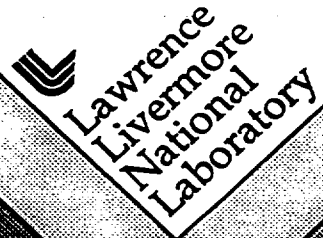# Molten Salt Destruction of Base Hydrolysate

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Introduction

As a result of the end of the Cold War and the shift in emphasis to a smaller stockpile, many munitions are scheduled for rapid dismantlement and demilitarization. Major components of these munitions are the explosives and propellants, or energetic materials. The DoD has several hundred million pounds of energetic materials in its demilitarization inventory, with millions more added each year. Although recycling and reusing is the preferred method of dealing with these surplus materials, there will always be the necessity of destroying intractable or unusable energetic materials. Traditionally, open burn/open detonation (OB/OD) has been the method of choice for the destruction of energetic materials. Public concerns and increasingly stringent environmental regulations have made open burning and open detonation of energetic materials increasingly costly and several states have banned OB/OD. Thus, the impetus to develop environmentally sound alternatives to dispose of energetic materials is great.

We have previously demonstrated the Molten Salt Destruction (MSD) Process for the destruction of HE and HE-containing wastes. MSD converts the organic constituents of the waste into non-hazardous substances such as carbon dioxide, nitrogen and water. Any inorganic constituents of the waste, such as binders and metallic particles, are retained in the molten salt. The destruction of energetic material waste is accomplished by introducing it, together with air, into a crucible containing a molten salt, a suitable mixture of sodium, potassium, lithium carbonates.

In addition to MSD other processes have been proposed to destroy energetic material waste. Each of these processes is unique and each is optimally effective for a different subset of the demilitarization inventory. Each of these processes produces solid, liquid and gaseous waste streams. Base hydrolysis is a demilitarization process that renders explosive materials non-reactive. This may be a cost effective process to demilitarize a fraction of the demil inventory, particularly for decontaminating large metal parts (bomb casings). The base hydrolysis process produces a hazardous liquid waste stream. This report describes experimental results of the destruction of base hydrolysate from four explosives (Tritonal, Octol, Comp B3, and PBXN-109) by molten salt.

Experimental

The Los Alamos National Laboratory (LANL) has investigated the use of base hydrolysis for the demilitarization of explosives. Cary B. Skidmore from LANL provided LLNL with the following samples:

Comp B hydrolysate   3 liters
Octol hydrolysate   3 liters
Tritonal hydrolysate   4 liters
PBXN-109 hydrolysate   4 liters

Appendix 1 describes how these samples were prepared. No data were provided for the Comp B experiments. Chemical analyses of the hydrolysate were not provided.

The hydrolysate was processed in the 7 foot tall pilot molten salt unit located in building 191 at the LLNL main site. An insulated downcomer (3.75 inches OD/1 inch ID) was used that ran from the top to within 6 inches of the bottom of the vessel. A 3/8 inch OD coaxial feed tube was contained within the downcomer that ran to within 4 inches of the bottom of the downcomer. The hydrolysate was pumped through the inner tube and air was delivered down the main downcomer. We found that is important to use this type of downcomer assembly to prevent evaporation of liquid and deposition of solid material in feed streams with a high loading of dissolved solids.

The hydrolysate was processed at 82 gram per minute into a carbonate salt bath at 735 to 770°C. Oxygen in the exhaust ran at 12 to 16% due to the low concentration of reduced carbon in the feed liquid. NOx and carbon monoxide emissions were low and are presented in Table 1. No other emissions, other than carbon dioxide were measured.

Table 1. Emissions from the molten salt destruction of base hydrolysate

Explosive	NOx (ppm)	CO (ppm)
Tritonal	51	40
Octol	52	140
PBXN-109	30	2777
Comp B-3	18	152

Results and Discussion

The processing of these base hydrolysate solutions proceeded in a straight-forward manner without notable occurrences. The emissions from these materials were quite low with one exception. The generally low emissions

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were due to the low concentration of dissolved organic and NOx generating inorganic components (such as nitrate/nitrite) in the solution.

In one case (PBXN-109) the emissions of carbon monoxide was quite high (2777 ppm). This material was hydrolyzed using 20 to 50% DMSO to swell the binder. This was necessary since the binder used in PBXN-109 is not hydrolyzed by sodium hydroxide and a limited reaction occurred in aqueous solutions. The resulting hydrolysate contained substantial quantities of DMSO, which does not burn cleanly at the operating temperature used to destroy explosives (750°C). The amounts of carbon monoxide could be reduced by operating the molten salt unit at higher temperatures (e.g. 900°C).

