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CONTRACTOR REPORT ARLCD-CR-78027

LABORATORY STUDY OF PYROLYSIS OF EXPLOSIVE CONTAMINATED WASTE

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FEBRUARY 1979

U.S. ARMY ARRADCOM

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

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ERRATA

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The attached table of contents was omitted from the above report. The title of the table on page 10 should be corrected to read as follows: Table 4. Noncondensible gases evolved during run no. 2139-2 (0.5% TNT)

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Army ammunition plants dispose of large quantities of neat explosives and chemical and explosive contaminated waste by either open air burning or incineration. These disposal techniques do not take advantage of the potential fuel value (7000 BTU/lb (15.7 MJ/kg)) of these wastes. This laboratory study was conducted to investigate the feasibility of utilizing a pyrolytic process to convert explosive contaminated waste into a useable, storable fuel. The study consisted of a series of laboratory scale pyrolysis runs on explosive contaminated waste. The data points for the runs were 0, 0.5, 1, and 2%

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20. explosive contamination by weight. The results of the study indicate that AAP waste can be safely processed with no adverse environmental impact, to produce a storable fuel having a heat content of 14,000 BTU/lb (31.3 MJ/kg) with an energy conversion efficiency of approximately 70%.

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PREFACE

The work described in this report was conducted at the Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia. The study was funded by the Manufacturing Technology Division, LCWSL, ARRADCOM, as part of MM&T Project No. 5774481 - Pyrolysis of Army Ammunition Plant Solid Waste. The objective of the project was to develop a system to convert explosive contaminated solid waste into synthetic fuel products (preferably liquid).

SUMMARY

Samples of mixed waste material and mixed waste material contaminated with levels of one-half percent, one percent, and two percent TNT were pyrolyzed at 650°C in a 15.2 cm tube furnace. The waste material was typical of contaminated waste disposed of by Army Ammunition Plants by either open air burning or incineration. The products of pyrolysis were all collected and analyzed. From the data, material and energy balances for each pyrolysis experiment were determined. Based on these experiments, 68 to 74 percent of the energy content of the input feed on a dry basis can be recovered in the char and oil, which are storable and transportable fuels. The data show that the energy content of the gases is in the range of 16 to 22 percent of the energy content of the input feed on a dry basis. The gases would have to be used on site.

Preliminary experiments with TNT contaminated waste did not produce any evidence of any explosion hazard in the thermal decomposition of the waste at 650°C. In the four pyrolysis experiments at 650°C in the 15.2 cm tube furnace there was no evidence of any explosion hazard with the contaminated waste. The data did not indicate that there would be any significant environmental impact from the pyrolysis of TNT contaminated waste.

INTRODUCTION

Objective. The objective of this project was to pyrolyze samples of waste contaminated with TNT on a batch basis in a 15.2 cm tube furnace and to analyze the feed material and pyrolytic products. Based on the data from these experiments, pyrolysis would be assessed as a means of energy recovery from the disposal of contaminated waste.

Background Information. Pyrolysis of carbonaceous material, such as agricultural, forestry and municipal wastes, produces char, oil, aqueous phase, and gas, and, therefore, provides a means for disposal of such materials and, at the same time, conversion into useful fuels. The Engineering Experiment Station at Georgia Tech has developed over the past several years, a continuous pyrolysis system for processing a wide variety of waste materials, and is capable of producing a liquid fuel product from solid waste with very little front-end preparation of feedstock. The process is licensed to the Tech-Air Corporation.[1] During the development of this process, four pilot plants were built and operated on campus at Georgia Tech. Two of these pyrolysis pilot plants are used for testing and research and development work with different of waste materials.

Pyrolysis offers the Army Ammunition Plants a potential means for disposal of contaminated wastes with recovery of a large part of the heating value of the waste. The useful fuels from the waste would be char, oil and gas. The char and oil are storable and transportable. The gas has a low BTU value and must be used on site.

EXPERIMENTAL WORK

Feed

The explosive shipping boxes material furnished by ARRADCOM and several corrugated paper boxes were sheared into one inch squares and stored separately in tightly closed plastic bags. A 9.1 kilogram sample of air dried pine chips from the laboratory's sample inventory was thoroughly mixed and stored in a tightly closed plastic bag. The liner paper supplied by ARRADCOM, a 908 gram lot of paper towels and a 454 grams of cotton rags were cut into small pieces and stored in separate containers.

The TNT (Eastman 268P[2]) was commercial grade 2,4,6-trinitrotoluene containing 10 percent water. Acetone solutions containing 0.222, 16.67, 33.33, and 66.67 grams, of the "wet" TNT were prepared and stored in tightly closed glass bottles for addition to a preliminary 10 gram pyrolysis sample and to 3,000 gram samples containing 0.5, 1.0, and 2.0 percent TNT for the tube furnace pyrolysis experiments.

A 100 gram composite sample for analysis and preliminary experiments was mixed using weighed portions of prepared materials:

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[1] Tech-Air Corporation, 2231 Perimeter Park, Suite 16, Atlanta, Georgia 30341, (404) 458-9096

[2] Eastman Organic Chemicals, Eastman Kodak Company, Rochester, New York, 14650

ARRADCOM explosive shipping box	63.0 g
ARRADCOM explosive liner paper	7.0 g
Pine wood chips	20.0 g
Corrugated paper box	3.33 g
Paper towel	3.33 g
Cotton rag	3.33 g

The weighed materials were mixed, passed through a Model 4 Wiley Mill using a 6-mm screen, remixed, and again passed through the mill with the same screen. The coarsely ground sample was passed twice through the Wiley Mill using a 2mm screen with thorough mixing after each pass. The ground sample was stored in a tightly closed glass container.

