PP660 -12

Extraction & Recycling of LOVA Propellants Using Supercritical Fluids.
PP-660 FY98 Annual Report*

Dr. Jeffrey B. Morris
Army Research Laboratory
AMSRL-WM-BD
Aberdeen Proving Ground, MD 21005-5066

Performing Organizations

Army Research Laboratory - Aberdeen Proving Ground
Naval Surface Warfare Center - Indian Head Division
Applied Analytical, Inc.

Abstract

In a cooperative effort involving the Army Research Laboratory (ARL), the Naval Surface Warfare Center (NSWC), and Applied Analytical, Inc., the scale-up of a process to separate the components of Composition B high explosive using a supercritical fluid (SF) extraction process was investigated. New solubility data for TNT and wax in SF CO_2 was measured as part of this study. Batch SF extraction runs were carried out up to the 100-gram level, with results substantially the same as in the previous laboratory-scale process.

---

*The timeframe covered in this interim report extends from 19 May 1998 through 30 September 1998.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **SEP 1998**	2. REPORT TYPE	3. DATES COVERED **19-05-1998 to 30-09-1998**

4. TITLE AND SUBTITLE **Extraction & Recycling of LOVA Propellants Using Supercritical Fluids**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Research Laboratory,AMSRD-ARL-WM-MD,4600 Deer Creek Loop,Aberdeen Proving Ground,MD,21005-5069**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

In a cooperative effort involving the Army Research Laboratory (ARL), the Naval Surface Warfare Center (NSWC), and Applied Analytical, Inc., the scale-up of a process to separate the components of Composition B high explosive using a supercritical fluid (SF) extraction process was investigated. New solubility data for TNT and wax in SF C02 was measured as part of this study. Batch SF extraction runs were carried out up to the 100-gram level, with results substantially the same as in the previous laboratory-scale process.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**10**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Background

In the past, waste and excess energetic materials have been disposed of through the means of open burning and open detonation (OB/OD). As an alternative to OB/OD, we have investigated the use of supercritical fluid (SF) technologies for the separation and recovery of valuable nitramine energetic materials from propellant and explosive formulations. The SF technologies we have investigated have involved the use of environmentally benign carbon dioxide (CO_2) as a process solvent. With recent increases in the procurement costs of virgin RDX, the use of reclaimed RDX is being given greater consideration.[1] Current RDX production costs are in the range of $12 to $15 per pound, as compared to $2 to $4 per pound several years ago. Two potential sources of RDX available for reclamation are Composition A-3, type I, and Composition B high explosives. The quantities of RDX potentially available for recovery from both existing industrial stocks and demilitarization inventories are much greater for Composition B than for Composition A-3. Composition B is a 60:40 mixture of RDX:TNT, with 1% added wax.

Objective

The primary objective of this project for FY98 was to demonstrate the scale-up of a process developed for the separation and recovery of RDX from Composition B high explosive. The process involves SF extraction (SFE) of the TNT and wax from Composition B. The TNT and wax components of Composition B are much more soluble in SF CO_2 than is RDX. RDX is recovered as a non-extractable material in this process.

Technical Approach

Recent work at the Army Research Laboratory (ARL) has demonstrated that RDX can be separated from Composition B high explosive, on the gram scale, via a SFE process.[2] For FY98, our planned approach was to incrementally scale this technology up to processing of 300 gram batches of Composition B. The Indian Head Division of the Naval Surface Warfare Center (NSWC) has the appropriate facilities to conduct the pilot-scale SF processing runs on energetic materials, using extraction vessels with volumes ranging from 0.5-liter up to about 20-liters. The services of Applied Analytical, Inc. were employed to generate quantitative TNT and wax solubility data in SF CO_2.

