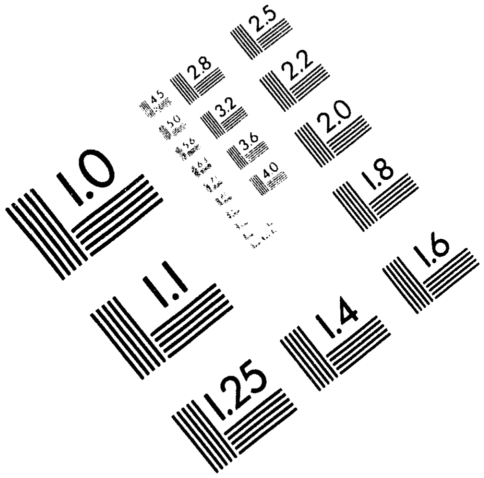

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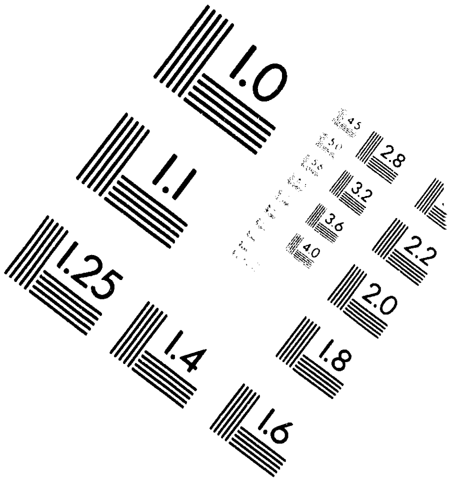

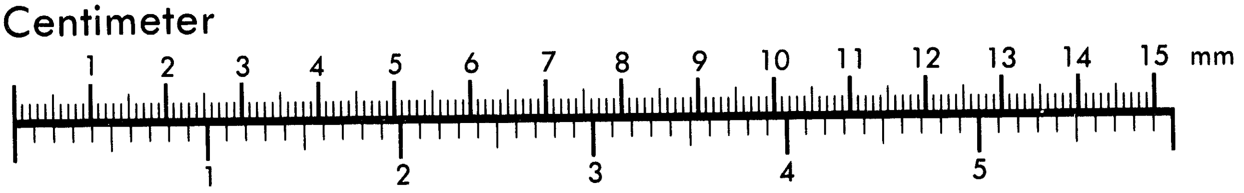

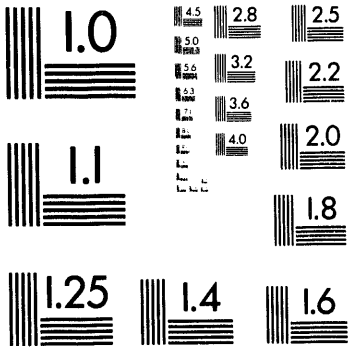

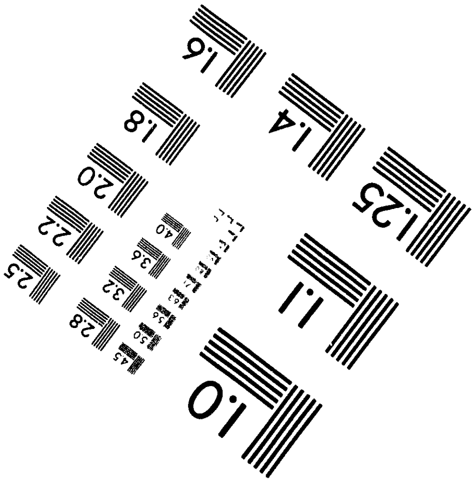

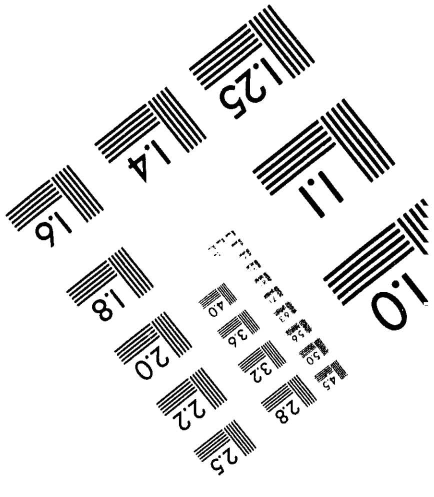

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LLNL Demonstration of Liquid Gun Propellant Destruction in a 0.1 Gallon Per Minute Scale Reactor

R.J. Cena, C.B. Thorsness, T. T. Coburn, and B.E. Watkins

Abstract

The Lawrence Livermore National Laboratory (LLNL) has built and operated a pilot plant for processing oil shale using recirculating hot solids. This pilot plant, was adapted in 1993 to demonstrate the feasibility of decomposing a liquid gun propellant (LGP), LP XM46, a mixture of 76% HAN (NH_3OHNO_3) and 24% TEAN ($(HOCH_2CH_2)_3\ NHNO_3$) diluted 1:3 in water. In the Livermore process, the LPG is thermally treated in a moving packed bed of ceramic spheres, where TEAN and HAN decompose, forming a suite of gases including: methane, carbon monoxide, oxygen, nitrogen oxides, ammonia and molecular nitrogen. The ceramic spheres are circulated and heated, providing the energy required for thermal decomposition. In addition to being an energy source, the spheres provide a large surface area for evaporation and decomposition to occur, avoiding problems of concentrating the LGP while undergoing processing.

We performed an extended one day (8 hour) test of the solids recirculation system, with continuous injection of approximately 0.1 gal/min of LGP, diluted 1:3 in water, for a period of eight hours. The apparatus operated smoothly over the course of the eight hour run during which 144 kg of solution was processed, containing 36 kg of LGP. Continuous on-line gas analysis was invaluable in tracking the progress of the experiment and quantifying the decomposition products. The reactor was operated in two modes, a "Pyrolysis" mode, where decomposition products were removed from the moving bed reactor exit, passing through condensers to a flare, and in a "Combustion" mode, where the products were oxidized in an air lift pipe prior to exiting the system.

In the "Pyrolysis mode, driver gases were recycled producing a small, concentrated stream of decomposition products. In this mode, 18% of the feed nitrogen was emitted as nitrogen bearing oxides: 11% as NO_2, 6% as N_2O and 1% as NO. (NO_2 trapped in the condensed liquid as NO_3^- is included). In the "Combustion mode, the driver gases were not recycled, resulting in 40 times higher gas flow rates and correspondingly lower concentrations of nitrogen bearing gases. In this mode, three times more of the feed nitrogen was emitted as nitrogen oxides: 29% as NO_2, 6% as N_2O and 19% as NO.

The bulk of the injected carbon was produced as CO_2 during experiment. Over 60% of the injected carbon is accounted for by CO_2 during the "Pyrolysis' portion of the test and 90% is accounted for during the "Combustion" portion of the test. The remaining portion of the injected carbon was produced as CO.