Each of the three kilogram pyrolysis samples was mixed separately using weighed portions of specified components:

ARRADCOM explosive shipping box	1900 g
ARRADCOM explosive liner paper	200 g
Pine wood chips	600 g
Corrugated paper box	100 g
Paper towels	100 g
Cotton rag	100 g
Total charge weight	3,000 g

No TNT was added to the first charge (No. 2139-1). Approximately one-quarter of the second charge (No. 2139-2) was moistened with 250 ml of the acetone solution containing 16.67 grams of "wet" TNT, (0.5% of charge weight of "dry basis" TNT). The solution storage bottle was rinsed with two 50 ml portions of acetone, and the washings were added to the charge. The treated portion of the charge was then thoroughly mixed with the remainder of the charge, and the mixture was spread to air dry overnight before being loaded into the pyrolysis tube. The same technique was employed to add 33.33 grams of "wet" TNT for the nominal one percent charge (No. 2139-3) and 66.67 grams of "wet" TNT for the nominal two percent charge (No. 2139-4).

Preliminary Pyrolysis Experiment. A 10.00 gram sample of the ground feed material was moistened with 10 ml of acetone containing 0.222 grams of dissolved "wet" TNT. The moistened sample was spread on a Teflon lined pan and air dried overnight.

Two 30-ml porcelain crucibles were packed with the dried material containing two percent TNT. As a control, two similar crucibles were packed with untreated (TNT-free) ground feed. The four crucibles were fitted with porcelain covers and placed on a wire rack in a cold muffle furnace. The furnace was heated to 650°C with the door open and held at 650°C for 1 hour. All personnel were excluded from the furnace room during this stage of the experiment, and the heating process was observed through a shatter proof window. At the end of the hour, the crucible covers were removed, and the samples were ignited to ash.

No evidence of detonation was observed during the course of this experiment. The crucible covers were not displaced during the heating stage. There was no difference in the appearance of the samples containing TNT and the control samples at any stage of the experiment. When the covers were removed, each crucible contained fibrous char with a thin layer of ash and light ash after complete ignition. These observations indicated that larger quantities of waste material containing two percent or less TNT could be carbonized in the tube furnace without risk of detonation if the explosive was widely dispersed throughout the charge.

<u>Tube Furnace Pyrolysis Experiments</u>. The four pyrolysis runs were carried out in a 15.2 cm tube furnace using an off-gas collection train. See Appendices A and B for detailed description of the equipment.

The first experiment (without TNT) was carried out as a cautious exploratory run to ascertain the reactive properties, e.g. heat transfer and gas evolution rates, of the mixed feed material. The furnace temperature was raised to 200°C held for 30 minutes, and then raised to 400°C. As the temperature inside the charge rose to 250°C, the gas evolution rate rose rapidly. After 45 minutes the furnace temperature was raised to 650°C, and the pyrolysis was completed. This experiment indicated that preheating the charge leads to a vigorous reaction when the rapid decompostion temperature is reached.

The remaining three pyrolysis runs were conducted with continuous heating to 650°C. This procedure established a temperature gradient within the charge and led to a less vigorous maximum rate of gas evolution than was observed in the initial run. Continuous heating of the tube with its temperature gradient within the charge is a more representative model of continuous pyrolytic converter conditions than the stepwise heating procedure used in the first experiment.

The maximum gas evolution rate in the first run exceeded 50 liters per minute for a brief period. This off-gas evolution rate exceeded the capacity of the train condensers, so that a relatively large amount of water vapor reached the drying tube. In the remaining runs, where steady heating was employed, the gas evolution rate did not exceed 25 liters per minute, and the weight increase of the drying tube was small.

Analytical Methods. The percent moisture and percent ash in the feeds and chars and the percent volatiles in the chars were determined by ASTM Method D1762-64. The acid insoluble ash in the feed and chars was determined by the method used for sand and insoluble silicates by the Association of Florida Phosphate Chemists. Heating values were determined by oxygen bomb calorimetry following the plain calorimeter method described in Parr Manual No. 130 (ref. 1). The bulk density of the chars was determined by weighing a measured volume of the unground material.

The heavy organic phases and the lighter aqueous phases were separated by decantation and weighed. The moisture content of each heavy organic phase and aqueous phase was determined by azeotropic distillation with toluene (Dean and Stark Method). The heating values of the heavy organic phases were determined by oxygen bomb calorimetry. The densities of these phases were determined by weighing well stirred 100 ml samples.

The yields of light oil in the dry ice traps were determined by weighing the condensates in tared, tightly stoppered polyethylene bottles. Heating values were determined by oxygen bomb calorimetry using a Parr volatiles cup.

The concentrations of the major gases in each of the collected samples for each of the four runs were determined separately by gas chromatography. Evolved gas yields were calculated by adding a volume of each gas in each of the collected samples. The gas remaining in the system at the end of each run was considered to have a composition corresponding to that of the final collected sample. The total volume of the final gas sample was taken to be the sum of the volume of the collection train and the volume of gas in the pyrolysis tube corrected to 101.33 kiloPascals at 25°C.

The concentration of nitrogen oxides in the gases evolved from the samples containing TNT were determined by a modification of ASTM Method D 1607 (ref. 2).

RESULTS AND DISCUSSION

Feeds and Recovered Chars. The yield weights of the chars and the detailed results of the laboratory analyses of the feed and recovered chars are summarized in table 1.