In the pressure-temperature (P-T) phase diagram of Figure 1, the lines separating the solid, liquid, and gas phases of CO_2 are equilibrium coexistence curves that represent phase boundaries. For fluid-based extractions, we are primarily concerned with the liquid and gas regions on the phase diagram. The liquid-gas coexistence curve extends between two well-defined points: the triple point and the critical point. At the triple point, the solid, liquid, and gas phases exist in equilibrium. The liquid-gas coexistence curve terminates abruptly at the critical point, where the densities of the gas and liquid phases in equilibrium become identical, and the demarcation between the gas and liquid disappears. For CO_2, the triple point occurs at 217 K and 5.18 bar, and the critical point occurs at 304 K (T_c) and 73.8 bar (P_c). A fluid with temperature and pressure greater than that at the critical point is referred to as supercritical fluid. In the supercritical region of the phase diagram, a single phase exists that is neither a gas nor a liquid, but has properties intermediate to those of gases and liquids. Supercritical fluids have gas-like viscosities (typically an order of magnitude below those of conventional solvents) and diffusivities (typically 1–2 orders of magnitude greater than those of conventional solvents), zero surface tension, and liquid-like densities. The gas-like viscosities and diffusivities of supercritical fluids imply superior mass transport characteristics for SFE as compared with conventional organic solvent extraction.

Figure 2 shows a block schematic diagram for a supercritical fluid extractor. A reservoir of liquid CO_2 supplies a pump that is used to bring the fluid to the operating pressure. The high-pressure liquid flows into a heated vessel that contains the material to be extracted. When the solute-rich fluid exits the extraction vessel, it passes through a pressure reduction valve, and into a separator, where the extracted material is collected. The CO_2 exiting the separator may be vented as a gas, or collected, recompressed, chilled, and used to replenish the liquid supply reservoir in a closed-loop operation. Omitted from Figure 2 are ancillary equipment, such as fluid pre-heaters, isolation valves, pressure and temperature gauges, and flow meters.

Supercritical fluid extraction equipment ranges from the analytical scale, with extraction vessel volumes of 1 ml or less, through process scale, with vessel volumes of greater than 100 liters.

Project Accomplishments

The milestones 1–5 were completed through the end of FY98, with modification as appropriate.

1. Initiate reconfigure and relocate SF–CO_2 equipment.
2. Initiate laboratory scale-up protocol—conduct base characterization on Comp B and Octol, and ingredients.
3. Initiate SF–CO_2 scale-up deployment for Comp B—define process parameters, temperature, pressure, and Comp B to CO_2 ratio.
4. Initiate large lab-scale process studies.
5. Scale-up process to 100-gram batches.

Initiate reconfigure and relocate SF–CO_2 equipment. Supercritical CO_2 processing equipment for 100-mL through 3-L vessel sizes was relocated within the Naval Surface Warfare Center–Indian Head Division (NSWC) in order to meet NSWC safety requirements.

Initiate laboratory scale-up protocol—conduct base characterization on Composition B and Octol, and ingredients. As part of the base characterization of Composition B, Dr. Larry Taylor of the Virginia Polytechnic Institute and Applied Analytical, Inc., completed more detailed laboratory studies on the solubilities of TNT and wax in CO_2[3] than were previously available in the literature[4]. The results of these studies are presented in Tables 1–2 and Figure 3–4. Each data point represents the average of 5 individual replicate measurements. For TNT, the data from Table 1 was converted to TNT mole fraction (X_{TNT}), and was fit as a function of density using a procedure similar to that used previously to fit RDX solubility data in CO_2[5]. Since waxes are oligomeric in nature, with a distribution of molecular weights, the solubility fitting analysis that was applied to RDX and TNT solubility data cannot be used. The data from Table 2 was plotted directly in Figure 4. It is expected that supercritical fluid extraction will tend to fractionate the wax. The data presented in Table 2 may not represent an even solubility distribution across the molecular weight distribution of the wax oligomers. In all likelihood, the lighter fractions of the wax will exhibit greater solubility in supercritical CO_2. No measurements of wax molecular weight distributions were made as part of this solubility study.

Table 1. Mass solubility of TNT in CO_2 (mg RDX/g CO_2) as a function of temperature and pressure.