Introduction

The Lawrence Livermore National Laboratory (LLNL) as part of the Energetic Materials Center, is developing methods for the safe, environmentally sound, destruction of explosives and propellants as a part of the Laboratory's ancillary demilitarization mission. As a result of the ending of the Cold War and the shift in emphasis to a smaller stockpile many weapons, both conventional and nuclear, are scheduled for dismantlement and are being rapidly retired. Energetic materials, both explosives and propellants, from these weapons must either be recycled or safely destroyed. Traditionally, open burn/open detonation has been the method of choice for the destruction of energetic materials. These methods are no longer considered to be environmentally acceptable and we and others are looking for alternative ways to dispose of energetic materials.

One such material for which an acceptable and economic destruction method is sought a liquid gun propellant (LGP), LP XM46, a mixture of 76% HAN (NH_3OHNO_3) and 24% TEAN ($(HOCH_2CH_2)_3$ $NHNO_3$. This material is being considered for use in a future automated battlefield and new regulations require cradle to grave accountability for all new energetic materials. Studies in LLNL's molten salt apparatus successfully demonstrated decomposition of this material. To further evaluate that process and provide a head-to-head comparison, LGP was also decomposed using the LLNL moving bed reactor described below.

Lawrence Livermore National Laboratory has built and operated a pilot plant for processing oil shale using recirculating hot solids. This pilot plant, shown in Figure 1, was adapted in the fall and winter of 1993 to demonstrate the feasibility of decomposing LGP. In the modified LLNL pilot plant, LGP diluted 1:3 in water was thermally treated in a moving packed bed of ceramic spheres, where TEAN and HAN decompose, forming a suite of gases including: methane, carbon monoxide, oxygen, nitrogen oxides, ammonia and molecular nitrogen. The ceramic spheres are circulated and heated, providing the energy required for thermal decomposition. In addition to being an energy source, the spheres provide a large surface area for evaporation and decomposition to occur, avoiding problems of concentrating the LGP while undergoing processing.

We performed an extended one day test of the solids recirculation system, with continuous injection of approximately 0.1 gal/min of LGP for a period of eight hours. Continuous on-line gas analysis was invaluable in tracking the progress of the experiment and quantifying the decomposition products. The reactor was operated in two modes, a "Pyrolysis" mode, where decomposition products were removed from the moving bed reactor exit, passing through condensers to a flare, and in a "Combustion" mode, where the gas was oxidized in an air lift pipe prior to exiting the system. The apparatus operated smoothly over the course of the eight hour run during which 144 kg of solution was processed, containing 36 kg of LGP.

Pilot Plant Description

The retort schematic, in Figure 2, shows the configuration of equipment for the LGP destruction test. The moving packed bed reactor contains approximately 90 kg of ceramic spheres with an additional 50 kg in the waste feed pipe and 55 kg in the moving bed heater. The spheres are circulated and maintained at a temperature at or above 550 °C to accomplish the decomposition. The spheres are discharged from the reactor at a rate of approximately 6 kg/min which gives a solids residence time in the reactor of 15 minutes. A gas actuated L-valve meters the spheres from the reactor to the pneumatic lift pipe. The spheres are lifted to the top of the tower and discharged into a gas/solid separator or classifier. The discharge gas passes though a cyclone separator and sintered metal dust filter and is then vented. The spheres, separated from the gas and dust in the classifier are recirculated back to the reactor after passing through a moving packed bed heater. In the reactor, steam and CO_2 are provided as reactants via an injection stinger which dispenses these gases along the centerline. Produced gas and steam pass through a cyclone and then enter a 2 stage condensing system to drop out water, soluble compounds and condensable gases. After condensing, the non-condensable gas is metered then vented.

Heat is picked up by the spheres during circulation. The energy is supplied via electric gas heaters, which preheat gas to 700 - 800 °C prior to contacting the spheres and electric heaters strapped to external vessel walls. The combined power input of 15 kW is enough to evaporate and bring to reaction temperature 0.1 gal/min of liquid feed.

The primary control of the experiment was to maintain the temperature at the exit of the moving bed reactor at or above 550 °C by adjustment of the liquid injection rate. For the test a liquid injection rate of 0.1 gal/min was achieved. Figure 3 shows a schematic of the moving bed reactor, with thermocouple positions noted.

LGP Injection Chronology

The experiment began at 9:00 and liquid feed was first injected beginning at 10:00. Figure 4 shows the progress of injection during the experiment. The "Pyrolysis" mode of the experiment lasted from approximately 10:00 to 11:00, at a feed injection rate of 0.06 gal/min. After 11:00 the injection was shutdown and the equipment was re configured for "Combustion" mode. Startup in "Combustion" mode was just after noon and the 0.06 gal/min rate was resumed. By removing a check valve, following a brief shutdown at 1:30 pm, we were able to increase the liquid injection rate to 0.1 gal/min, which we held till the end of the experiment at 5:00 pm.

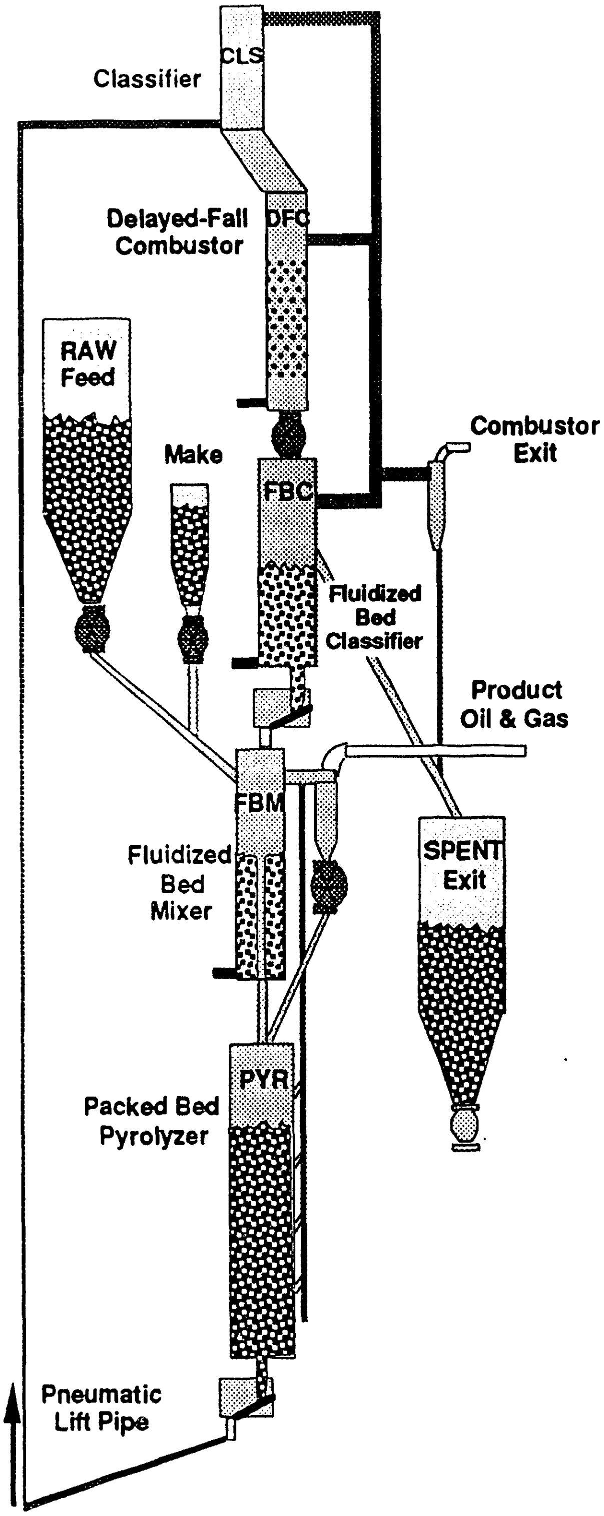

Figure 1. Schematic of LLNL Hot-Recycled-Solid (HRS) Oil Shale Retorting Pilot Plant

