Study on Stripping-down TNT-based Explosives from Waste Munitions by Supercritical CO_2 Fluid for Industrial Applications

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ABSTRACT

The applications of supercritical fluid for chemical industry are rapid developing in recent years. Using CO_2 as a solvent have some advantages like low pollution, low cost, well chemical stability and low operating temperature. This research explores the industrial process for using the supercritical CO_2 fluid to strip and recover the TNT and Composition B explosive (containing RDX and TNT) from the waste munitions. The industrial-grade supercritical fluid stripping apparatus with container of 50 liters is engineered specifically to evaluate the feasibility of practical industrial application for stripping-down explosives from the waste munitions by supercritical CO_2 fluid. The 155 mm artillery projectiles filled with TNT and the 105 mm artillery projectiles filled with Composition B explosive are used to test the removal percentages of TNT and Composition B explosive through the supercritical CO_2 fluid under different temperature, pressure and residence time conditions. The experimental results show that TNT and Composition B explosive can be completely removed from 155 mm and 105 mm artillery projectiles, respectively. It is expected this new technology will be able to solve the problems of industrial safety and environmental protection on disposal of waste munitions in the future.

Keywords: Disposal of waste munitions, Trinitrotoluene, Supercritical fluid technology, Stripping-down, Industrial applications.

以超臨界二氧化碳流體脫除廢彈 TNT 系炸藥的工業應用之研究

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摘　要

超臨界流體萃取技術是近年來化學工業迅速發展的技術，若搭配以 CO_2 為溶劑，則具有低汙染、低成本、化學安定性良好及可在低溫操作等優點。本研究探討利用超臨界 CO_2 流體從廢舊彈頭脫除及回收 TNT 及 B 炸藥（包含 TNT 及 RDX）的工業程序，由於已證實 TNT 在超臨界 CO_2 流體中有熔點降低的現象，因此特別設計具有 50 公升容器的工業級超臨界流體萃取設備，藉以評估以超臨界 CO_2 流體從廢舊彈頭脫除炸藥之工業應用的可行性，測試樣品使用裝填 TNT 的 155 公厘彈頭及裝填 B 炸藥的 105 公厘彈頭，分別在不同的溫度、壓力及滯留時間的條件下，使用超臨界 CO_2 流體測試 TNT 及 B 炸藥的移除率，實驗結果顯示 TNT 及 B 炸藥能完全從 155 及 105 公厘彈頭移除，未來新的技術預期將能解決廢舊彈藥處理衍生的工安及環保問題。

關鍵詞：廢舊彈藥處理、TNT、超臨界流體技術、脫除、工業應用。

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Ⅰ. INTRODUCTION

All munitions have a finite lifetime. Storage of these munitions can be costly and potentially hazardous when they reach the end of their lives through ageing processes or deterioration. The conventional methods for the disposal of obsolete and aged munitions include open burning/open detonation (OB/OD), controlled incineration, hot water washout, autoclave meltout, water jet cutting, cryofracture, supercritical water oxidation, plasma waste converter, etc. These disposal methods may be used because of their simplicity, low cost, effectiveness and safety, but the environmental impacts also should be taken into consideration. Furthermore, the potentially valuable energetic materials will be destructed by these disposal methods. Therefore, alternative technologies need to be developed in an environmentally-friendly manner. The resource recovery of the energetic materials also should be an important consideration in the new disposal technologies [1, 2, 3].

Trinitrotoluene (TNT) is one of the most commonly explosives used for military applications [4]. Many formulations of military high explosives are based on TNT and used in a variety of military ordnance applications, like bursting charges for projectile warheads or land mines. But the disposal of munitions containing cast explosives (TNT and Composition B explosive) are a really troublesome problem. Typical methods include melting out, steaming/water washout and solvent washout of the TNT-based explosive from the projectile casing [5]. Melting out and steaming/water washout are operated at a temperature above the melt point of TNT and take high explosive phase transition from solid to slurry. Solvent washout is solution high explosive to be separated. These three methods have some disadvantages like time consuming, inappropriate for reclaiming high explosives, generating too much polluted waste water which is required to treat in prohibitively high cost, and low efficiency.