P (bar)	Solubility @ 308 K	Solubility @ 323 K	Solubility @ 343 K
139	5.3	4.2	13.3
253	11.0	13.7	25.6
375	14.9	18.0	30.3

Table 2. Mass solubility of wax in CO_2 (mg wax/g CO_2) as a function of temperature and pressure.

P (bar)	Solubility @ 308 K	Solubility @ 328 K	Solubility @ 343 K
139	0.34	0.39	0.46
253	0.40	0.62	0.79
375	0.62	1.21	1.61

Initiate large lab-scale process studies and scale-up process to 100 gram batches. The Composition B SFE process was scaled up to the 100 gram level with a moderate degree of success. However, as was noted on the gram-scale SFE runs [2], the recovered RDX had the appearance of beach sand, rather than the preferred white appearance of virgin RDX. A small number of post-processing solvents were used without much success in an attempt to whiten the appearance of the recovered RDX. In the opinion of the technical POC at NSWC, on the basis of the discoloration, no formulator would choose to use this material. It was decided not to scale this process up to the 300-gram level until recovered RDX with a more agreeable appearance could be recovered. It is expected that scale-up from the 100-gam to 300-gram level would involve minimal complications.

High performance liquid chromatographic (HPLC) analysis of the recovered RDX revealed removal of the TNT component, and gravimetric analysis confirmed the removal of the wax.

Given the processing and morphology of Composition B, it was concluded that this discoloration was due to a small amount of material that was coated on the surface of the recovered RDX crystals. It is anticipated that recrystallization of the recovered RDX would result in that same white appearance is seen with virgin RDX. However, recrystallization of the recovered RDX would add an additional processing cost of \$3 to \$6 per pound.[1]

Papers that resulted from this FY98 study will be presented at the 1999 JANNAF Propellant Development & Characterization Subcommittee and Safety & Environmental Protection Subcommittee Joint Meeting; the citations for these papers are listed in Appendix A. Future plans involve a transition from ARL to NSWC for continued investigation of a CO_2-based extraction process for the recovery of RDX from Composition B. Since FY98 was the final year of SERDP funding for this project, a more detailed project final report is currently under preparation.

Acknowledgments

This research was supported wholly by the U. S. Department of Defense, through the Strategic Environmental Research and Development Program (SERDP) and through in-house labor matching funds provided by NSWC. The author of this report would also like to acknowledge the following people for their contributions to the FY98 portion of this project: Mr. George W. Nauflett, Mr. Robert E. Farncomb, and Ms. Sibyl L. Turner of the Naval Surface warfare Center, and Dr. Larry T. Taylor and Dr. Medhi Ashraf-Khorassani of Applied Analytical, Inc.

References

1. Newman, K. E.; Kenar, K. T.; Rosenberg, S. J.; Yim, K. B. *Feasibility of Reclamation and Reuse of RDX for Joint Mine Countermeasures Programs.* IHTR 2036, Naval Surface Warfare Center, Indian Head, MD, 31 October 1997.

2. Morris, J. B. Separation of RDX from Composition B Via a Supercritical Fluid Extraction Process. *Proceedings of 1997 JANNAF Safety and Environmental Protection Subcommittee Meeting*, CPIA Pub. 647, vol. I, Sunnyvale, CA, March 1997, pp. 283-290.

3. Ashraf-Khorassani, M.; Taylor, L. T.; Nauflett, G. W.; Farncomb, R. E. Solubility of TNT and Wax in Supercritical Carbon Dioxide. To be published in *Proceedings of 1999 JANNAF Propellant Development & Characterization Subcommittee and Safety & Environmental Protection Subcommittee Joint Meeting*, Johns Hopkins University/Chemical Propulsion Information Agency, April, 1999.

4. Teipel, U.; Gerber, P.; Kreause, H. H. Characterization of the Phase Equilibrium of the System Trinitrotoluene / Carbon Dioxide. *Propellants, Explosives, Pyrotechnics*, vol. 23, pp 82–85 (1998).

5. Morris, J. B. Solubility of RDX in Dense Carbon Dioxide at Temperatures between 303 K and 353 K. *Journal of Chemical and Engineering Data*, vol. 43, pp 268-273 (1998).