The HRS Oil Shale Pilot Plant

The Hot-Recycled-Solid (HRS) process is an innovative concept for obtaining oil efficiently from crushed oil shale in an above-ground plant with no moving parts in hot, corrosive areas. Processing begins as raw feed and recycled shale are mixed in a fluidized bed, at a ratio of approximately 1:3. This compact unit rapidly mixes the two streams with a 30 second average solids residence time. The combined stream, leaving the mixer in thermal equilibrium at retorting temperature (approx. 500°C), next spends 2-3 minutes in a gravity flow pyrolyzer, where complete pyrolysis takes place. This moving packed bed has the advantage of uniform solid residence time and the ability to hold and process fines, which would be rejected from fluidized bed pyrolyzers. The pyrolyzer also serves as a surge tank with excess capacity to accommodate temporary process upsets. The condensable oil and gas, containing water and dust, pass through staged coolers for product recovery. After cooling, the gas is either discharged or recycled back to fluidize the mixer. The solid leaving the pyrolyzer enters the pneumatic lift-pipe, where residual carbon on the spent shale is combusted during transport to the top of the tower. The lift discharges into a delayed-fall combustor, which provides an additional 5 s residence time for shale combustion in a compact 2.5 m unit. Below the delayed-fall combustor, the gas and solid is separated with the solid entering a fluid-bed classifier. This unit classifies the shale, discharges the smaller material into the spent shale hopper while recycling the larger shale back to the fluidized bed mixer. The unit also provides a pressure block which separates the combustion and pyrolysis atmospheres within the process.

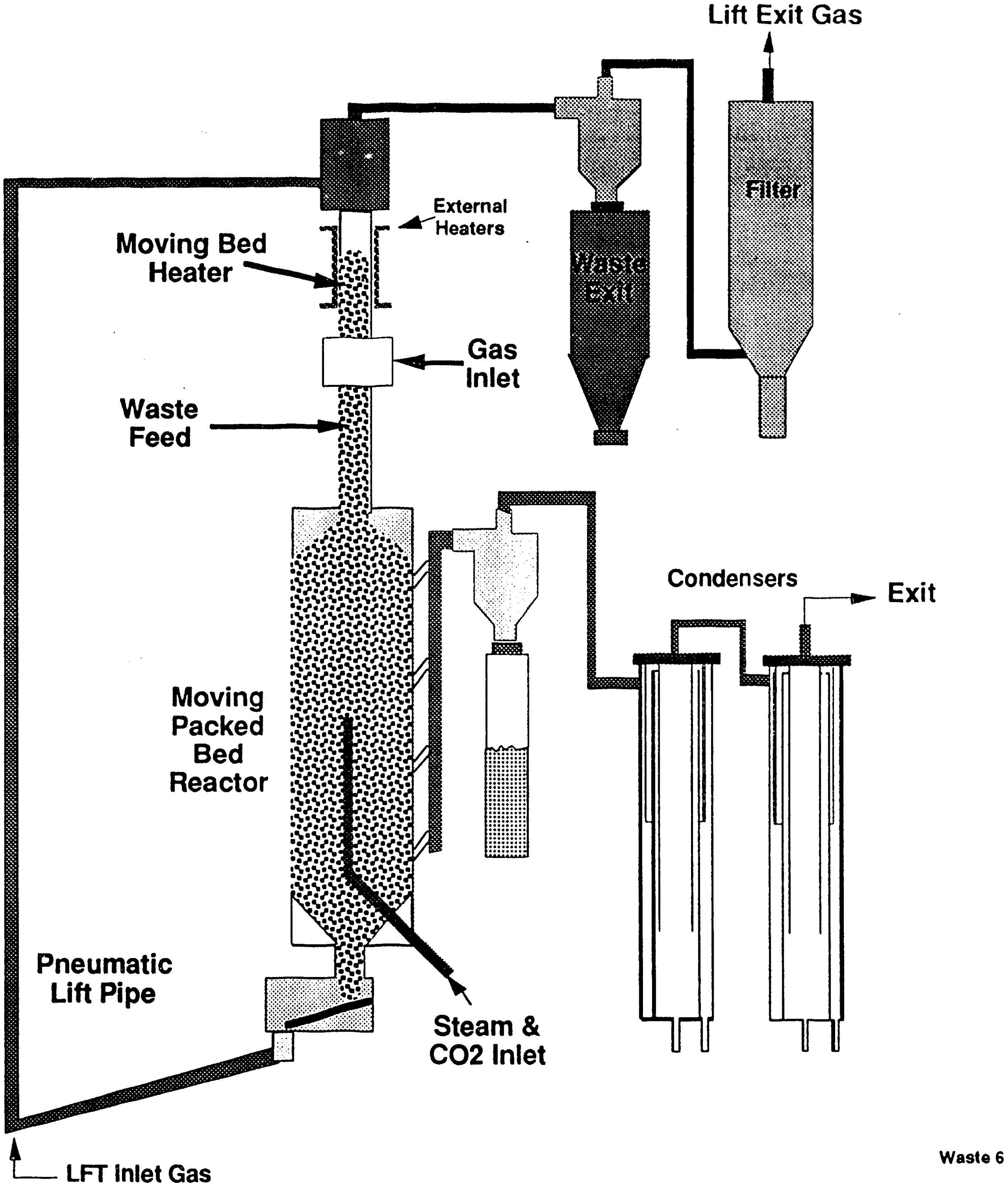

Figure 2. Schematic of Hot-Recycled-Solid Pilot Plant for Demonstration of LGP Destruction

Reactor Temperatures

The temperature exiting the moving bed reactor over the course of the runs is shown in Figure 5. As shown, the thermal capacity exceeded the liquid injection rate during the first part of the experiment, with the reactor temperatures above 600 °C. After the check valve was removed, the liquid injection was increased to 0.1 gal/min which cooled the reactor down to the 550 °C operating temperature maintained for the remainder of the experiment.