Table 1. Analysis of feed and recovered chars

	Feed	Run No. 1 (0%TNT)	Run No. 2 (0.5% TNT)	Run No. 3 (1% TNT)	Run No. 4 (2% TNT)
Yield Weight (g)	--	735.0	758.4	770.1	763.2
Percent Moisture					
Sample 1	6.21	.36	.33	.28	.33
Sample 2	6.53	.51	.29	.34	.43
Average	6.37	.44	.31	.31	.38
Percent Volatiles					
Sample 1	--	5.04	6.39	5.22	6.61
Sample 2	--	5.19	6.25	5.20	6.26
Average	--	5.12	6.32	5.21	6.44
Percent Ash					
Sample 1	1.48	6.20	6.23	6.21	6.21
Sample 2	1.54	6.12	6.34	6.32	6.32
Average	1.51	6.16	6.29	6.27	6.27
Percent Acid Insoluble Ash					
Sample 1	.29	1.40	1.96	1.38	1.57
Sample 2	.32	1.54	1.87	1.46	1.66
Average	.31	1.47	1.92	1.42	1.62
Higher Heating Value cal/g					
Sample 1	3,981	7,857	7,431	7,848	7,858
Sample 2	3,958	7,814	7,421	7,817	7,866
Average	3,970 (7,143)*	7,836 (14,104)*	7,426 (13,367)*	7,833 (14,098)*	7,862 (14,152)*
Bulk Density g/cm^3	--	7.7	6.5	7.2	7.3

---

*(Btu/lb)

These results are "as determined," i.e. not corrected for moisture. The bulk densities were determined using unground and uncompacted char. The char particles resulting from ARRADCOM explosive shipping box and liner paper and the wood retained the shapes of the original feed particles. The rag and paper towel char tended to powder on handling. The observed bulk densities could be greatly increased by compaction or grinding.

None of the observations made during the four pyrolysis runs can explain the relatively low heating value of the char from run no. 2.

Liquid Condensates. The yields and details of the laboratory analyses of the condensates are shown in table 2.

The relatively high amount of water reaching the dryer in run no. 1 is attributed to a vigorous reaction and high gas evolution rate in the preheated charge. The exceptionally high heating value of the light oil collected in the dry ice traps during run no. 2 is conspicuous. Occasional unusually high values in this condensate fraction have been observed in successive pyrolyses of wood or wood and bark feeds, but a suitable explanation is not obvious.

The organic phase was free flowing, and based on visual observation its viscosity increased only slightly with decreasing temperature. With these condensates the liquid phase layers from the four runs were readily separated in a separatory funnel.

Noncondensible Gases. The gases were analyzed by gas chromatography and the calculated compositions (major components) and heating values of the gases evolved during the four pyrolysis runs are shown in tables 3, 4, 5 and 6. The values shown include only the major gases evolved during each pyrolysis.

The average molecular weights of the gases evolved from each run are within the 28.5 to 29.5 range typical of gases from lignocellulosic materials carbonized near 650°C. The relatively low yield and heating value for the gases from run no. 1 are attributed to the slow, stepwise heating program.

The nitrogen oxide analyses are summarized in table 7. The sample numbers refer to the six 90 liter samples taken from each pyrolysis run and to the seventh or final sample. If all of the TNT nitrogen were evolved as nitrogen dioxide, the concentrations of nitrogen oxides evolved in the off-gases from runs 2, 3, and 4 would have been 8,100, 18,400, and 31,700 parts per million by volume, respectively.

Table 2. Analysis of liquid condensates

Pyrolysis Run No.	1	2	3	4
Organic Phase				
Yield Weight (g)	210.9	198.0	238.1	182.2
Percent Moisture				
Sample 1	10.3	17.5	17.8	14.1
Sample 2	10.4	17.2	17.6	14.1
Average	10.4	17.4	17.7	14.1
High Heating Value cal/g				
Sample 1	6,552	6,208	6,021	6,359
Sample 2	6,559	6,314	6,052	6,347
Sample 3	--	6,260	--	--
Average	6,556	6,261	6,037	6,353
	(11,800)*	(11,269)*	(10,866)*	(11,436)*
Density (g/ml)	9.2	9.1	9.2	9.2
lb/gal	1.103	1.091	1.103	1.103
Aqueous Phase				
Yield Weight (g)	1,166.8	1,184.5	1,200.8	1,255.4
Percent Moisture				
Sample 1	82.4	87.5	84.8	80.0
Sample 2	81.4	87.3	84.4	80.6
Average	81.9	87.4	84.6	80.3
Density g/ml	1.043	1.019	1.031	1.031
lb/gal	8.7	8.5	8.6	8.6
Dryer Condensate (g**)	113.9	11.0	20.7	21.7
Light Oil (Cold Trap)				
Yield Weight (g)	43.7	62.4	49.1	44.4
Higher Heating Value cal/g				
Sample 1	7,651	10,229	7,575	7,851
Sample 2	7,737	10,208	7,319	7,852
Sample 3	7,737	---	7,473	--
Average	7,708	10,219	7,456	7,852
	(13,875)*	(18,393)*	(13,408)*	(14,134)*

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[*] (Btu/lb)

[**] Assumed to be water.

Table 3. Noncondensible gases evolved during run no. 2139-1 (0%TNT)

Component	Liters	Volume Percent Zero% Air	Molecular Weight	Grams Per Mole Mixture	Mass Fraction	HHV* cal/g (BTU/LB)	HHV* cal/g Mixture (Btu/lb)
Carbon monoxide	147.4	32.7	28	9.156	.3115	2,415 (4,347)	752 (1,354)
Carbon dioxide	166.1	36.8	44	16.192	.5509	0	0
Hydrogen	46.0	10.2	2	.204	.0069	33,944 (61,100)	234 (422)
Methane	77.1	17.1	16	2.736	.0931	13,266 (23,879)	1,235 (2,223)
Ethane ethylene	8.37	1.86	30	.558	.0190	12,400 (22,320)	236 (424)
Propane propylene	4.69	1.04	44	.458	.0156	12,034 (21,661)	188 (338)
Butanes butenes	.62	.14	58	.081	.0028	11,838 (21,308)	33 (60)
Total liters:	451.1		$\bar{M}$:	29.39 (1)		Cal/g (BTU/lb)	2,678 (4,821)

