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LLNL Demonstration of Base Hydrolysate Decomposition in a 0.035 Gallon Per Minute Scale Reactor

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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 base hydrolysate, a mixture of sodium nitrite, sodium formate and other constituents. This material is the waste stream from the base hydrolysis process for destruction of energetic materials, being studied by researchers at Los Alamos National Laboratory (LANL). In the Livermore process, the waste feed is thermally treated in a moving packed bed of ceramic spheres, where constituents in the waste decompose, in the presence of carbon dioxide, to form solid sodium carbonate and a suite of gases including: methane, carbon monoxide, oxygen, nitrogen oxides, ammonia and possibly 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 sticking and agglomeration of the waste while undergoing processing.

We performed an extended one day (8 hour) test of the solids recirculation system, with continuous injection of approximately 0.035 gal/min of waste for a period of seven hours. Continuous on-line gas analysis was invaluable in tracking the progress of the experiment and quantifying the decomposition products. Analyses showed the primary solid product, collected in the lift exit cyclone, was indeed sodium carbonate, as expected. For the reactor condition studied in this test, N_2O was found to be the primary nitrogen bearing gas species. However, other experimental results indicate that in a more oxidizing environment, with longer residence times, the production of N_2O can be limited. In the test, approximately equal quantities of ammonia and nitrogen bearing oxide gases were produced (NO , NO_2 and N_2O). Under proper conditions, this ammonia and NO_x can be recombined downstream to form N_2 and O_2 as the primary effluent gases. The evaporated liquid waste was condensed and analyzed following processing and determined to be non-hazardous and sewerable by Federal and State standards.

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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.

The Los Alamos National Laboratory (LANL) has developed a process to demilitarize energetic materials by treatment in boiling aqueous sodium hydroxide. This process is referred to as base hydrolysis and is an excellent way to render these materials non-detonable and non-reactive. However the base hydrolysis does produce large volumes hazardous waste that is corrosive and potentially toxic. The base hydrolysate is a mixture of sodium nitrite, sodium formate as well as other, including some unknown, constituents.

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 base hydrolysate. In the modified LLNL pilot plant, a sample of Los Alamos National Laboratory's base hydrolysate was thermally treated in a moving packed bed of ceramic spheres, where constituents in the waste decompose, in the presence of carbon dioxide, to form solid sodium carbonate and a suite of gases including: methane, carbon monoxide, oxygen, nitrogen oxides, ammonia and possibly 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 sticking and agglomeration of the waste while undergoing processing. We performed an extended one day test of the solids recirculation system, with continuous injection of approximately 0.035 gal/min of waste for a period of seven hours. Solid sodium carbonate, methane, carbon monoxide, nitrogen oxides and possibly molecular nitrogen were the major products.

Pilot Plant Description

The retort schematic, in Figure 2, shows the configuration of equipment for the waste 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 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 1. Schematic of LLNL Hot-Recycled-Solid (HRS) Oil Shale Retorting Pilot Plant

Waste 6

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

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 through 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 CO₂ 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 8 kW is enough to evaporate and bring to reaction temperature 0.04 gal/min of waste 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 waste injection rate. For the test a waste injection rate of 0.035 gal/min was achieved. Figure 3 shows a schematic of the moving bed reactor, with thermocouple positions noted.

Base hydrolysate composition

A hemisphere of PBX 9405 weighing approximately 15 pounds was dissolved in 15 gallons of hot 1 M sodium hydroxide. This material contained 26.3 g/L of sodium, 11.9 g/L formate, 0.53 g/L of chloride and 2.82 g/L of nitrite. It showed a pH of greater than 12 and a strong base concentration of 0.596 M. It also contained an unknown amount of partial hydrolysis products of the HMX in the PBX 9404.

Waste Injection Chronology

The experiment began at 9:30 and waste was first injected beginning at 10:04. Progress of both the waste and steam injection was followed using bubblers to record the liquid level in each of the two supply vessels. Figure 4 shows the progress of injection during the experiment. As shown in the figure, after initial startup, the waste injection was adjusted at 11:20 and then held steady for the duration of the test, which was terminated at 5:00 PM. Steam injection was held constant for the entire period. The average steam injection rate during the run was 0.03 gal/min and the average waste injection rate was 0.035 gal/min.

Reactor Temperatures

The temperature exiting the moving bed reactor over the course of the runs is shown in Figure 5. At 11:00 the feed of circulating solids became sluggish requiring adjustment of the slope of the L-valve. During this time excess liquid cooled the solid causing the thermal response observed at T-4 at 11:30. Following this time, no other adjustments were made in major run parameters for the duration of the run.