Gas Composition

The composition of gas species produced during the decomposition test was monitored on-line throughout the run. The on-line instruments included a quadrupole mass spectrometer (MS), a fourier transform infrared spectrometer (FTIR), several individual IR meters for CO, CO_2 and NOx and an O_2 analyzer. On-line analysis of gas phase components included: NO, NO_2, N_2O, NH_3, O_2, CO, CO_2 and H_2O. N_2 levels were dominated by the air and N_2 used as working fluids for pneumatic lifting, pressure balance and L-valve operation. Therefore, N_2 produced from the decomposition was not detectable. Two gas exit streams were monitored. During "Pyrolysis" mode, the retort exit gas stream was monitored and during "Combustion mode, the lift exit gas stream was monitored.

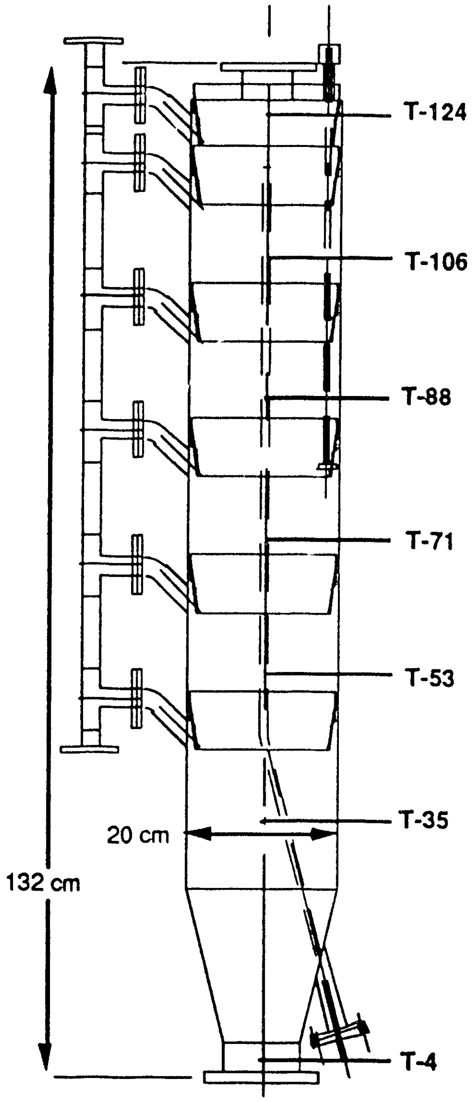

Figure 3. Schematic of Moving Packed Bed Reactor Showing Thermocouple Locations

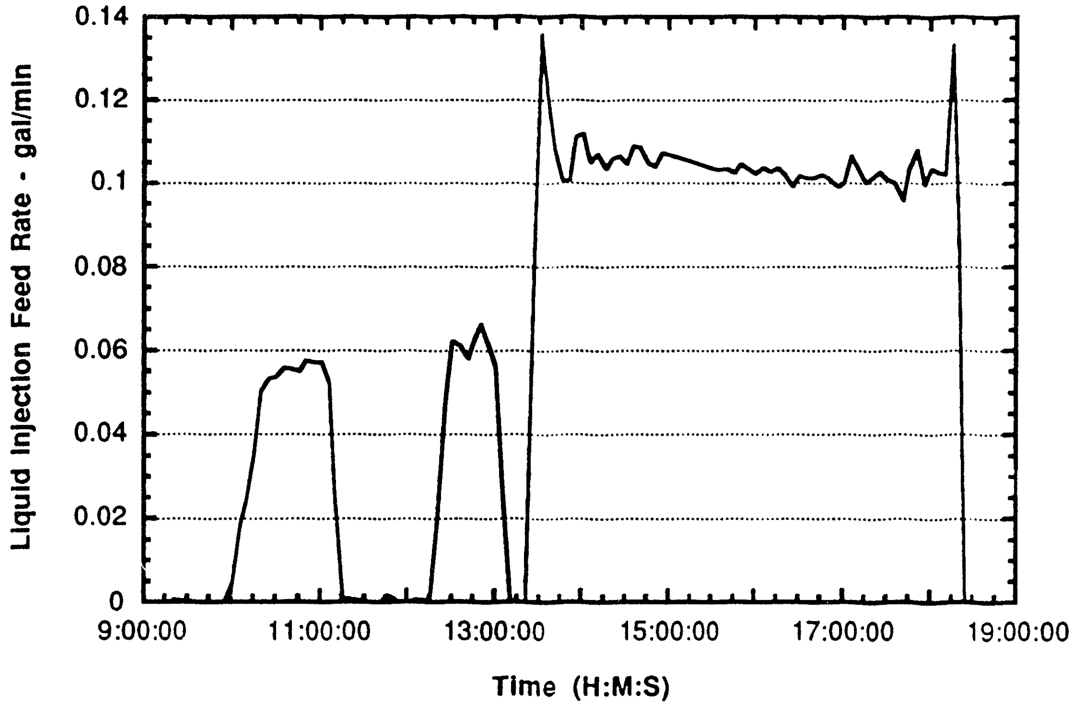

Figure 4. Rate of Injection of 1:3 Diluted Liquid Gun Propellant During Test

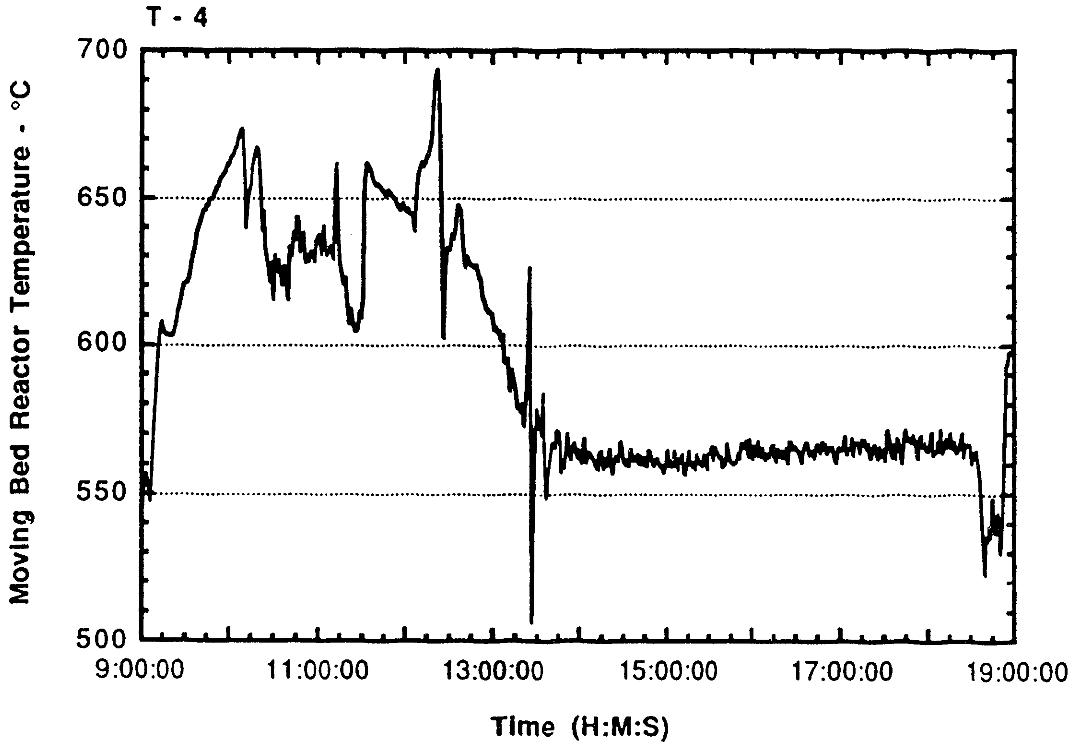

Figure 5. Thermal Response at Bottom of Reactor (T-4).