These experiments processed base hydrolysate at 1.4 gallons per hour, and the time required to process the liquid from all four explosives required 3.5 hours. This was insufficient time to reach steady state. The feed material was not completely characterized, so any conclusions drawn from these experiments must be considered as preliminary. However, 14 liters of material was processed is a short amount of time without incident. With one exception (noted above) the gaseous emissions from the molten salt destruction of base hydrolysate were low. We are, therefore, hopeful that molten salt destruction is an ideal method to process waste from a large-scale base hydrolysis program.

Appendix 1. Preparation of base hydrolysate
(Provided by Cary B. Skidmore of Los Alamos National Laboratory)

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Experimental Summary for the DOD Explosives: Base Hydrolysate was a mixture of all the experiments using the same explosive

Effectiveness of base hydrolysis on Octol:

| Experiment #	Mass of Explosive	Description	Concentration of Base	Volume of Base	Peak Temp.	Time at Temp.	% reacted	Date
CSX-46*	16.935 g	Scrap	1.5M NaOH	200 mL	93°C or >	106 minutes	99.7	2/15/96
CSX-47*	23.831 g	1 piece	3M NaOH	200 mL	80°C or >	30 minutes	99.8	2/20/96
CSX-58^S	105.55 g	2 cylinders	3M NaOH	1000 mL	150°C	~1 minute**	99.0	2/26/96
CSX-59	181.51 g	2 cylinders	3M NaOH	1000 mL	80°C or >	28 minutes	94.6	2/27/96

* A Solid salt of TNT is formed in the ammonia experiment, so the determination of how much Octol was reacted is difficult to determine.
** Due to a rapid exotherm (see temperature profile for CSX-58) the time at temperature was not accurately determined.
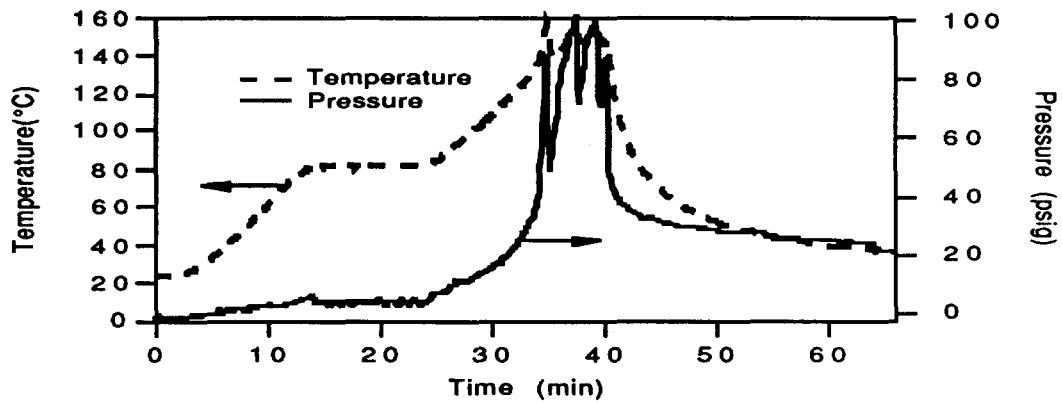^{S} Stirring was used.