Gas Composition

The composition of gas species produced during the base hydrolysate 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, CO₂ and NO_x and an O₂ analyzer. On-line analysis of gas phase components included: NO, NO₂, N₂O, O₂, CO, CO₂ and H₂O. N₂ levels were dominated by the air and N₂ used as working fluids for pneumatic lifting, pressure balance and L-valve operation. Therefore, N₂ produced from the decomposition of NaNO₂ was not detectable. Two gas exit streams were monitored. On-line meters (CO, CO₂ & O₂) and the FTIR and MS primary monitored the main reactor exit gas stream, downstream of the condensing system. The second, lift exit gas stream, was in general monitored by on-line meters only (CO, CO₂, O₂ and NO_x). For two short periods at 1:30 pm and 4:00 pm the FTIR and MS were switched to monitor the lift exit gas. These two

periods are noted in the following reactor exit plots as "Off Line".

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

Figure 4. Steam and Waste Injection Tank Levels 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 NO₂ and N₂O. The FTIR is capable of quantitatively measuring all three of these species and monitored their evolution in the reactor exit gas throughout the test. Figure 6 shows the NO, NO₂ and N₂O production in the reactor exit gas during the test as measured by FTIR, in ppm. Figure 7 shows CH₄ and CO concentration in the reactor exit. Figure 8 shows the three major reactor exit gases produced, CO₂, N₂ and O₂. CO₂ was injected into the reactor at a rate of 42 mMol/s. N₂ and O₂ reach the reactor exit through gas exchange with the pneumatic lift and/or packed bed heater system. Finally, H₂O in the reactor exit gas is shown in Figure 9. In the lift exit gas, concentrations of NO_x and N₂O were below detectable limits. However, this is understandable given the high dilution (40 to 1) of lift exit gas to reactor exit gas coupled with the low concentrations of these species in the reactor exit gas. Figures 10 and 11 show the only species present in sufficient quantities for measurement. As shown, the mass spectrometer and FTIR were on-line for two short periods over the course of the experiment.

Comparison of the lift exit CO₂ from the on-line meter and mass spectrometer is shown in Figure 12. We can also compare the CO₂ and O₂ on-line meters on the reactor exit gas to concentrations reported by the mass spectrometer. These are shown in Figures 13-14. Finally, we can compare the FTIR and mass spectrometer for nitrogen response. The mass spectrometer does not distinguish between NO, NO₂ and N₂O however by summing the three FTIR responses we can qualitatively compare responses. This is shown in Figure 15. The lower response of the mass spectrometer is to be expected, since the cracking pattern for N₂O yields about 50% response at mass 30, compared with nearly 100% response for NO and NO₂.

Figure 6. Reactor Exit NO, NO₂ and N₂O by FTIR Instrument

Figure 7. Reactor Exit CO and CH₄ by FTIR Instrument

Figure 8. Reactor Exit CO₂, N₂ and O₂ by Mass Spectrometer

Figure 9. Reactor Exit H₂O by Mass Spectrometer

Figure 10. Lift Exit CO₂, N₂ and O₂ by Mass Spectrometer

Figure 11. Lift Exit H₂O by Mass Spectrometer

Figure 12. Comparison of Lift Exit CO₂ by IR Meter Versus Mass Spectrometer

Figure 13. Comparison of Reactor Exit CO₂ by Meter Versus Mass Spectrometer

Figure 14. Comparison of Reactor Exit O₂ by Meter Versus Mass Spectrometer

Figure 15. Comparison of Reactor Exit "NO" by FTIR Versus Mass Spectrometer

System Response to Termination of Waste Feed

Figure 16 shows the system response in the reactor exit gas to termination of the waste feed. The analytic instruments have approximately a 3 minutes sample line lag time.

Using the response in Figure 16, we can estimate the time required for a fifty percent decay in concentration of "NO" following termination of waste injection. In the reactor exit gas, the response time on Day 3 for a 50% decay in NO concentration is estimated to be 8 minutes. If the decomposition follows a first order rate law, this estimated response time would equate to a reaction rate constant, k , of 0.0015 sec^{-1} . A first order rate constant for sodium nitrate decomposition in a small-scale fluidized bed has been measured to be 0.0023 sec^{-1} .

Figure 17 shows the flow of product gas exiting the reactor through the condensing system. This flow is small compared to the pneumatic lift system flows and the flow rate is influenced by gas leaking between the two systems. Thus, as the figure shows, the flow is not steady. However, a flow of 0.039 mol/s is representative of the product flow over the course of the experiment.