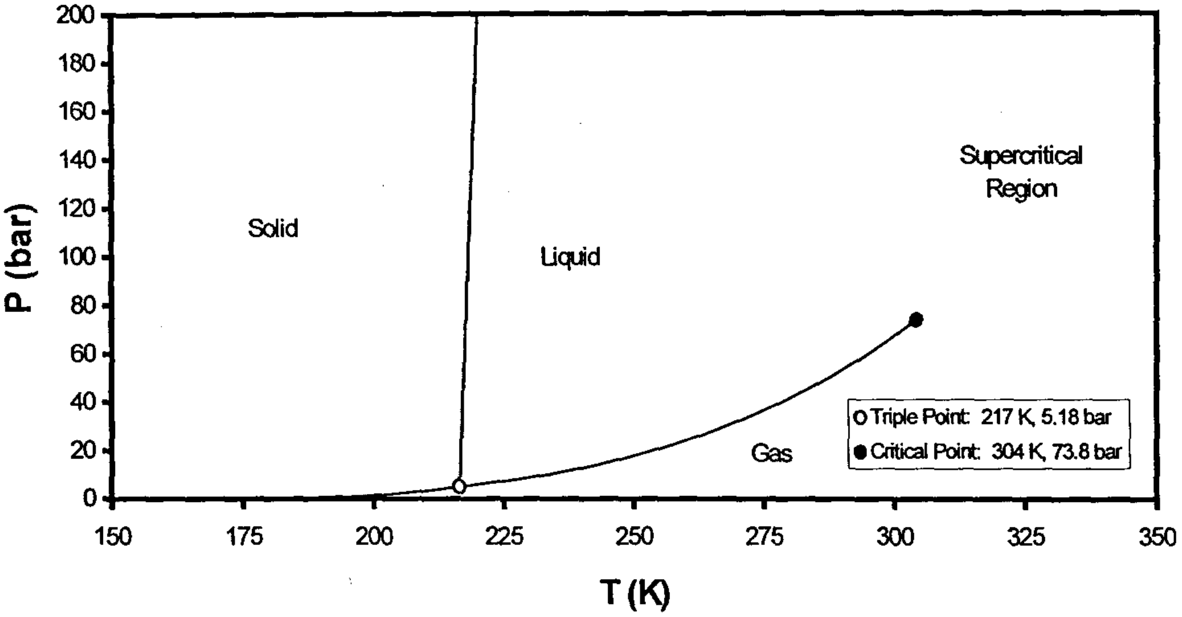

Figure 1. Pressure-temperature phase diagram for CO_2.