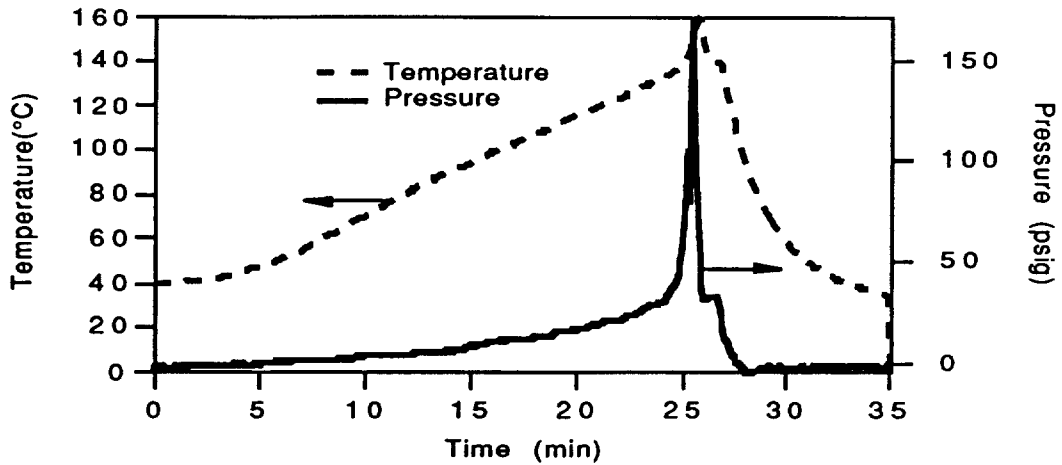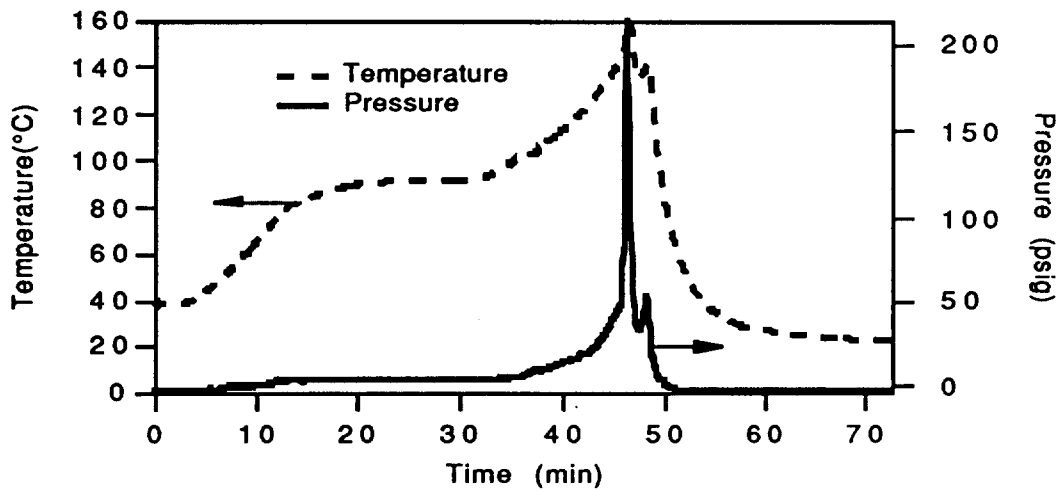## Temperature and pressure profiles for the Octol experiments

CSX-46

CSX-47

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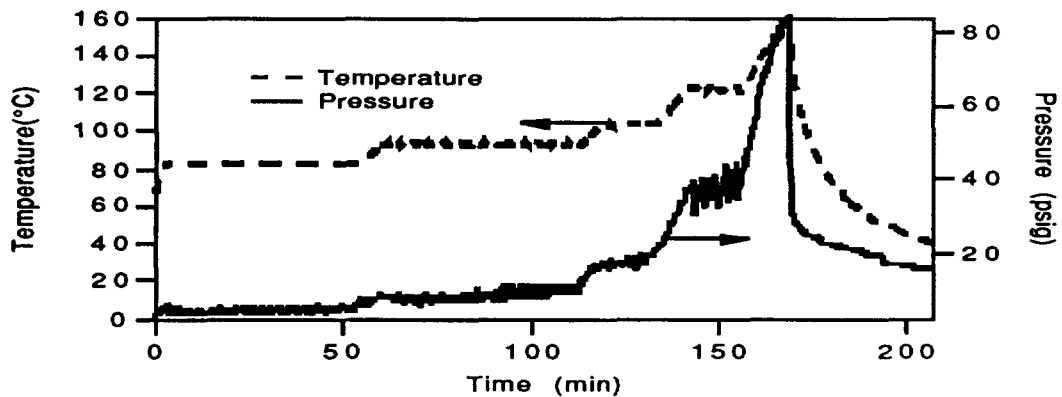
CSX-58

CSX-59

Gas Chromatograph Results for Octol Experiments (Air Free)

Experiment	CO_2	H_2	N_2O	N_2	CO	O_2	Unknown
CSX-46	Trace		94.8%		0.128%		5.07%
CSX-47		Trace	90.9%	6.86%	0.122%		2.12%
CSX-49			~100%	0%	0.38%		0%
CSX-50			~100%	0%	0.28%		0%
CSX-59	0.182%		67.4%	10.83%	0.096%	0.210%	21.28%

CSX-58 did not have a GC run on it because of the release of some liquid out of the relief valve, and the presence of a partial vacuum in the reactor system.

Percent of starting nitrogen reacted, converted to N_2O and N_2

Experiment#	% N_2O	% N_2	% Total
CSX-46	31		31
CSX-47	52	0.13	52.13

The stoichiometry used for octol is that 0.6 grams of NaOH is needed per gram of octol. The best results were when the reaction was directly heated to 150°C. The only problem with this method is that an adequate relief valve must be present in order to handle the large quantity of gas released during the experiment. Roughly 110 cm^3 (STP) of gas is produced for every gram of Octol. The average values of the gas components for the treatment of Octol with NaOH is 84.4% N_2O, 5.90% N_2, 0.12% CO. All gas percentages are air free.

