seems $COCl_2$ was not the major concern because its concentration was very low.

3.3 Some Thoughts on Toxicity Assessment of Combustion Product Gas

Combustion product gas produced by burning polymers in a high-pressure oxygen system contains a high percentage of oxygen. In this study, combustion product gases contained more than 94.2 percent oxygen. Since the toxicity (in terms of LC_{50}) of combustion product gas is determined primarily for the "air-based" gas mixtures, the use of the reported LC_{50} to assess the toxicity of the "oxygen-enriched" combustion product gas may not be necessarily appropriate. In the first-aid treatment of fire gas victims, administering 100 percent oxygen by mask is strongly recommended.²¹ The high oxygen concentration may have a "smoothing" effect on the toxicity.

It has been stated in the Materials and Test Methods section that the amount of oxygen reacted with polymers was 12-ml oxygen at 17.2 MPa (equivalent to 0.084 moles oxygen). This amount of gas represents 2.05 L of gas at 101.3 kPa (one atmosphere) pressure. The gas flow rate in a medical cylinder is usually about 2 to 15 L/min, depending on the doctor's prescription. In the worst-case condition (i.e. 2 L/min flow rate), the exposure time for the patient is only about 1 min. Hence, it is suggested to consider the "small dose" and "short exposure time" when one attempts to assess the toxicity of combustion product gas produced from the burning of polymers in a high-pressure medical oxygen cylinder.

4. CONCLUSIONS

This study has demonstrated that the NASA pneumatic-impact system is an appropriate test system to conduct adiabatic-compression combustion tests and to collect the combustion product gases for further chemical analyses.

The burning of Zytel 42 and Buna N in a high-pressure oxygen system was relatively complete. The major combustion product was CO₂. Only a small amount of NO₂ (~20 ppm) was found in the combustion product gas. The burning of Viton A produced a significant amount of HF and a moderate amount of COF₂. The burning of Teflon produced significant amounts of COF₂ and HF. The combustion product gas of Neoflon was complex; it contained significant amounts of COF₂ and HF, and moderate amounts of F₂, HCl, and Cl₂. For the combustion toxicity assessment of the polymers used in high-pressure medical oxygen cylinders the following factors should be considered: the amount of polymer to be consumed, the length of exposure time, and the high oxygen concentration in combustion product gas.

REFERENCES

1. NASA, *Guide for Oxygen Hazards Analyses on Components and Systems*, TM 104823, October 1996.
2. ISO/DIS 15001.3, *Anesthetic and Respiratory Equipment - Compatibility with Oxygen*, International Organization for Standardization, Geneva, Switzerland, March 2001.
3. Hshieh F-Y, D. B. Hirsch, H. D. Beeson, "Toxic Combustion Products Testing of Polymers Used in Oxygen Systems - A Review of Testing at WSTF." In *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: ASTM STP 145*. Steinberg, T.A., Beeson, H.D., Newton, B.E. eds. pp. 27-45. ASTM International, West Conshohocken, PA, 2003.
4. NASA, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*. NASA STD-6001. Office of Safety and Mission Quality, Washington, DC, 1998.
5. ASTM, *Standard Test Method for Ignition Sensitivity of Materials to Gaseous Fluid Impact*. ASTM G 74. American Society for Testing and Materials: Philadelphia, PA, 2001.
6. NIOSH 6011: *Chlorine and Bromine, NIOSH Manual of Analytical Method*. NMAM, 4th edition, 1994.
7. NIOSH 7903: *Acids, Inorganic, NIOSH Manual of Analytical Methods*. NMAM, 4th edition, 1994.
8. NIOSH 6014: *Nitric Oxide and Nitrogen Dioxide, NIOSH Manual of Analytical Methods* (NMAM), 4th edition, 1994.
9. http://en.wikipedia.org/wiki/Human_lung
10. Hshieh, F-Y, J. H. Williams. "Pneumatic Impact Ignition of Selected Polymers in High-Pressure Oxygen Environments." *Fire and Materials*, in press.
11. ISO 10298 *Determination of Toxicity of a Gas or Gas Mixture*, International Organization for Standardization, Geneva, Switzerland, 1995.
12. www.mal.uic.edu/MSDS/N2O.pdf
13. Proctor, N. H., J. P. Hughes, M. L. Fischman. *Chemical Hazards of The Workplace*, 2nd ed, J.B. Lippincott Company, Philadelphia, PA 1998, p.454.
14. http://physchem.ox.ac.uk/MSDS/TH/thionyl_fluoride.html
15. www.wapa.gov/rm/psmmCHAP-04.pdf
16. www.swantek.com/html/msds/405.htm
17. Proctor, p.130.