The gas species of primary interest are the oxides of nitrogen, NO and NO_2 and N_2O. The FTIR is capable of quantitatively measuring all three of these species. Figure 6 shows the NO, NO_2 and N_2O production in the reactor exit gas during the "Pyrolysis" portion of the test as measured by FTIR, in ppm. Figure 7 shows the same species during the "Combustion" portion of the test, where gas flow rates were 40 times higher, requiring a scale changes in the figures. In Figure 6, N_2O appears to be the primary effluent gas produced during the "Pyrolysis" phase of the experiment. However, this is due to the fact that much of the produced NO_2 was captured as nitrates and nitrites in the condensed water. If condensation did not occur, the ratio of NO_2 to N_2O during the "Pyrolysis portion of the test would be approximately 2:1. During the "Combustion" portion of the test, NO_2 is shown to be the primary nitrogen bearing species followed by NO and lastely N_2O, which appears to decline over the course of the run.

Figures 8 and 9 show CO_2 and CO production during the "Pyrolysis" and "Combustion" portions of the test. The ratio of produced CO_2 to CO is roughly 3:1 for both portions of experiment. Figure 10 compares the production of CO2 during the "Combustion" portion of the experiment as measured by IR meter versus the mass spectrometer. This comparison shows the same trend in the data with approximately a factor of two discrepancy in measured value. This discrepancy is explained by the fact that the IR meter was operating at the lower limit, (bottom one percent) of it's range, whereas the mass spec had no limitation. Thus, the true measure of CO2 concentration is better represented by the mass spectometer and the ratio of CO2 to CO during the "Combustion" portion of the test cannot be fully quantified.

Figure 11 shows ammonia production during the "Combustion phase of the experiment. Ammonia production during the "Pyrolysis" phase was trapped in the condensers. And finally, major driver gases and water produced during the "Combustion" portion of the test are shown in Figures 12 and 13.