The TNT appears to melt and react at roughly 90°C allowing for the HMX to contact the base. This is the reason for the large jump in temperature and pressure during the reaction. Overall, octol is very suitable for base hydrolysis. The hydrolysate is a reddish-black liquid that does not lend itself to analysis by NMR. This might be due to the theory that the hydrolysate products of TNT are in a fine colloidal suspension, and not completely soluble with the base solution. Recent work by T. Spontarelli hopefully will solve this problem. Ammonia hydroxide was found to not be as effective as NaOH, and tended to form insoluble salts with TNT.

Experimental Summary for Tritonal Experiments

Experiment #	Mass of Explosive	Description	Concentration of Base	Volume of Base	Peak Temp.	Time at Temp.	% Reacted	Date
CSX-54	50.154 g	1 piece	3M NaOH	250 mL	>80°C	33 minutes	12.1**	2/23/9
CSX-55*	41.965 g	Flat Disk	3M NaOH	500 mL	95°C	21 minutes	68.8	2/23/9
CSX-56*	51.27 g	1 piece	1.5M NaOH	750 mL	95°C	19 minutes	83.5	2/24/9
CSX-56-2*	20.234 g	scrap	1.5M NaOH	400 mL	95°C	20 minutes	14.9***	2/24/9
CSX-57*	49.404 g	1-piece	1.5M NaOH	1000 mL	95°C	30 minutes	99.5	2/26/9

* A solid disk formed on the bottom of reactor. Acetone was needed to remove the solid disk. Mass reacted
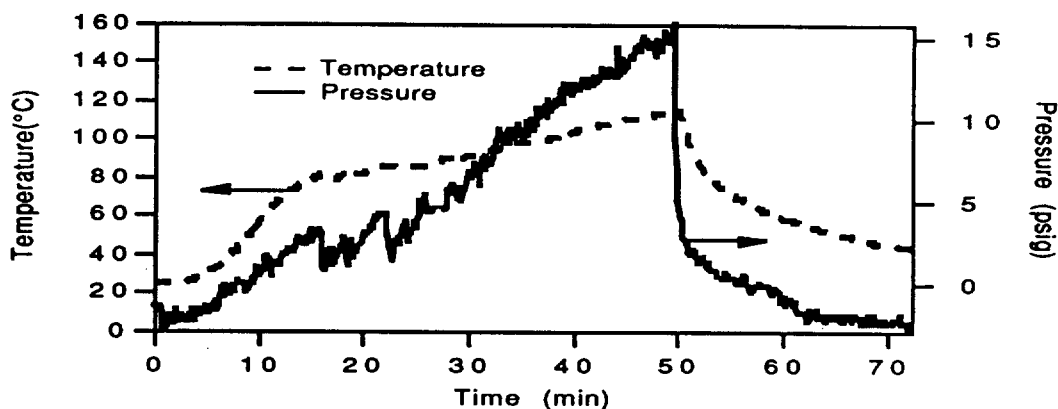   was determined after acetone evaporated. No stirring was used in this experiments

** A solid disk formed, but was easily removed. This disk was used in CSX-55. No stirring was used in
    this experiment.

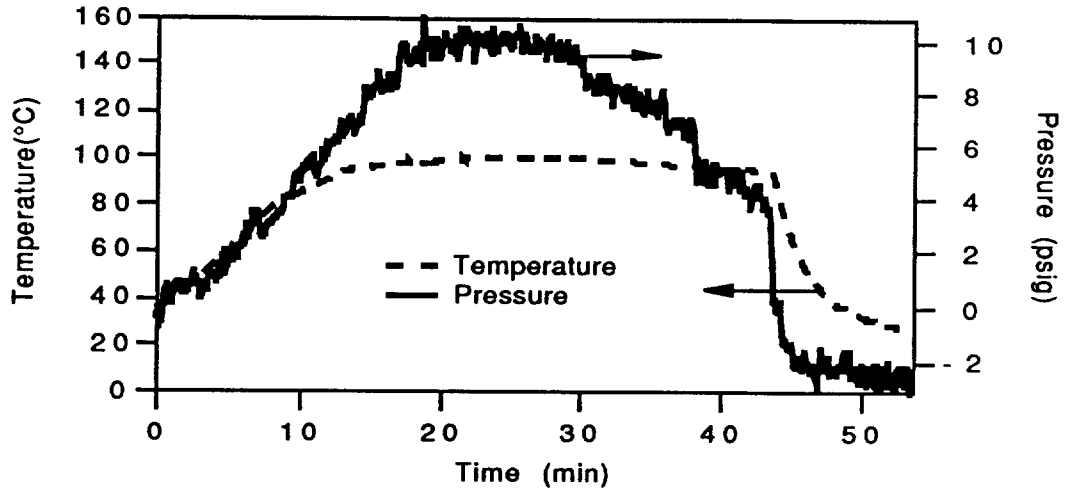*** Liquid level was not sufficiently high enough for good mixing.