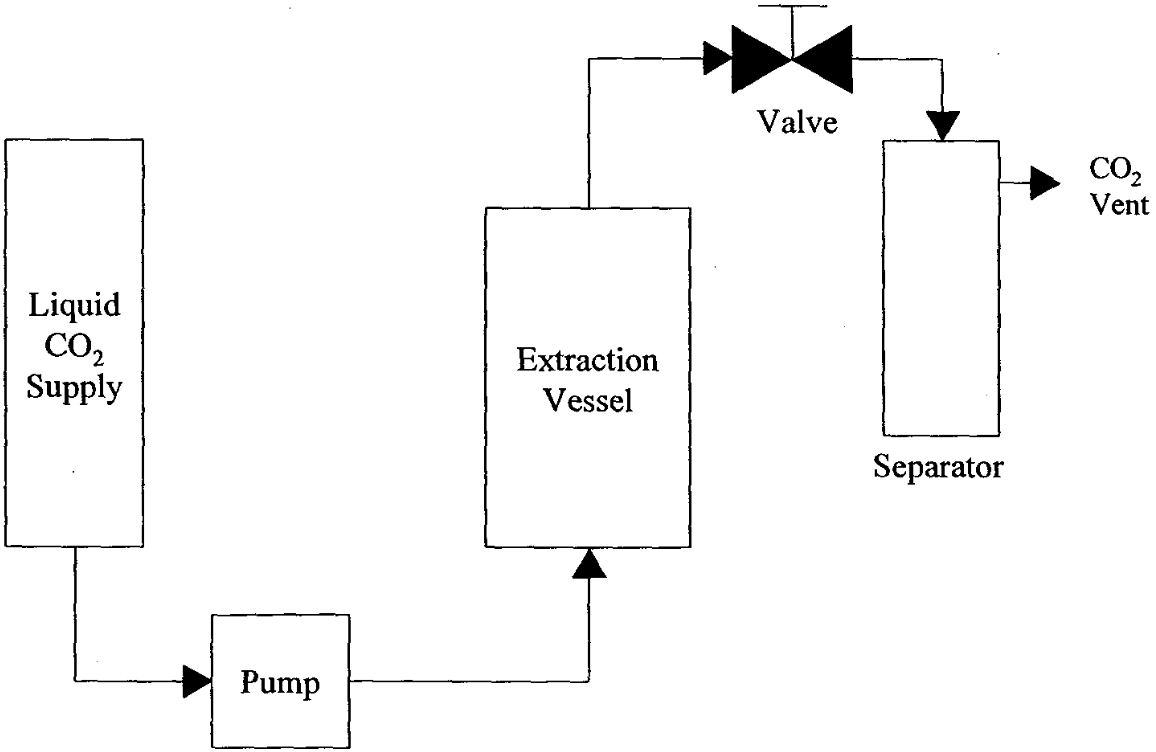

Figure 2. Schematic of supercritical fluid extraction apparatus.

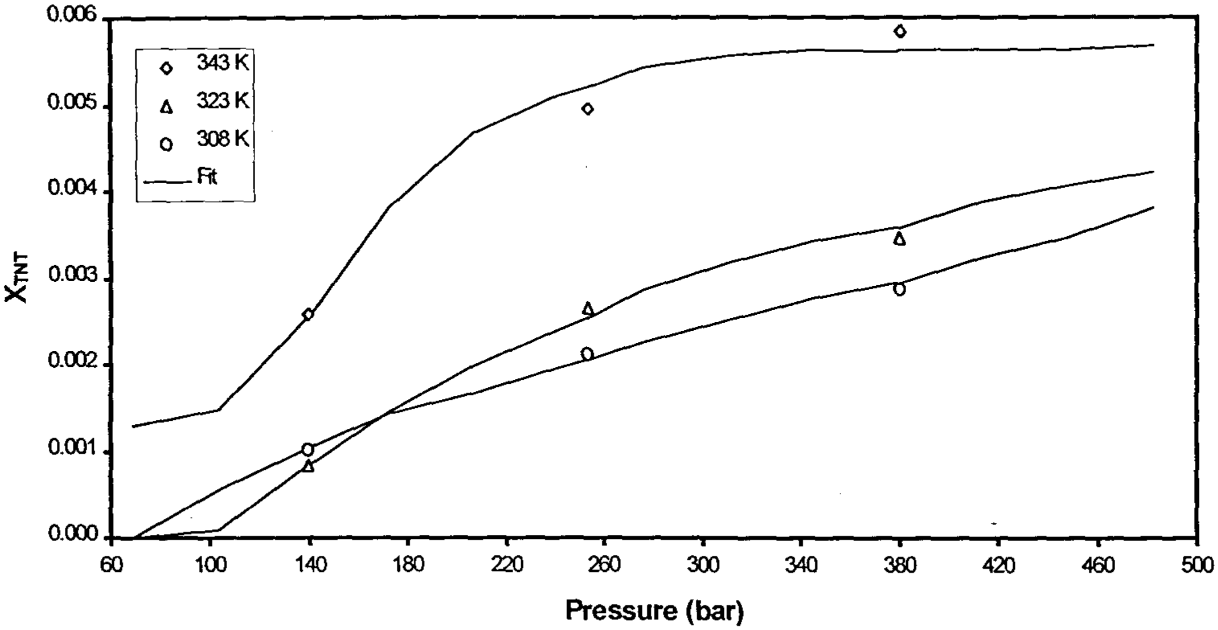

Figure 3. TNT solubility isotherms in CO_2.