DENSITY @ STP = $\frac{(29.4)}{(22.4)}$ = 1.3125 g/l (2,3,4)

HEATING VALUE = 1.3125 X 2,678 = $\frac{3,515}{(368)}$ $\frac{\text{kcal/m}^3}{(\text{BTU/SCF})}$

NONCONDENSIBLE GAS YIELD = 29.4 X $\frac{451.1}{22.4}$ = 592.1 grams

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1. $\bar{M}$ - "average molecular weight" of evolved gases
2. STP - standard temperature and pressure
3. 22.4 liters/mole of gas
4. 28.9 taken as "molecular weight" of air

* Higher heating value

Table 3. Noncondensible gases evolved during run no. 2139-~~1~~2 ~~(0%TNT)~~ (0.5%TNT)

Component	Liters	Volume Percent Zero% Air	Molecular Weight	Grams Per Mole Mixture	Mass Fraction	HHV* cal/g (BTU/LB)	HHV* cal/g Mixture (Btu/lb)
Carbon monoxide	178.4	32.4	28	9.072	.3181	2,415 (4,347)	768 (1,383)
Carbon dioxide	193.0	35.0	44	15.400	.5400	0	0
Hydrogen	66.5	12.1	2	.242	.0085	33,944 (61,100)	289 (520)
Methane	98.9	18.0	16	2.880	.1010	13,266 (23,879)	1,340 (2,412)
Ethane ethylene	7.88	1.4	30	.420	.0147	12,400 (22,320)	182 (328)
Propane propylene	5.99	1.1	44	.484	.0170	12,034 (21,661)	204 (368)
Butanes butenes	.19	.03	58	.017	.0006	11,838 (21,308)	7 (13)
Total liters:	550.9		$\bar{M}$: 28.52 (1)			Cal/g (BTU/lb)	3,290 (5,024)

DENSITY @ STP = $\frac{(28.5)}{(22.4)}$ = 1.2723 g/l (2,3,4)

HEATING VALUE = 1.2723 X 3,290 = 4,186 kcal/m^3 (372) (BTU/SCF)

NONCONDENSIBLE GAS YIELD = 28.5 X $\frac{550.9}{22.4}$ = 700.9grams

---

1. $\bar{M}$ - "average molecular weight" of evolved gases
2. STP - standard temperature and pressure
3. 22.4 liters/mole of gas
4. 28.9 taken as "molecular weight" of air

*Higher heating value

Table 5. Noncondensible gases evolved during run no. 2139-3 (1%-TNT)

Component	Liters	Volume Percent Zero% Air	Molecular Weight	Grams Per Mole Mixture	Mass Fraction	HHV* cal/g $\left(\frac{BTU}{LB}\right)$	HHV* $\frac{cal}{g}$ Mixture (Btu/lb)
Carbon monoxide	182.1	31.5	28	8.82	.3007	2,415 (4,347)	726 (1,307)
Carbon dioxide	203.9	35.3	44	15.53	.5295	0	0
Hydrogen	52.9	9.16	2	.18	.0061	33,944 (61,100)	207 (373)
Methane	109.2	18.9	16	3.02	.1030	13,266 (23,879)	1,367 (2,460)
Ethane ethylene	19.8	3.43	30	1.03	.0351	12,400 (22,320)	435 (783)
Propane propylene	7.8	1.35	44	.59	.0201	12,034 (21,661)	242 (435)
Butanes butenes	1.6	.28	58	.16	.0055	11,838 (21,308)	65 (117)
Total liters:	577.3		$\bar{M}$: 29.33 (1)			Cal/g (BTU/lb)	3,042 (5,475)

DENSITY @ STP $= \frac{(29.3)}{(22.4)} =$ 1.3080 g/l (2,3,4)

HEATING VALUE = 1.3080 X 3,042 = $\frac{3{,}979}{(416)}$ $\frac{\text{kcal/m}^3}{\text{(BTU/SCF)}}$

NONCONDENSIBLE GAS YIELD = 29.3 X $\frac{577.3}{22.4}$ = 755.1 grams

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1. $\bar{M}$ - "average molecular weight" of evolved gases
2. STP - standard temperature and pressure
3. 22.4 liters/mole of gas
4. 28.9 taken as "molecular weight" of air

* Higher heating value

Table 6. Noncondensible gases evolved during run no. 2139-4 (2%-TNT)

Component	Liters	Volume Percent Zero% Air	Molecular Weight	Grams Per Mole Mixture	Mass Fraction	HHV* cal/g (BTU/LB)	HHV* cal/g Mixture (Btu/lb)
Carbon monoxide	178.9	32.0	28	8.96	.3068	2,415 (4,347)	741 (1,334)
Carbon dioxide	195.1	34.9	44	15.36	.5260	0	0
Hydrogen	59.2	10.6	2	.21	.0072	33,944 (61,100)	244 (440)
Methane	89.6	16.0	16	2.56	.0877	13,266 (23,879)	1,157 (2,082)
Ethane ethylene	30.7	5.5	30	1.65	.0565	12,400 (22,320)	701 (1,261)
Propane propylene	5.5	1.0	44	.44	.0151	12,034 (21,661)	182 (328)
Butanes butenes	.2	.04	58	.02	.0007	11,838 (21,308)	8 (15)
Total liters:	559.2		$\bar{M}$: 29.20 (1)			Cal/g (BTU/lb)	3,033 (5,460)

DENSITY @ STP $= \frac{(29.2)}{(22.4)} =$ 1.3036 g/l (2,3,4)

HEATING VALUE = 1.3036 X 3,033 = 3,954 kcal/m^3 (413) (BTU/SCF)

NONCONDENSIBLE GAS YIELD $= 29.2 \times \frac{559.2}{22.4} =$ 729.0 grams

---

1. $\bar{M}$ - "average molecular weight" of evolved gases
2. STP - standard temperature and pressure
3. 22.4 liters/mole of gas
4. 28.9 taken as "molecular weight" of air

* High heating value

Therefore, the nitrogen oxides levels shown in table 7 are uncorrected values determined on the gases as collected. No corrections were made for the nitrogen initially present in the system or for the difference between the corrected volume of the final gas sample and the 90 liters collected in the first six samples of each run. The average values shown are simple arithmetic averages, i.e, one-seventh of the sum of the parts per million nitrogen oxides found in the separate collection bags.