• Stirring was used.

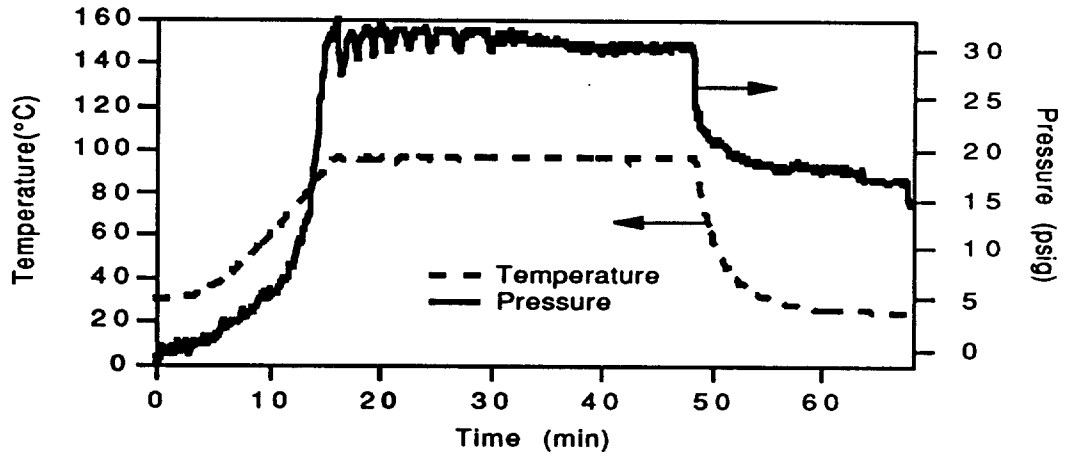## Temperature and Pressure Profiles for Tritonal Experiments

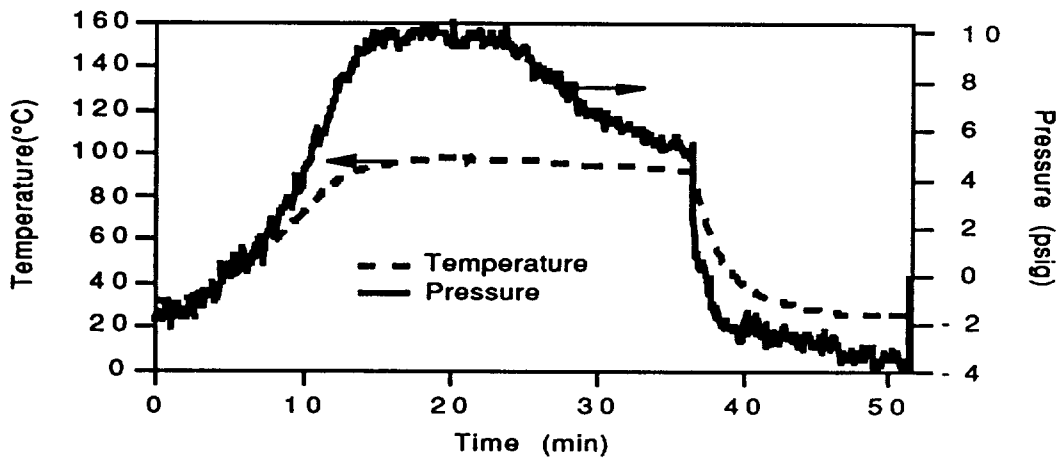### CSX-54

CSX-55

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CSX-56

CSX-56-2

CSX-57
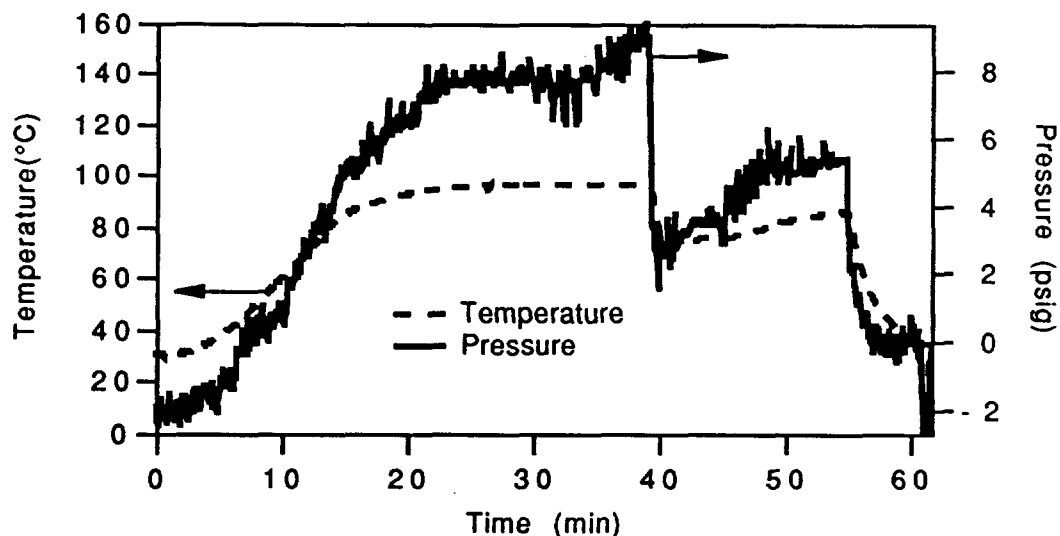
GC Results for Tritonal Experiments (Air Free)