18. Purser, D.A. "Recent Developments in Understanding the Toxicity of PTFE Thermal Decomposition Products." *Fire and Materials*, 1992; 16:67-75.
19. www.borealisgroup.com/public/pdf/customer_centre/0202toxicity_FRCC.pdf
20. www.fluorideaction.org/pesticides/carbon.tetrafluoride.abs.htm
21. Braker, W., A. L. Mossman. *Effects of Exposure to Toxic Gases - First Aid and Medical Treatment*, Matheson Gas Products, East Rutherford, New Jersey, 1970.

Table I. LC₅₀ and TLV of Target Toxic Compounds

Target Compound	Chemical Formula	LC ₅₀ (ppm)	TLV (ppm)
Carbon monoxide	CO	3760	50
Carbon dioxide	CO ₂	88000	5000
Hydrogen cyanide	HCN	140	10
Nitric oxide	NO	115	2.5
Nitrogen dioxide	NO ₂	115	5
Nitrous oxide	N ₂ O	593 ¹²	50 ¹²
Ammonia	NH ₃	7338	25
Hydrogen sulfide	H ₂ S	712	10
Sulfur dioxide	SO ₂	2520	5
Sulfuryl fluoride	SO ₂ F ₂	3020 ¹³	5 ¹³
Thionyl fluoride	SOF ₂	260 ¹⁴	1 ¹⁵
Carbonyl fluoride	COF ₂	360	2 ¹⁶
Carbon tetrafluoride	CF ₄	N/A ^a	1000 ¹⁵
Fluorine	F ₂	185	1
Hydrogen fluoride	HF	996	3
Carbonyl chloride	COCl ₂	5	0.05
Chlorine dioxide	ClO ₂	N/A	0.1 ¹⁷
Chlorine oxide	Cl ₂ O	N/A	N/A
Chlorine	Cl ₂	293	1
Hydrogen chloride	HCl	3120	5
Carbonyl chloride-fluoride	COClF	N/A	N/A

^a N/A = not available

Note: Except the data marked by the reference number, all other data were obtained from ISO 10298.¹¹ The reported LC₅₀ of SOF₂ was, essentially, the lowest published lethal concentration (LCLO).

Table II. Combustion Product Gas Analysis of Zytel 42 (sample weight: 0.033 g)

Combustion Product	Quantity (ppm)
CO	2
CO ₂	2733
HCN	ND ^a
NO	ND
NO ₂	15
N ₂ O	ND
NH ₃	ND

^a ND = Non Detected

Note: Adiabatic compression tests were performed at 17.2 MPa (2500 psia) oxygen.

Table III. Combustion Product Gas Analysis of Buna N (sample weight: 0.031 g)

Combustion Product	Quantity (ppm)
CO	1
CO ₂	4400
HCN	ND ^a
NO	ND
NO ₂	24
N ₂ O	ND
NH ₃	ND
H ₂ S	ND
SO ₂	6

^a ND = Non Detected

Note: Adiabatic compression tests were performed at 17.2 MPa (2500 psia) oxygen.

Table IV. Combustion product gas analysis of Viton A (sample weight: 0.051 g)

Combustion Product	Quantity (ppm)
CO	8
CO ₂	21000
COF ₂	105
CF ₄	2650
HF	1090
F ₂	4
H ₂ S	ND ^a
SO ₂	1
SO ₂ F ₂	51
SOF ₂	6

^a ND = Non DetectedNote: Adiabatic compression tests were performed at 17.2 MPa (2500 psia) oxygen; SO₂F₂ and SOF₂ were quantified as COF₂.**Table V. Combustion Product Gas Analysis of Neoflon (sample weight: 0.059 g)**

Combustion Product	Quantity (ppm)
CO	10
CO ₂	6618
COF ₂	2967
CF ₄	45000
COCIF	3
Cl ₂	16
F ₂	108
HCl	209
HF	2562
COCl ₂	1
ClO ₂	18
Cl ₂ O	ND ^a

^a ND = Non DetectedNote: Adiabatic compression tests were performed at 17.2 MPa (2500 psia) oxygen; COCIF was quantified as COF₂, and ClO₂ was quantified as SO₂.