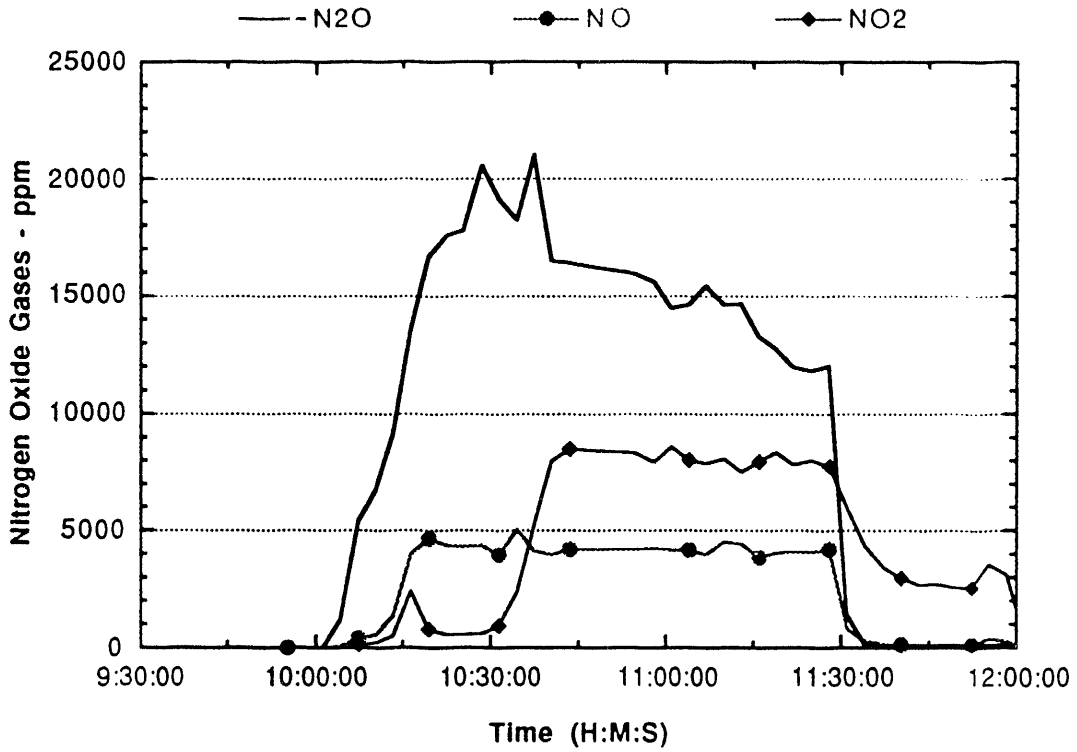

Figure 6. Reactor Exit NO, NO_2 and N_2O by FTIR During "Pyrolysis" Mode

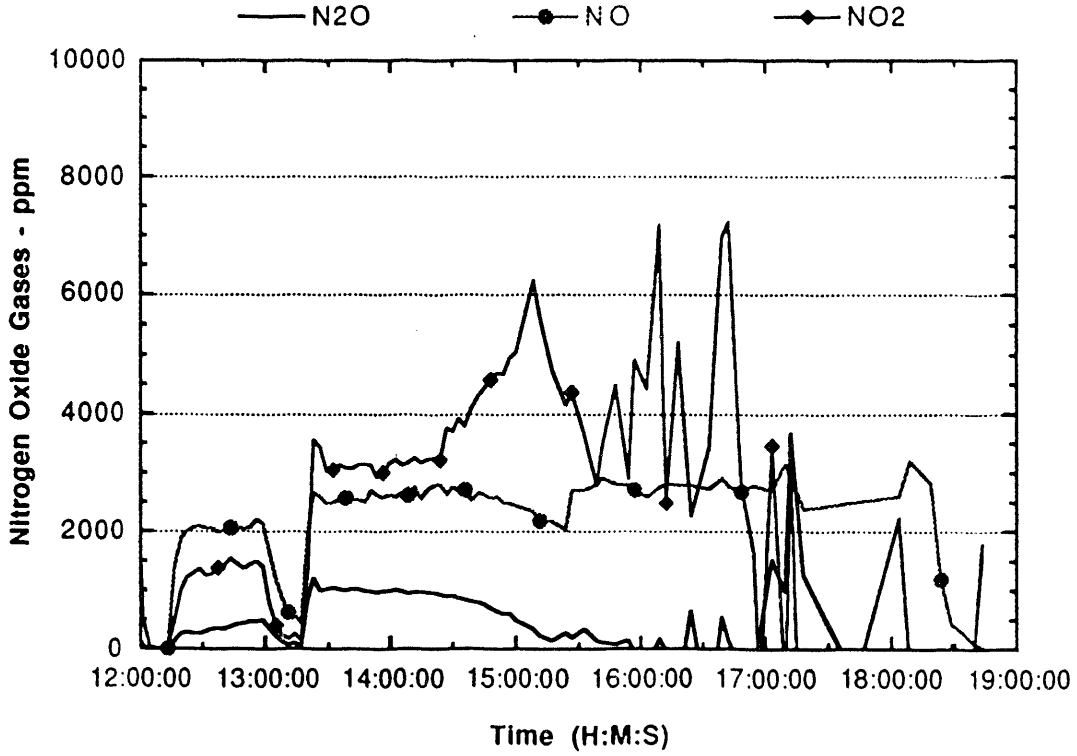

Figure 7. Lift Exit NO, NO_2 and N_2O by FTIR During "Combustion" Mode

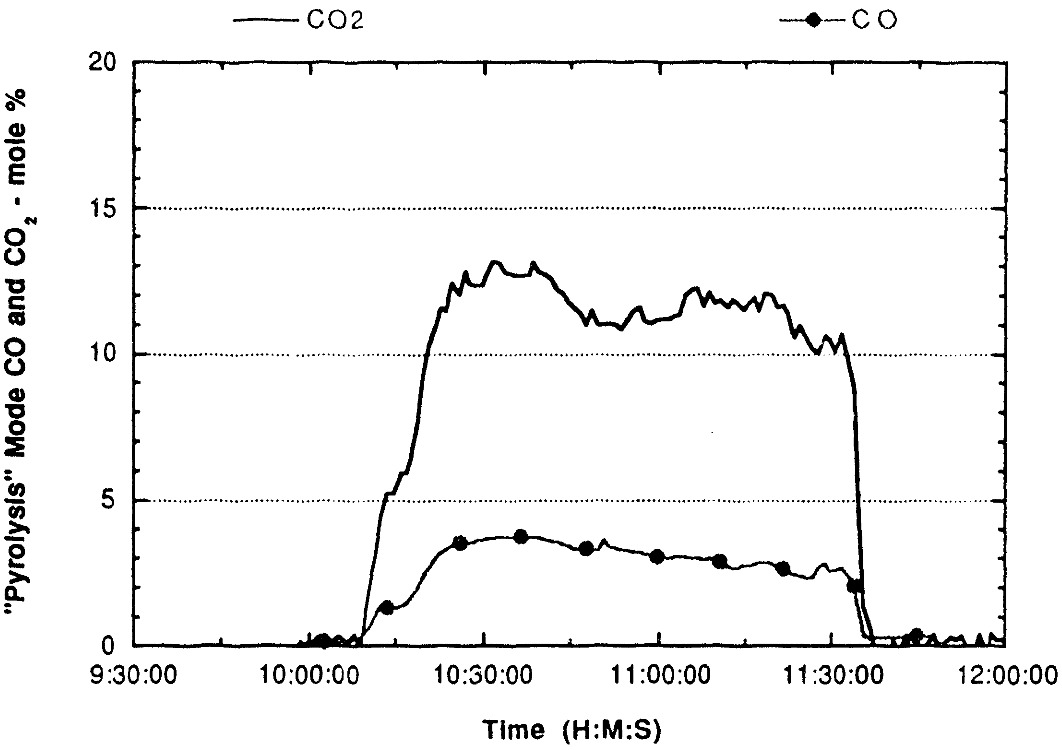

Figure 8. Reactor Exit CO, CO_2 by On-Line Meter During "Pyrolysis" Mode

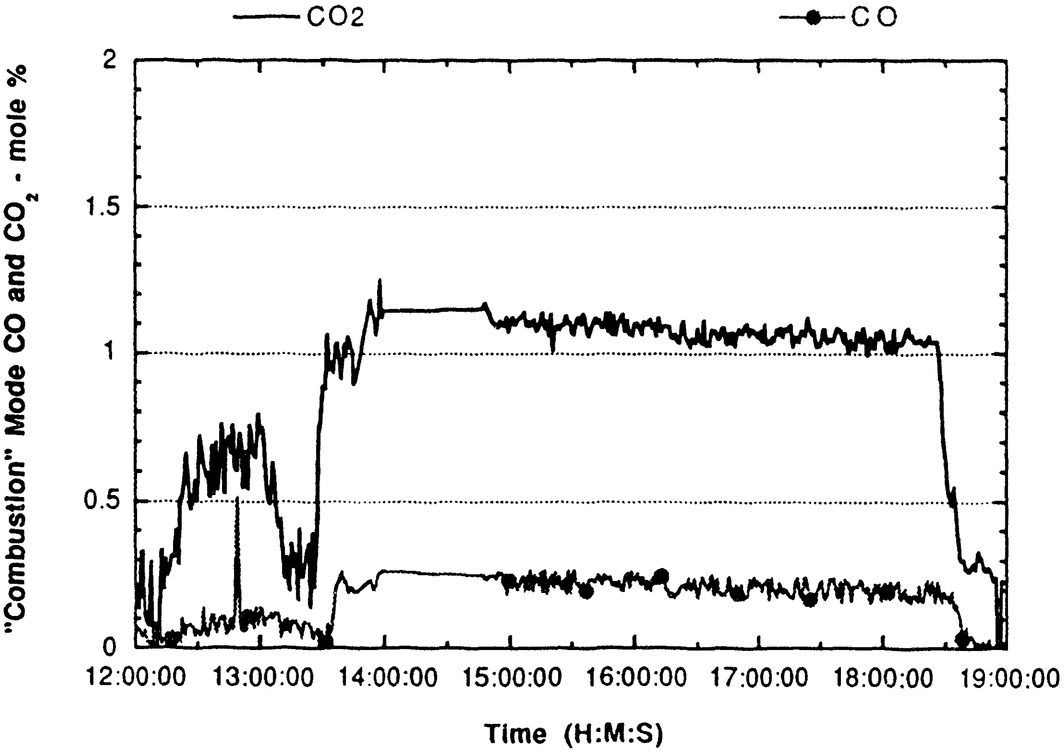

Figure 9. Lift Exit CO, CO_2 by On-Line Meter During "Combustion" Mode

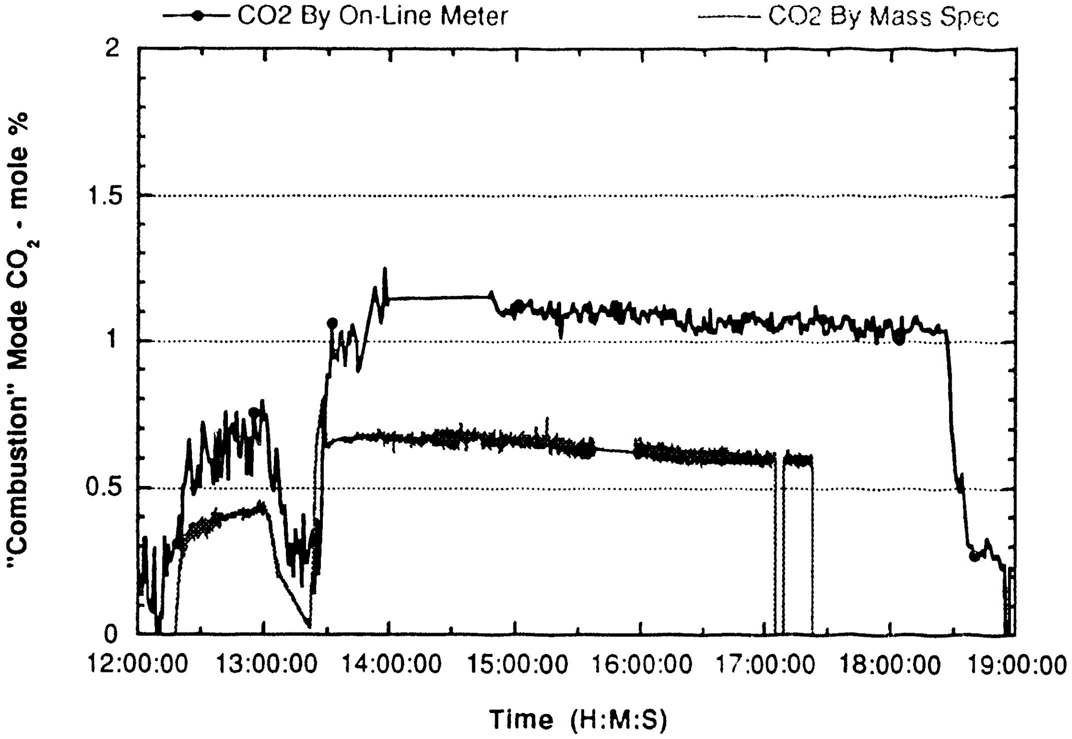

Figure 10. Comparison of "Combustion" CO_2 by Mass Spec and On-Line Meters

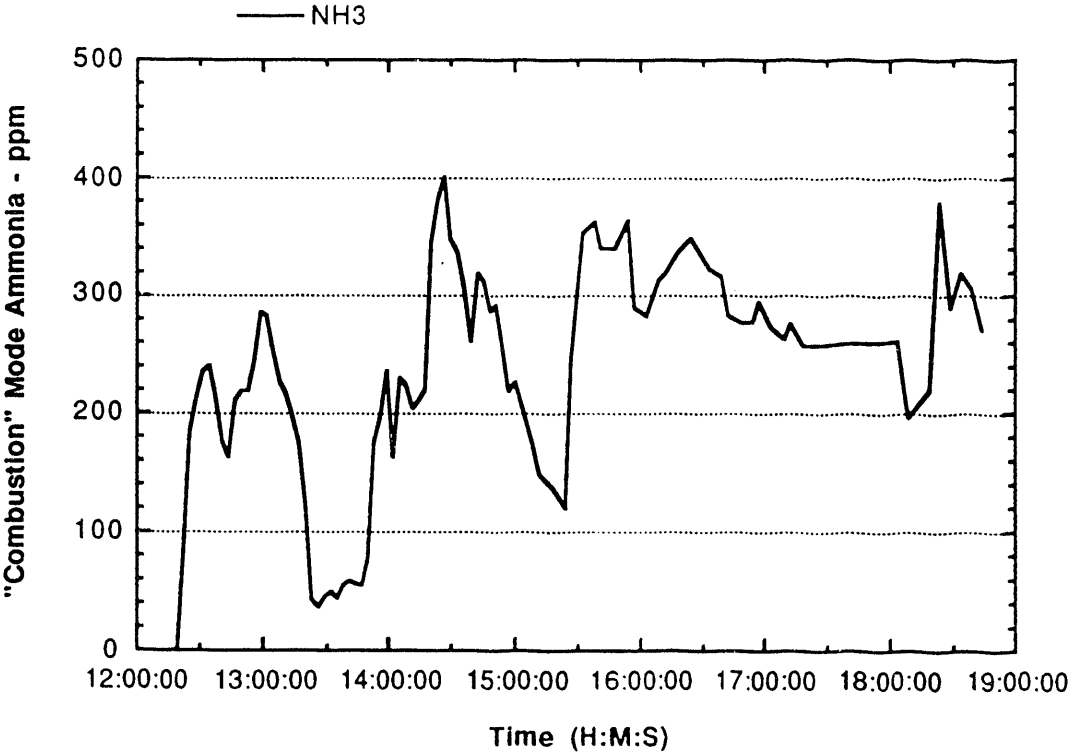

Figure 11. Lift Exit Ammonia by FTIR During "Combustion" Mode

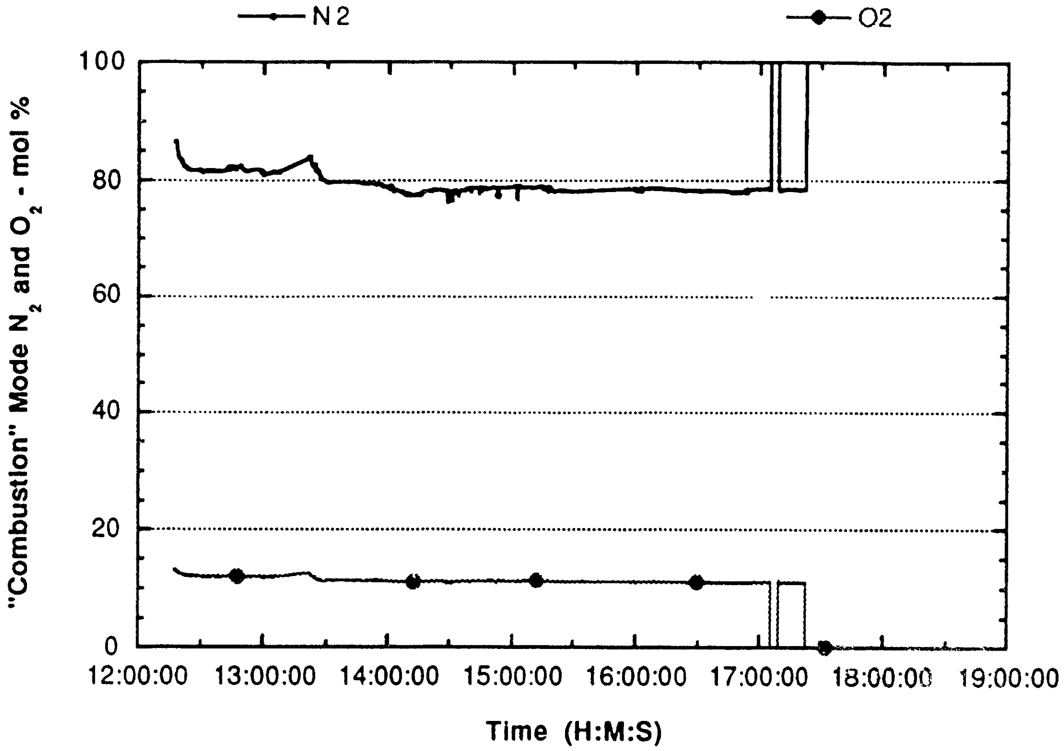

Figure 12. Lift Exit N_2 and O_2 by Mass Spectrometer

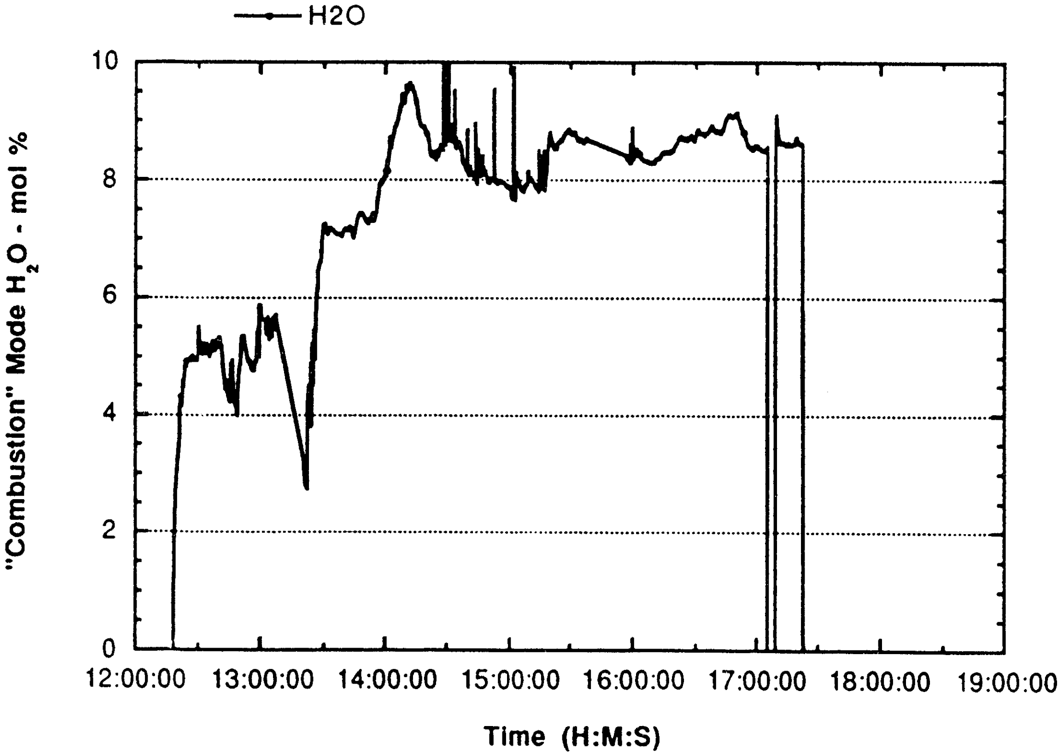

Figure 13. Lift Exit H_2O by Mass Spectrometer

Summary Tables

Tables 1 and 2 summarize nitrogen balances for the two portions of the test. In Table 1, two categories are given for NO_2 production. The first is the NO2 as measured in the gas phase by FTIR. The second is NO_2 which was trapped in the condensed liquid. This second NO_2 value has been converted to a ppm equivalent value as it would have appeared in the gas phase. As shown, 18% of the injected nitrogen was produced as nitrogen bearing gases during the "Pyrolysis" phase of the experiment. This compares with 56% produced during the "Combustion" phase.

Table 1. Nitrogen Balance During "Pyrolysis" or Recycle Mode

Item	Units	Value
Product Flow	moles/s	0.045
Duration	Hours	1.07