Figure 18 shows the flow of gas exiting the lift system. This is the combined flow from the lift inlet, moving bed heater inlet and the L-valve flow and includes approximately five percent steam. At the beginning of the experiment, the average flow was 1.53 mol/s , whereas, after 11:30 to shutdown the flow averaged 1.73 mol/s .

Figure 16. Decay of NO_x in Reactor Exit Gas After Waste Stopped

Figure 17. Reactor Exit Gas Flow During Experiment

Figure 18. Lift Exit Gas Flow During Experiment

Summary Tables

Tables 1-5 summarize the major operating data for the test. In each of the tables, the large type numbers are averaged data over a suitable time period, whereas the smaller type numbers are standard deviation (σ) of these averages. Table 1 shows the relative magnitude of gas flows into and out of the system over the course of the experiment. Good agreement is obtained in overall inlet and exit flow measurements. Table 2 shows the amount of base hydrolysate and steam injected into the system and the amount of condensate collected in the reactor exit. As shown in a later table, the remaining water left the system in the lift exit gas. Table 3 shows pertinent process temperatures. And finally, Tables 4 and 5 give average compositions for reactor exit and lift exit gases.

Table 1. Injection and Production Gas Flows

Experiment W1 - Gas Flows					
	mMol/s	σ		mMol/s	σ
Lift In Flow	1118	2			
Bed Heater In Flow	352	8	Reactor Exit Flow	39	9
CO ₂ In Flow	42	1	Combined Lift Exit	1725	37
L-Valve In Flow	168	12			
Total In	1681		Total Out (Dry Basis)	1678	

Table 2. Injected Liquid Flow Rates and Totals

Experiment W1 - Liquid Flows			
	gal/min	mMol/s	Total - kg
Liquid Waste In	0.034	118	52
Steam In	0.029	100	52
Condenser Out			52

Table 3. Process Temperatures

Experiment W1 - Temperatures					
	°C	σ		°C	σ
Pyrolyzer @ 106 cm	623	10	Top of Lift Pipe	636	9
Pyrolyzer @ 88 cm	616	10	Top of Heater	592	11
Pyrolyzer @ 71 cm	641	7	Prior to Liquid Inj.	610	10
Pyrolyzer @ 53 cm	631	8	After Liquid Inj.	353	38
Pyrolyzer @ 35 cm	617	9	Reactor Gas Exit	520	11
Pyrolyzer @ 4 cm	557	22	Lift Exit @ Filter	261	2

Table 4. Reactor Exit Gas Composition

Experiment W1 - Reactor Exit Gases					
	ppm	σ		mole %	σ
N ₂ O	617	107	CO ₂	25	6
NO	152	36	N ₂	58	5
NO ₂	98	24	O ₂	14	1
CO	216	26	H ₂ O	1	0.1
CH ₄	41	7			

Table 5. Lift Exit Gas Composition

Experiment W1 - Lift Exit Gases					
	mole %	σ		mole %	σ
CO ₂	1.2	0.1	O ₂	8.7	0.1
N ₂	84	0.3	H ₂ O	5.3	0.3

Post Run Sample Analysis and Balances

After final shutdown, we began emptying the vessels of the 195 kg of sphere inventory used. The spheres were removed from the process using the reactor L-valve and during discharge showed no signs of sticking, tacking or agglomeration. The final inventory of the spheres recovered from the process totaled the same 195 kg added during the course of the test.

During the tests, 51.9 kg of solution was injected along with 52.3 kg of steam. The injected species are accounted for in effluents from the process and accumulation within the process. The effluents include: 1) the collected condensate, 2) the collected solid in the reactor exit and lift exit cyclones and 3) the reactor and lift exit gas streams. Accumulation within the process includes: 1) the circulating spheres and 2) the solid accumulation on vessel walls.

A number of analytic samples were collected during the run and after shutdown. These included: 1) four samples of condenser condensate, 2) a sample of circulating spheres and 3) lift exit cyclone solid sample. Presented below are material balances based on key constituents measured in the collected samples. These included sodium content, measured using inductive coupled plasma atomic emission spectrometry (ICP-AES), NO₂- and NO₃- content, measured by ion chromatography, and carbonate content, using a TOC analyzer.