Table VI. Combustion Product Gas Analysis of Teflon (sample weight: 0.060 g)

Combustion Product	Quantity (ppm)
CO	4
CO ₂	7920
COF ₂	3000
CF ₄	34667
HF	2857
F ₂	4

Note: Adiabatic compression tests were performed at 17.2 MPa (2500 psia) oxygen.

Table VII. Comparison of the Major Toxic Combustion Products Produced by Viton A, Neoflon, and Teflon (concentrations were calculated based on 0.10 g sample weight)

Material	Concentration of Toxic Compounds (ppm)						
	COF ₂	HF	F ₂	SOF ₂	COCl ₂	HCl	Cl ₂
Viton A	206	2137	8	12	ND ^a	ND	ND
Neoflon	5029	4342	183	ND	2	354	27
Teflon	5000	4762	7	ND	ND	ND	ND

^a ND = Non Detected

Note: Adiabatic compression tests were performed at 17.2 MPa (2500 psia) oxygen.

LC₅₀ are as follows: COF₂ (360 ppm), HF (996 ppm), F₂ (185 ppm), SOF₂ (260 ppm), COCl₂ (5 ppm), HCl (3120 ppm), Cl₂ (293 ppm).

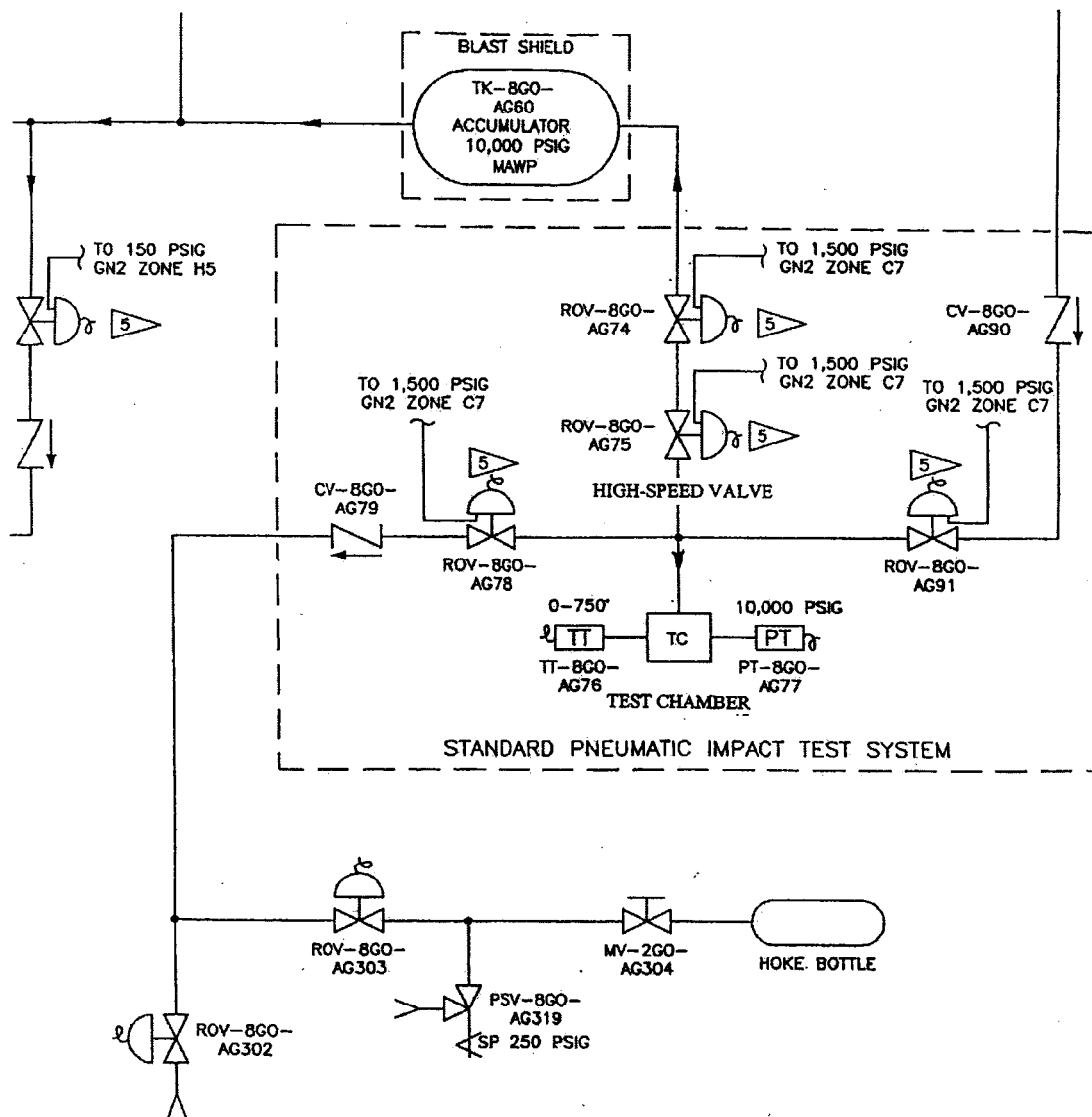


Figure 1. Schematic Diagram (partial) of Adiabatic-Compression (pneumatic-impact) Combustion Test System.

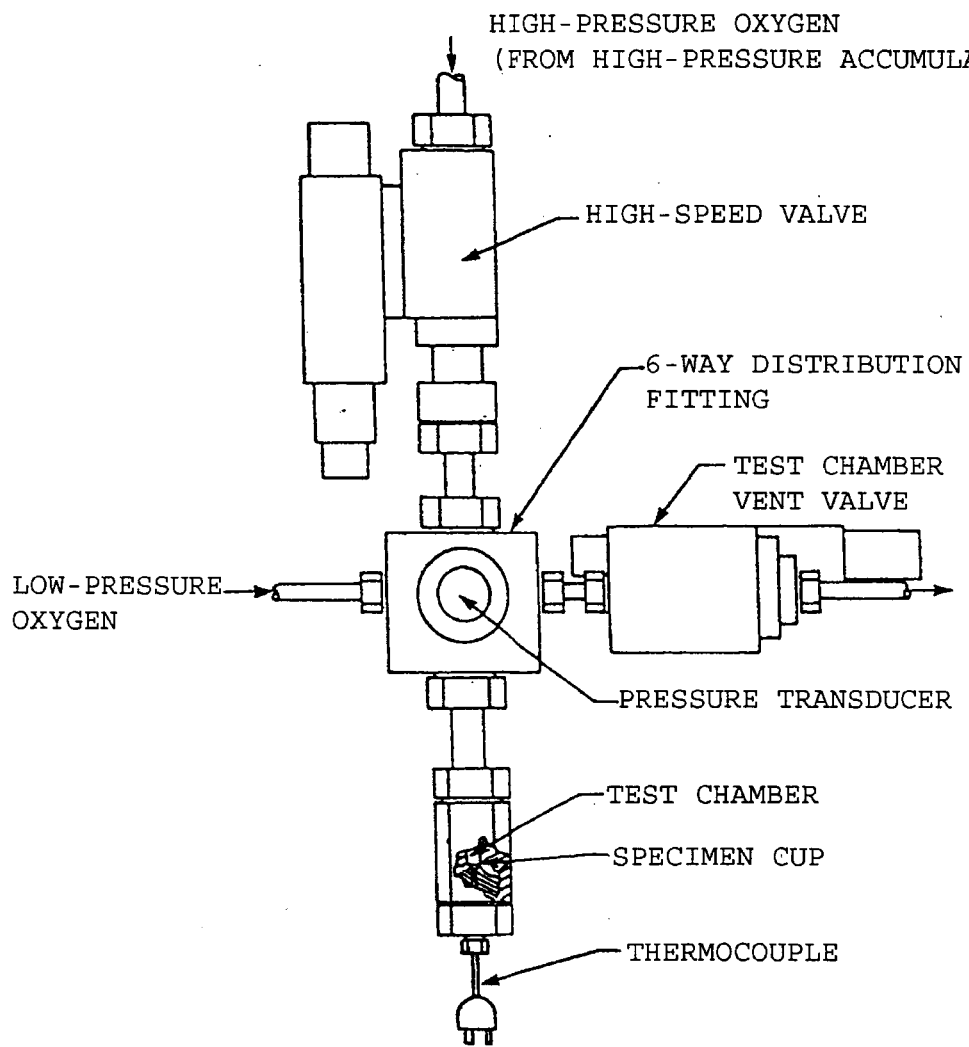


Figure 2. Detailed Diagram of the Adiabatic-Compression (pneumatic-impact) Test Assembly.