The "uncorrected" values shown in table 7 adequately demonstrate that the TNT nitrogen is almost quantitatively reduced to nitrogen and possibly a trace of ammonia.

Dry Basis Data. Dry basis yield and analytical data were calculated from the experimental data shown in the preceding tables. The results of these calculations are summarized in Table 8.

In calculating the percent yield and heating value of the heavy organic condensate it was assumed that the oils dissolved in the aqueous phase (dissolved oils) are similar to those in the organic phase. The weight of the oil in the organic phase was therefore added to that of the dissolved oil to obtain a combined yield of heavy organics.

Mass and Energy Balance. A mass and energy balance based on one gram of bone dry mixed waste feed was calculated for each run. These data are given in table 9, and presented graphically in figures 1 and 2. Each of the quantities listed is the result of an independent determination, i.e. none of the values are estimated by difference, and the results are not normalized. The differences between the total percent yields and 100 percent and between the calculated energy yield and input energy, therefore, provide an approximation of the algebraic sum of the cumulative experimental errors in preparation, pyrolysis, and analytical work for each of the four pyrolysis experiments.

The latent heat values shown are based on 539.6 calories per gram as the heat of vaporization of water at 25°C. The sensible heats of the pyrolysis products are neglected, as they are believed to be small in comparison to the heat input from the furnace and the heat losses to the coolants in the condensation train and to the atmosphere from the exposed ends of the pyrolysis tube.

Table 7. Nitrogen oxides evolved

Gas Sample No.	Nitrogen Oxides (PPM)*		
	Run No. 2	Run No. 3	Run No. 4
1	1.9	50.0	44.0
2	0.7	5.0	8.5
3	0	2.6	2.2
4	0.8	1.3	1.4
5	0	1.1	0.8
6	0	0	0
7	0.5	0.7	0
Average	0.6	8.7	8.1

---

*PPM by volume.

Table 8. Calculated dry basis analytical data*

Pyrolysis Run No.	1	2	3	4
Feed				
Weight of Input	2,808.9	2,808.9	2,808.9	2,808.9
cal/g	4,238	4,238	4,238	4,238
	(7,629)†	(7,629)†	(7,629)†	(7,629)†
TNT				
Weight** Input	0	15.0	30.0	60.0
cal/g	3,613	3,613	3,613	3,613
	(6,504)†	(6,504)†	(6,504)†	(6,504)†
Char				
Weight of Yield	731.8	756.0	767.7	760.8
Percent Yield	26.1	26.9	27.3	27.1
Percent Volatiles	5.14	6.34	5.23	6.46
Percent Ash	6.9	6.31	6.29	6.29
Percent A. I. Ash††	1.48	1.93	1.42	1.63
cal/g	7,870	7,616	7,857	7,892
	(14,166)†	(13,709)†	(14,142)†	(14,206)†
Heavy Organic				
Weight of Organic Phase Oils	189.0	163.5	195.6	156.5
Weight of Dissolved Oils	211.2	150.4	184.9	247.3
Weight of Combined Yield	400.2	313.9	380.5	403.8
Percent Yield	14.2	11.2	13.5	14.4
cal/g	7,317	7,579	7,335	7,396
	(13,170)†	(13,643)†	(13,203)†	(13,313)†
Light Oils (Cold Trap)				
Weight of Yield	43.7	62.4	49.1	44.4
Percent Yield	1.6	2.2	1.7	1.6
cal/g	7,708	10,218	7,449	7,852
	(13,875)†	(18,393)†	(13,408)†	(14,134)†
Water				
Weight of Yield	900.3	888.4	887.6	841.1
Percent Yield	32.1	31.6	31.6	29.9
Noncondensible Gases				
Weight of Yield	592.1	700.9	755.1	729.0
Percent Yield	21.1	24.9	26.9	26.0
cal/g	2,678	2,791	3,042	3,033
	(4,281)†	(5,024)†	(5,475)†	(5,460)†

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* All weights in grams.

** Calculated from 820.7 Kg cal./gm. mole. Ref. R. A. Lange, ed. Handbook

†† Acid insoluble ash

† (BTU/1b)

Table 9. Mass and energy balances*

	Run No. 1			Run No. 2			Run No. 3			Run No. 4		
	%(wt)	g/ g	cal/ g	%(wt)	g/ g	cal/ g	%(wt)	g/ g	cal/ g	%(wt)	g/ g	cal/ g
Inputs												
Feed		1.00	4,238		1.00	4,238		1.00	4,238		1.00	4,238
TNT		0	0		.005	18		.01	36		.02	72
Total		1.00	4,238		1.005	4,256		1.01	4,274		1.02	4,310
Yields												
Char	26.1	.261	2,054	26.9	.269	2,049	27.3	.273	2,145	27.1	.271	2,139
Heavy Oil	14.2	.142	1,039	11.2	.112	849	13.5	.135	990	14.4	.144	1,065
Light Oil	1.6	.016	123	2.2	.222	225	1.7	.017	127	1.6	.016	126
Water	32.1	.321	--	31.6	.316	--	31.6	.316	--	29.9	.299	--
Gases	21.1	.211	565	25.0	.250	698	26.9	.269	818	26.0	.260	789
Latent Heat	--	--	173	--	--	171	--	--	171	--	--	161
	95.1	.951	3,954 (93.3%)	96.9	.969	3,992 (93.8%)	101.0	1.010	4,251 (99.4%)	99.0	0.99	4,280 (99.3%)

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*Basis on lb dry feed.

g/g Expressed as g input or yield per g of dry feed.
cal/g expressed as calories per gram of dry feed.