Supercritical fluid extraction using carbon dioxide (CO_2) has been recognized as a green technology, which is also a rapidly developing technique for chemical industry in recent years. It is a clean and versatile solvent with gas-like diffusivity and liquid-like density in the supercritical phase, which has provided an excellent alternative to the use of chemical solvents. Morris et al. [6, 7, 8] have presented a method for the extraction of TNT from the high explosives through the use of supercritical CO_2 fluid. This method can recover TNT at temperature above the melting point of TNT. Considering the factors of environmental protection and resource recovery, the supercritical fluid extraction may be a better method for the disposal of munitions containing TNT. However, Teipel et al. [9] have reported an extensive set of data that the solubility of TNT in supercritical CO_2 fluid is very low. Agrawal et al. [10, 11] have used isothermal-isobaric Monte Carlo (NPT–MC) simulations and the Widom test particle method to predict the solubilities of TNT and RDX in supercritical CO_2 fluid. The results also reveal that the solubilities of TNT and RDX are very low. Therefore, this method needs a great volume of CO_2 and much extraction time for recovering TNT at high temperature, and then increases the operation cost.

There is a particularly noteworthy phenomenon that the solid can be melted at temperatures lower than its normal melting point in the presence of a supercritical fluid [12-14]. Lucien and Foster [12] have pointed out that the melting point of a pure solid can be depressed significantly under the influence of high pressure CO_2 and a similar phenomenon exists in the case of eutectic points of solid mixtures. Lian et al. [13] have developed a method based on the Clapeyron equation for predicting the maximum melting point depression of a compound in the presence of a supercritical fluid. Pasquali et al. [14] have demonstrated that the melting temperature decreases linearly with pressure at low pressure and is followed by an approximately constant region at higher pressure. Therefore, a novel method of stripping-down explosive from the simulated warhead in laboratory scale is proposed based on the melting point depression of solid explosives in supercritical CO_2 fluid [15].

In this study, the phenomenon of melting point depression of TNT in supercritical CO_2 fluid is applied to strip down explosives (TNT and Composition B explosive) from the warhead at relatively lower temperature. The industrial-grade supercritical fluid stripping apparatus is engineered specifically and the 155 mm artillery projectiles filled with TNT and the 105 mm artillery projectiles filled with

Composition B explosive are used to test the removal percentages of TNT and Composition B explosive through the supercritical CO_2 fluid under different temperature, pressure and residence time conditions. It is expected this new technology could be able to solve the problems of disposal of waste munitions on the industrial safety and environmental protection in the future. Furthermore, the explosives stripped from waste munitions can also be recovered to reuse.

Ⅱ. EXPERIMENTAL

2.1 Materials

The 155 mm artillery projectiles (about 43.5 kg) filled with 6.6 kg of TNT and the 105 mm artillery projectiles (about 19.9 kg) filled with 2.2 kg of Composition B explosive were obtained from the Ammunition Disposal Center (ADC) in Taiwan, as shown in Figure 1. These two kinds of artillery projectiles were used to evaluate the feasibility of practical industrial application for stripping-down explosives from the waste munitions by supercritical CO_2 fluid. Furthermore, the analytical grade TNT (2,4,6-trinitrotoluene) and RDX (1,3,5-Trinitro-1,3,5-triazacyclohexane) were obtained from the 203rd Arsenal in Taiwan and used to construct the HPLC calibration line.

(A) (B)

Fig. 1. 155 mm (A) and 105 mm (B) artillery projectiles.

2.2 Apparatus and Procedures

The experimental apparatus for stripping-down explosive from waste munitions was SC-50L supercritical fluid stripping equipment from Taiwan Supercritical Technology Co., Ltd. as shown in Figures 2-3. This industrial-scale apparatus with a stripping vessel of 50 liters was engineered specifically to evaluate the feasibility of practical industrial application for stripping-down explosives from the waste munitions by supercritical CO_2 fluid. The maximum operating pressure and temperature were 30 MPa and 80 ℃, respectively. The metal bracket was designed specifically to hold up a warhead and recover the stripping-down explosive as shown in Figure 4. Li [15] had demonstrated that the melting temperatures of TNT in supercritical CO_2 fluid at 50, 15, 10 MPa are approximately 35, 45 and 55 ℃, respectively. Therefore, the removal percentages of TNT from 155 mm artillery projectile through the supercritical CO_2 fluid were experimentally explored over the pressure, temperature and residence time ranges of 25 MPa, 50-65 ℃ and 30-120 minutes, respectively. The process included the steps of loading metal bracket with a warhead in the stripping vessel; supplying a supercritical CO_2 fluid to the stripping vessel, and contacting the high explosive with the supercritical CO_2 fluid at a preset temperature, pressure and residence time to strip down the high explosive. There were nine preset testing conditions as shown in Table 1. Furthermore, the removal percentages of Composition B explosive from 105 mm artillery projectile through the supercritical CO_2 fluid were also experimentally explored over the pressure, temperature and total residence time ranges of 25 MPa, 55-65 ℃ and 90-120 minutes, respectively. The stripping-down of Composition B explosive was carried out in a two-stage process, which is different comparing with the stripping-down of TNT. The two-stage process means that the same stripping-down process is repeated two times. The total residence time was the sum of two stage residence time. There were nine preset testing conditions as shown in Table 2.