N_2O Concentration	ppm	16,450
NO Concentration	ppm	4262
NO_2 Concentration	ppm	5249
NO_2 in Condensate	ppm equivalent	50,000
Injected Nitrogen	kg	1.3
N_2O	% of injected N	6
NO	% of injected N	1
NO_2	% of injected N	11
All N Species	% of injected N	18

Table 2. Nitrogen Balance During "Combustion" or Once Through Mode

Item	Units	Value
Product Flow	moles/s	1.86
Duration	Hours	6
NH_3 Concentration	ppm	227
N_2O Concentration	ppm	412
NO Concentration	ppm	2653
NO_2 Concentration	ppm	3989
Injected Nitrogen	kg	7.77
NH_3	% of injected N	2
N_2O	% of injected N	6
NO	% of injected N	19
NO_2	% of injected N	29
All N Species	% of injected N	56

Table 3 gives the results for the production of carbon as CO and CO_2 during the "Pyrolysis" portion of the test. The ratio of CO_2 to CO is shown to be approximately 4:1. Using a rough balance, based on the average measured concentration and approximate operating time, 75% of the injected carbon is accounted for by the two gases over this portion of the test.

Table 4 gives the carbon balance results during the "Combustion" portion of the test. The CO_2 is shown to account for as much as 90% of the produced carbon. In this case we choose to report the CO_2 measured by mass spectrometer, as this instrument is more accurate at the low concentrations encountered. We believe that the remaining carbon can be accounted for as CO, but the dilution was too high for us to obtain an accurate CO measurement.

Table 3. Carbon Balance During "Pyrolysis" or Recycle Mode

Item	Units	Value
Product Flow	moles/s	0.045
Duration	Hours	1.07