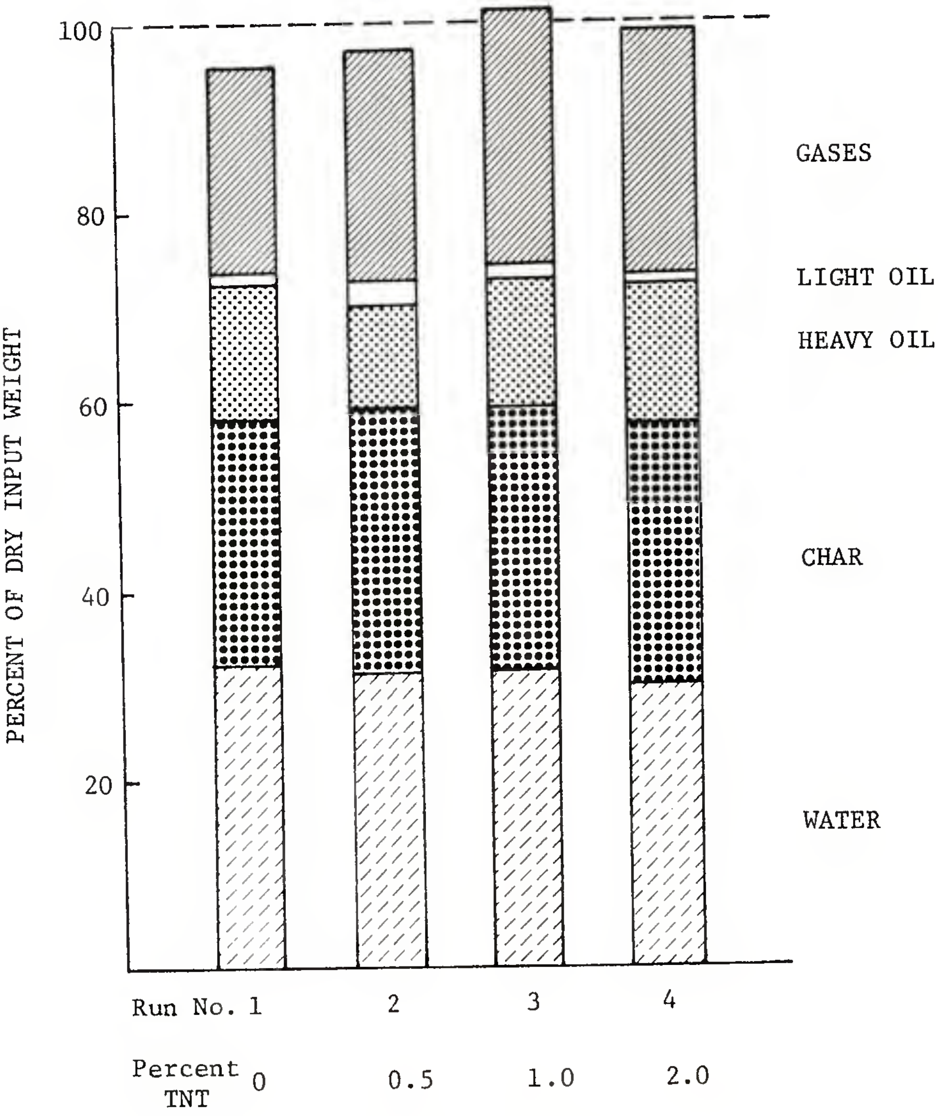


Figure 1. Mass yield distribution.