Experiment	CO_2	H_2	N_2O	N_2	CO	O_2	Unknown
CSX-53			0.96%	58.5%	0.04%		40.5%
CSX-56		~100%			0.22%		

The stoichiometry used for the reaction of tritonal with NaOH is that 1.2 grams of NaOH is needed for every gram of tritonal. The large difference in stoichiometry between tritonal and octol is due to the presence of aluminum, which consumed two moles of NaOH per mole of aluminum. The best results were when the solution was heated to ~95°C. Good mixing is very important, if mixing is poor the TNT in the tritonal will melt and sit on the bottom of the reactor as a solid lump. When this happens, the mass transfer is poor enough, that the reaction does no proceed to any great degree. Very little gas is produced from the TNT, but in one run, a large amount of hydrogen gas was produced from its reaction with aluminum.

It appears that the large discrepancies between the off gas analysis of different runs of tritonal is due to the samples not being completely homogeneous. The hydrolysate is dark red in color, and does not lend itself to analysis by NMR for the same reason as octol (see note on T. spont on page 3). Overall tritonal is very ideal for base hydrolysis using NaOH and can be performed at fairly low temperatures. Ammonia was not found to be as effective as NaOH, and tended to form insoluble salts with TNT.

Effectiveness of base hydrolysis on PBXN-109

PBXN-109 is one of the two explosives that contains HTPBD as a binder. Due to the resistance that the binder has to base, DMSO will be used to hopefully swell the binder, and allow access to the RDX. One problem that has come up is that the DMSO does not easily become separated from the binder after the experiment. This makes it difficult to determine the weight of the explosive after the reaction is complete. The temperature and pressure curves for the DMSO experiments are listed below the table.

20% DMSO Experimental Summary

| Experiment #	Mass of Explosive	Description	Concentration of Base	Volume of Base	Peak Temp.	Time at Temp.	% Reacted	Date
CSX-60*	51.958 g	1 piece	3M NaOH	500 mL	150°C	1hr	~4.5	2/28/96
CSX-61*	51.585 g	1 piece	3M NaOH	500 mL	150°C	1hr	~5.9	2/29/96
CSX-62*	51.49g	1 piece	3M NaOH	500mL	150°C	3 hr		2/29/96

50% DMSO experiment

Experiment #	Mass of Explosive	Description	Concentration of Base	Volume of Base	Peak Temp.	Time at Temp.	% Reacted	Date
CSX-63*	51.557g	1 piece	3M NaOH	500 mL	150°C	4hr	~<38.3	3/1/96

46% DMSO Experiment

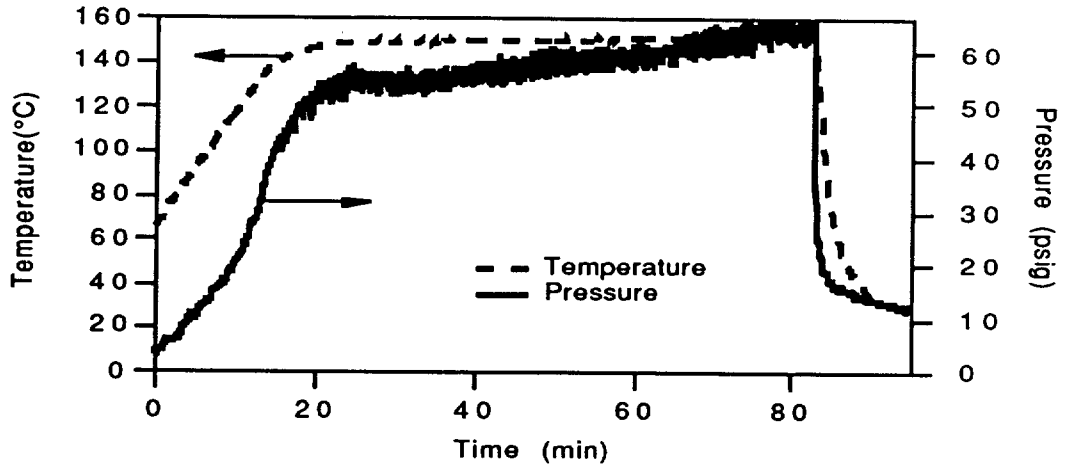| Experiment #	Mass of Explosive	Description	Concentration of Base	Volume of Base	Peak Temp.	Time at Temp.	% Reacted	Date
CSX-64*	51.606	1 piece	3M NaOH	500 mL	150°C	6hr	~34.6	3/2/96