CO Concentration	mol %	3
CO_2 Concentration	mol %	12
Injected Carbon	kg	0.42
CO	% of injected C	15
CO_2	% of injected C	60

Table 4. Carbon Balance During "Combustion" or Once Through Mode

Item	Units	Value
Product Flow	moles/s	1.86
Duration	Hours	5.5
CO_2 Concentration	mol %	0.6
Injected Carbon	kg	2.9
CO_2	% of injected C	91

Conclusions

Based on results of the first test of propellant decomposition, using the Hot-Recycled-Solid (HRS) pilot plant, the following conclusions are drawn:

- **The Hot-Recycle-Solid circulation system has been shown to be a safe and effective method for destroying LP XM46 in a simple and robust system.**

- **Continuous on-line gas analysis was invaluable in tracking the progress of the experiment and quantifying the decomposition products.**

- **The analyses showed that 18% of the nitrogen in the feed is emitted as nitrogen bearing species during the "Pyrolysis" portion of the test, where products are swept out of the retort through a condensing system.**

- **The analyses showed that 56% of the nitrogen in the feed is emitted as nitrogen bearing species during the "Combustion" portion of the test, where products are forced through an air blown lift pipe prior to exiting**

- The bulk of the carbon in the feed was emitted as CO_2 during both portions of the test. A rough material balance shows that produced CO_2 accounts for over 60% of the carbon injected during the "Pyrolysis" portion of the test and 90% of the carbon injected during the "Combustion" portion of the test.

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