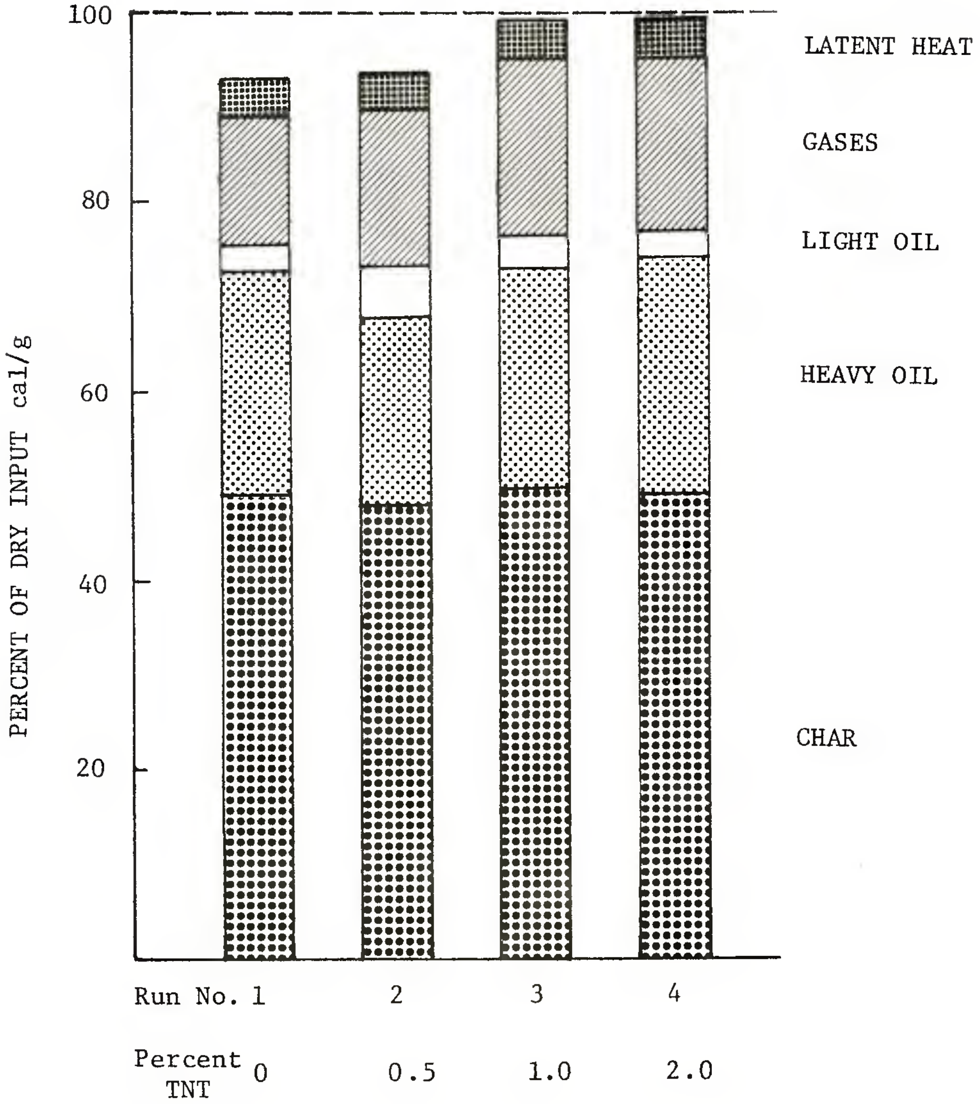


Figure 2. Energy yield distribution.

CONCLUSIONS

Based on the results of these bench scale studies, pyrolysis is a potentially useful method for disposal of TNT contaminated wastes from Army Ammunition Plants with recovery of approximately 70% of the input energy of the waste on a dry basis in the char and oil. Approximately 50% of the input energy of the feed is in the char with the remainder in the oil. The char and oil are storable and transportable fuels.

From the results of this work with waste contaminated with up to two percent TNT, no explosion hazard would be likely in a continuous pyrolysis system of the type developed at the Georgia Tech Engineering Experiment Station.

The results of the study do not indicate that there would be any significant emission problems from pyrolysis of TNT contaminated waste.

REFERENCES

1. Parr Manual No. 130, Parr Instrument Company, Moline, IL, 1960.

2. Methods of Air Sampling and Analysis, American Public Health Association, Washington, DC, 1969.

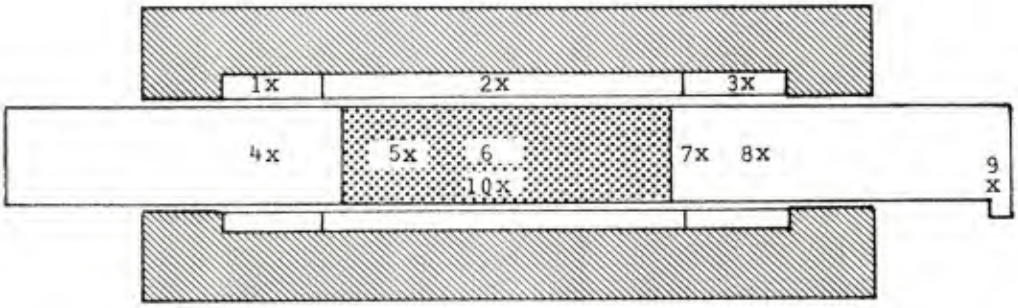
3. R.A. Lange, ed., Handbook of Chemistry, 6th edition, Handbook Publishing Company, Sandusky, OH, 2946.

APPENDIX A

15.2 CENTIMETER TUBE FURNACE APPARATUS

APPARATUS

The 15.2 cm pyrolysis unit consists of a 152.4 cm length of Schedule 40 six-inch stainless steel pipe heated by a three-zone Lindberg tube furnace. The ends are closed by means of heavy aluminum plates tightly compressed against silicone rubber gaskets. Stainless steel spacers are provided to confine the feed material to the uniformly heated center zone of the apparatus. The temperatures of the three separately controlled furnace zones and of selected locations within the tube are measured by chromel-alumel thermocouples and recorded. A schematic diagram of the tube furnace arrangement is shown in the figure with the location of thermocouples numbered 1 through 10.



Schematic diagram of tube furnace

The upstream end of the apparatus (left hand end in the diagram) is raised slightly to promote gravitational flow of the liquid products toward the 2.5 cm stainless steel exit tube located at the bottom of the downstream end of the pyrolysis tube. The spacer on the downstream end of the charge is slotted at the bottom to permit liquid flow. The exit tube ends in a one-inch stainless steel Whitey ball valve. This valve, which is used to exclude air from the pyrolized charge during cooling, is fitted to accept the upstream end of the condensate collection train.

OPERATION

The thermocouple leads were connected to a multi-channel recorder located above the furnace control panel outside of the pyrolysis laboratory. To avoid any possibility of premature ignition leading to detonation of the TNT in the charge, the furnace and the gas collection train were thoroughly purged with nitrogen before heating was begun.

With the ball valve at the downstream end of the furnace open heating was begun and continued until the rate of gas evolution decreased to less than two liters per hour and the thermocouples inside the charge recorded a sustained decrease in temperature for at least 15 minutes. The ball valve was then closed, and the furnace power was turned off. The furnace and the sealed tube containing the charge were cooled for 24 hours by a stream of forced air passed between the tubes and the refractory material of the furnace. The cooled furnace was then opened, and the carbonized charge was recovered.