* Stirring was used

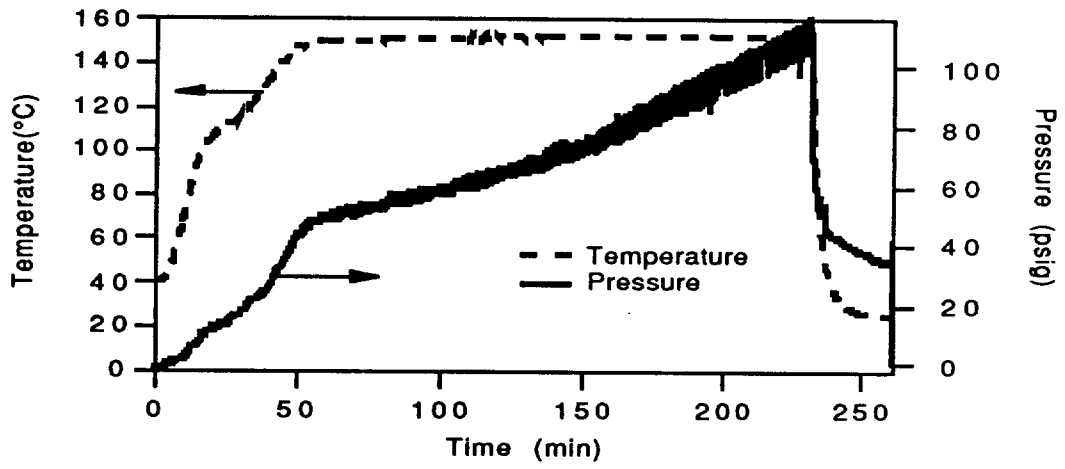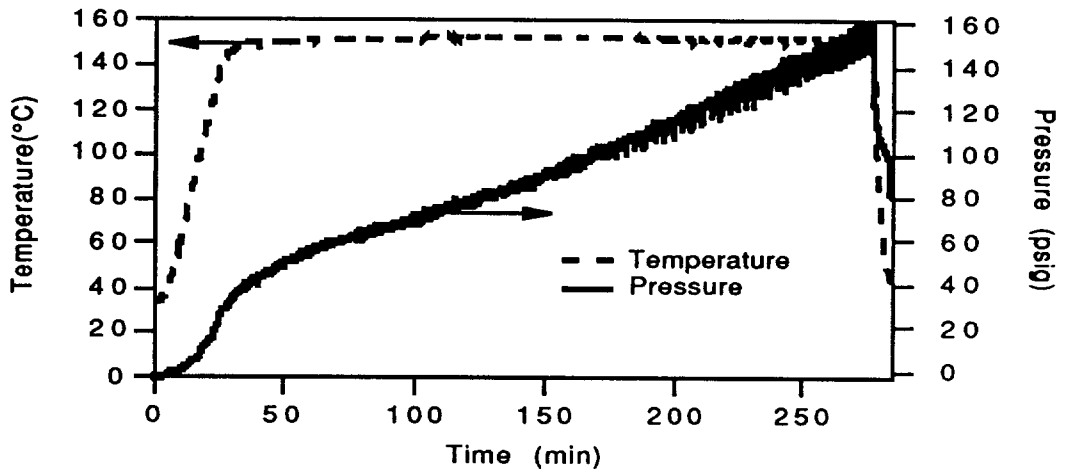## Temperature and Pressure Plots for the PBXN-109 Experiments