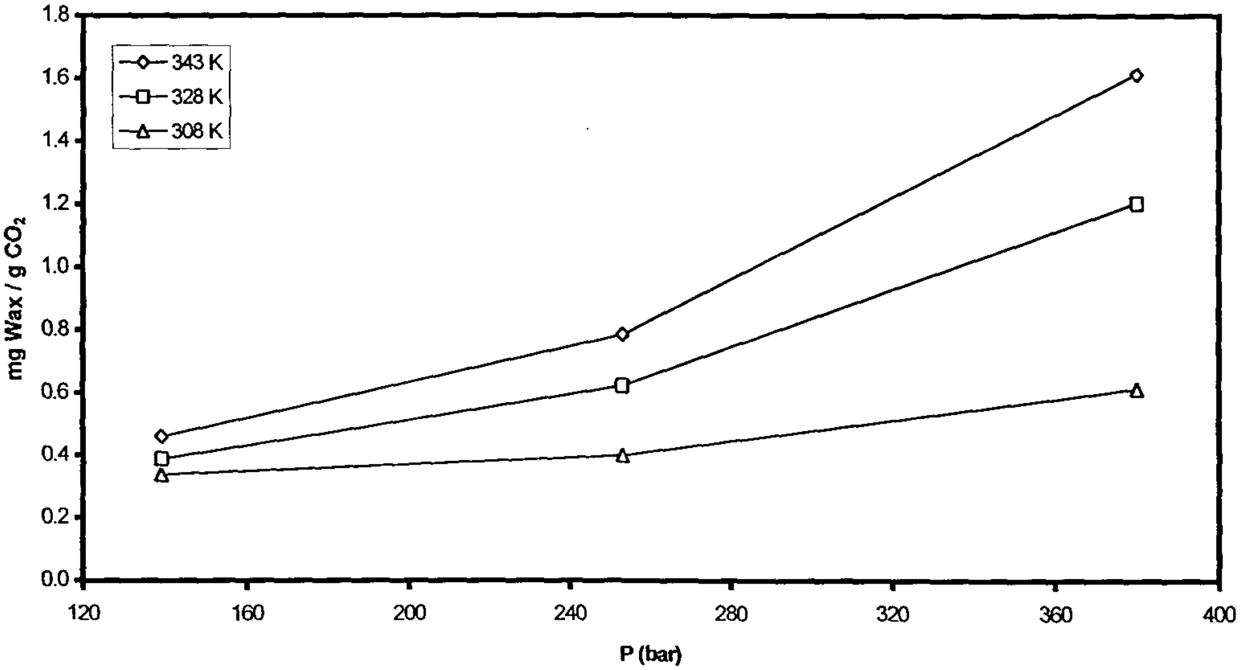

Figure 4. Wax solubility isotherms in CO_2.

Appendix A – Publications

Turner, S. L.; Farncomb, R. E.; Nauflett, G. W.; Taylor, L. T. Fractionation of TNT, Wax and RDX from Comp B with Supercritical Carbon Dioxide. To be published in *Proceedings of 1999 JANNAF Propellant Development & Characterization Subcommittee and Safety & Environmental Protection Subcommittee Joint Meeting*, Johns Hopkins University/Chemical Propulsion Information Agency, April, 1999.

Ashraf-Khorassani, M.; Taylor, L. T.; Nauflett, G. W.; Farncomb, R. E. Solubility of TNT and Wax in Supercritical Carbon Dioxide. To be published in *Proceedings of 1999 JANNAF Propellant Development & Characterization Subcommittee and Safety & Environmental Protection Subcommittee Joint Meeting*, Johns Hopkins University/Chemical Propulsion Information Agency, April, 1999.

Morris, J. B. Supercritical Fluid Extraction of Triple-Base and LOVA Gun Propellants. To be published in *Proceedings of 1999 JANNAF Propellant Development & Characterization Subcommittee and Safety & Environmental Protection Subcommittee Joint Meeting*, Johns Hopkins University/Chemical Propulsion Information Agency, April, 1999.