APPENDIX B

TUBE FURNACE OFF-GAS COLLECTION TRAIN

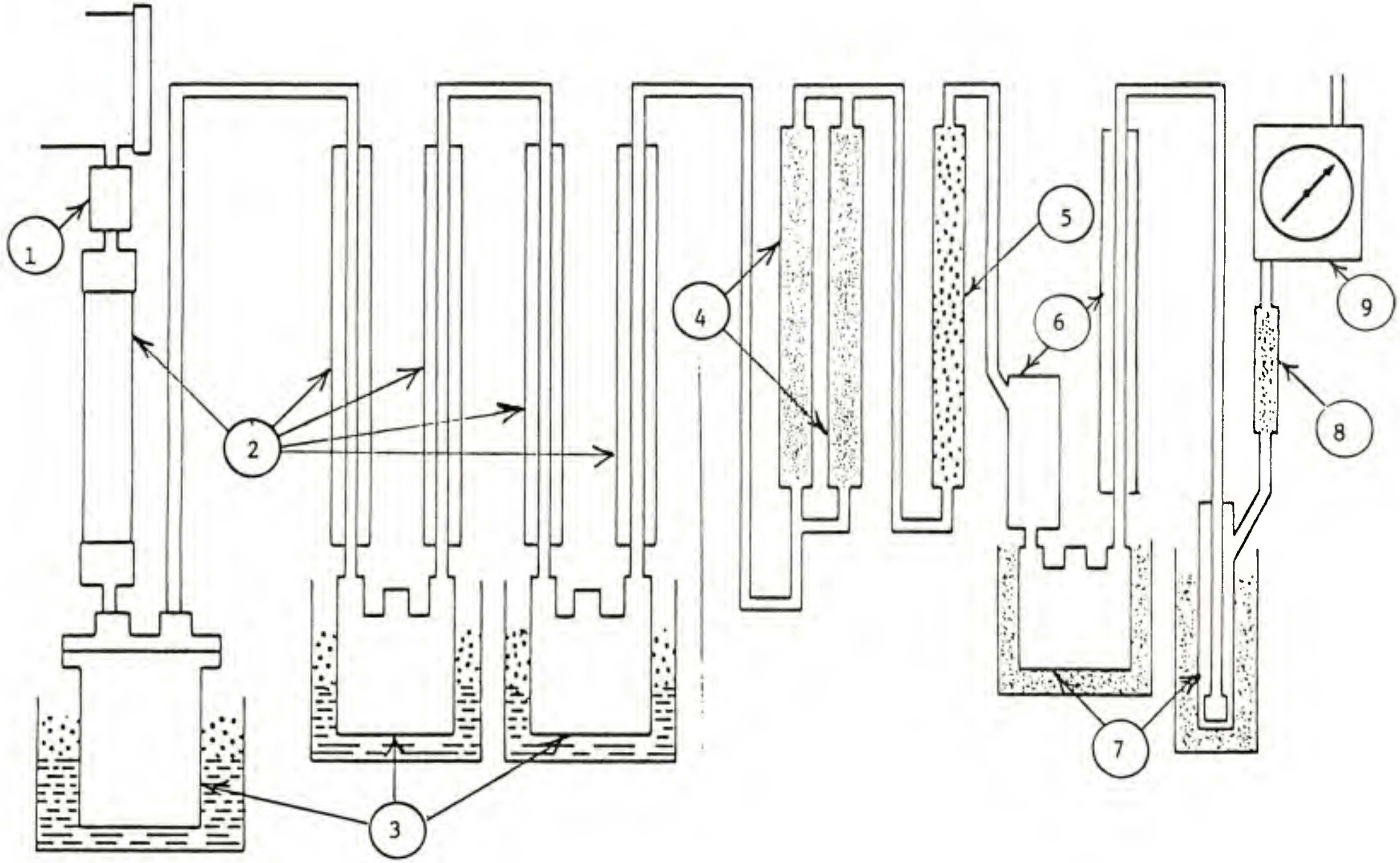
APPARATUS

A schematic diagram of the tube furnace off-gas collection is shown in the figure. Liquids and gases emerge from the pyrolysis tube through a stainless steel ball valve (1) into a series of water cooled condensers (2) and ice cooled traps (3). The first condenser is a jacketed stainless steel tube, which minimizes the risk of breakage that might occur in a heated metal-to-glass joint. The first trap is a resin kettle rather than a flask so that viscous condensates may easily be recovered. The gas stream then passes through a glass wool demister (4) and a calcium sulfate ("Drierite) column (5) into a series of cold condensers (6) and cold "light oil" traps (7). The condensers are chilled by ethanol circulating through a heat exchanger coil immersed in dry ice and ethylene glycol for most experiments or in dry ice and acetone when a large quantity of hydrogen sulfide is anticipated. The traps are immersed in a bath of dry ice and acetone. From the cold traps, the gases pass through a magnesium perchlorate drier (8) and a calibrated dry test meter (9) into a series of 96-liter gas collection bags. The quantity of magnesium perchlorate, which is necessary to prevent subsequent fouling of gas chromatographic columns, is held to a minimum to reduce possible explosion hazards.

OPERATION

After assembly and thorough leak testing, the train is connected to the pyrolysis tube and the refrigerants are added. The ball valve is opened at the start of the run and closed when the run is completed. During the run, 90-liter quantities of non-condensible gas are collected successively in a series of 96-liter gas collection bags.

After each bag is filled, it is kneaded to mix its contents and then emptied by aspiration through a gas collection tube. When the bag is approximately half-emptied, the gas collection tube is closed and labelled for laboratory analysis. If sulfur gases are of interest, a measured portion of the of the gas is drawn through a special sulfur gas absorption train. The remainder of the gas from each bag is then pumped to an exhaust fan.



Schematic diagram of the condensation train

On completion of the run the ball valve is closed and the weights of the condensates are determined. The condensates are then transferred to tightly closed containers and transported to the wet chemistry laboratory for analysis. The heavy organic and aqueous condensates are stored in a refrigerator. The light oils (from the dry ice traps) are stored in a freezer.

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