Material Balances

The first key performance parameter to be determined by material balance is the amount of waste processed. This can be conservatively estimated by determining the amount of sodium found in the reactor effluent condensing system versus the amount of sodium injected in the waste feed. Analyses showed that less than 0.5% of the injected sodium reached the reactor exit condensing system, therefore over 99.5% of the injected sodium remained in the system and was processed.

Table 6 summarizes the atomic balance for sodium. During the test, a total of 1.37 kg of sodium was injected into the system. As shown, 10% of the injected sodium was collected in the lift exit cyclone and 29% was deposited as a coating on the circulating spheres. The remaining sodium is assumed to have formed a thin coating on internal vessel walls. Post run inspection of the vessels substantiates this claim, although no quantitative material balance was attempted.

Table 6. Sodium Balance

	Concentration	Units	Sample Size	Net Sodium	% of Total
			kg	gm	%
Condensate 1	0.037	gm/kg	15	0.5	0.0%
Condensate 2	0.074	gm/kg	10	0.7	0.1%
Condensate 3	0.095	gm/kg	17	1.6	0.1%
Condensate 4	0.131	gm/kg	10	1.3	0.1%
Spheres	2.00	gm/kg	196	392	28.7%
Lift Cyclone	345.0	gm/kg	0.4	132	9.7%
Total Produced				528	38.7%
Total Injected	26.3	gm/kg	51.9	1365	

Analysis of the lift exit cyclone solid showed that sodium carbonate (Na_2CO_3) made up 76% of the total sample weight. The remainder consisted of inorganic compounds from ware of the spheres and vessel walls.

Table 7 summarizes the atomic balance for nitrogen. During the test, a total of 45 gm of nitrogen was injected into the system in the form of nitrite (NO_2^-). As shown, 27% of this injected nitrogen is accounted for in the condenser condensate, primarily in the form of ammonia (NH_4^+). An additional 27% is accounted for in three nitrogen containing gases exiting the reactor, with N_2O being the most abundant species. Due to the high dilution in the lift system, detection of nitrogen gases was not possible. However, based on the most abundant species (N_2O), we estimate that no more than 13% of the nitrogen exited in this stream. This leaves 35% of the nitrogen unaccounted for and assumed to be ammonia leaving the system with in the lift exit gas.

Table 7. Nitrogen Balance

	Concentration	Units	Sample Size	Units	Net N	% of Total
					gm	
Condensate - Nitrate	0.072	gm/kg	52	kg	1	2%
Condensate - Nitrite	0.036	gm/kg	52	kg	1	1%
Condensate - Ammonia	0.263	gm/kg	52	kg	11	24%
Reactor Gas - N_2O	617	ppm	7 & .039	hrs & mol/s	8	19%
Reactor Gas - NO	152	ppm	7 & .039	hrs & mol/s	2	5%
Reactor Gas - NO_2	98	ppm	7 & .039	hrs & mol/s	1	3%
Lift Exit Gas - N_2O	10	ppm	7 & 1.7	hrs & mol/s	6	13%
Total Produced				gm	29	65%
Total Injected				gm	45	

* Maximum value - Below detectable limits of instrument

The last balance concerns water injected versus water collected in the reactor exit condensing system. Table 8 summarizes these results which shows that 96% of the injected water is accounted for.

Table 8. Water Balance

	Value	Units	Total - kg	% Total
Liquid Waste In	0.034	gal/min	52	50%
Steam In	0.029	gal/min	52	50%
Total In	-	-	104	-
Condenser Out	-	-	52	50%
Lift Exit Gas	1.7	% & 8.5 hrs	48	46%
Reactor Exit Gas	1.5	% & 8.5 hrs	0.3	0.3%
Total Out	-	-	100	96%

Conclusions

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

- The Hot-Recycle-Solid circulation system operated successfully for 7 hours during which 55 kg of base hydrolysate was processed.
- The primary solid product was sodium carbonate, which is removed from the system as as fine dust, collected in a gas/solid cyclone separator.
- Continuous on-line gas analysis was invaluable in tracking the progress of the experiment and quantifying the decomposition products.
- The analyses showed that N₂O was the major nitrogen oxide species measured in this test. Other experiments in a more oxidizing environment and longer residence times produces NO and NO₂ as the primary nitrogen oxide species.
- Ammonia production was equivalent to nitrogen oxide production. The ammonia and NO_x could be combined in a downstream reactor producing N₂ and O₂ as the primary effluent gases.
- Inspection of solids removed from the process following shutdown showed no signs of sticking, tacking or agglomeration.
- Analyses showed the liquid condensate produced in in this process to be non-hazardous and sewerable by Federal and State standards.

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