CSX-60
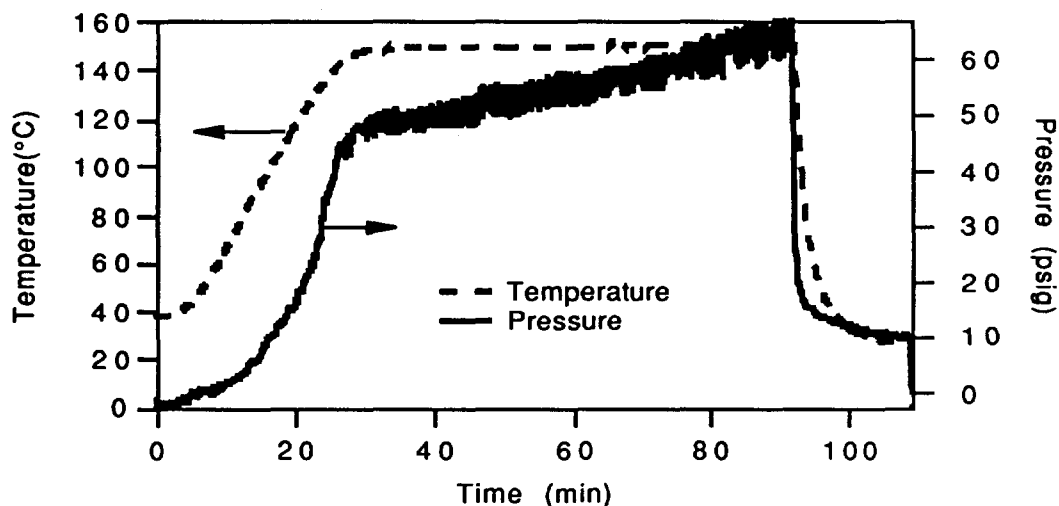
CSX-61

CSX-62

CSX-63

CSX-64
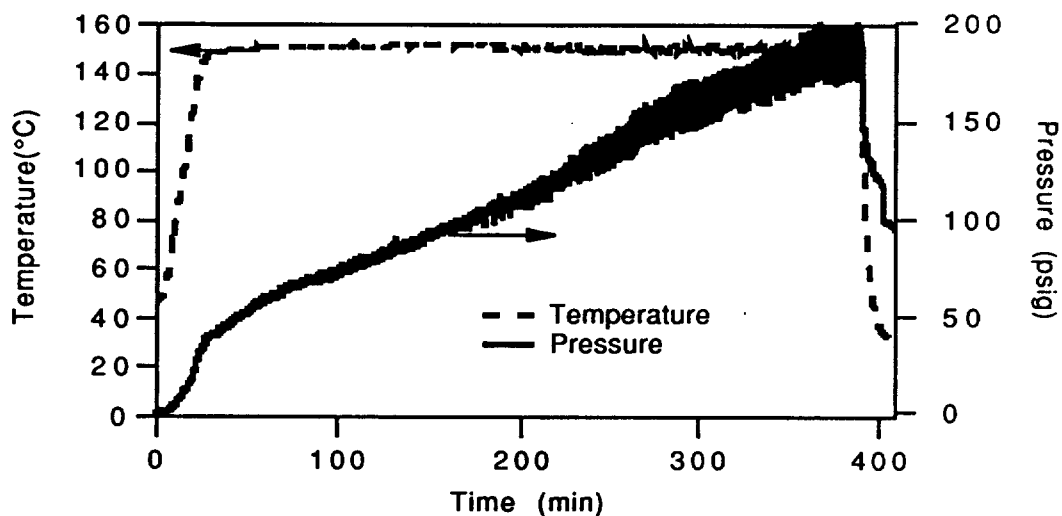
GC Results for PBXN-109 (Air Free)

Experiment	CO$_2$	H$_2$	N$_2$O	N$_2$	CO	O$_2$	Unknown
CSX-60		~61.1%	38.9%				
CSX-61		~61.3%	35.0%	2.69%			
CSX-62		~49.0%	34.1%	12.5%	0.088%		4.31%
CSX-63		~52.2%	5.84%	38.0%	0.078%		3.88%
CSX-64		~54.8%	2.86%	38.9%	0.079%		3.36%

The stoichiometry used for these experiment was 0.6 grams of NaOH per gram of PBXN-109. As the reaction proceeded, so did the percentage of hydrogen gas. Carbon monoxide and nitrogen gas stayed fairly constant, while the percentage of N$_2$O dropped. The sold left after CSX-64 was split into pieces had a very definable band between the reacted and the unreacted RDX was present. It appears that the reaction penetrated the solid only ~1/8" on each side, after six hours. PBXN-109 is a very difficult explosive to process, and pre-treatment will most likely be needed. The explosives could be sliced into smaller pieces to help to alleviate some of the mass transfer problems. A different solvent could also be used, but it is difficult to find one that works well with hot base, and it not a disposal problem. PBXN-109 might not be well suited for base hydrolysis. For a two inch piece, estimate between 50 and 70 hours for complete destruction of the RDX and aluminum. Neither ammonia hydroxide or sodium carbonate has been tried at this time.