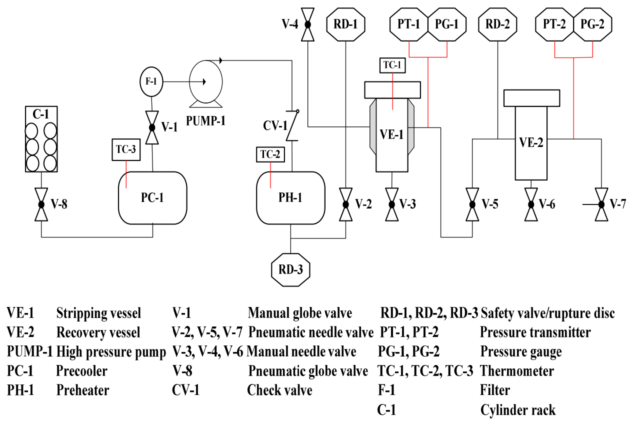


Fig. 2. The schematic diagram of the SC-50L supercritical fluid stripping equipment.

Fig. 3. The photograph of the SC-50L supercritical fluid stripping equipment.

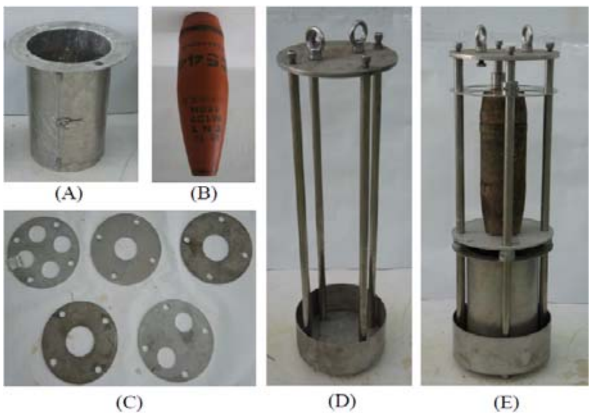


Fig. 4. The metal bracket for stripping-down and recovering explosive.

Table 1. Experimental conditions for removal percentage of TNT from 155 mm artillery projectile through supercritical CO_2 fluid.

Test No.	Pressure (MPa)	Temperature (℃)	Residence time (min)	Number of the test
1-3	25	55	60, 90, 120	3
4-6	25	60	60, 75, 90	3
7-9	25	65	30, 45, 60	3

Table 2. Experimental conditions for removal percentage of Composition B explosive from 105 mm artillery projectile through supercritical CO_2 fluid.

Test No.	Operating pressure (MPa)	Operating temperature (℃)	Residence time(min) 1st	2nd	Number of the test
1-3	25	55, 60, 65	120	-	3
4	25	65	60	60	1
5-6	25	65	45, 30	60	2
7-8	25	65	60	45, 30	2
9	25	65	45	45	1

High Performance Liquid Chromatography (HPLC) was used to analyze the content variation of TNT and RDX in Composition B explosive during stripping-down process. The experimental apparatus was Waters Alliance 2695 type from Waters Corporation. The column type was 4.60 mm×150 mm Cronusil-M C18 with a particle size of 3 *um* and the operating temperature was maintained at 25 ℃. A mobile phase consisting of 50% (vol./vol.) of HPLC grade methanol and 50% (vol./vol.) of distilled water was used at a flow rate of 1.0 mL/min. The UV-detector was set at a wavelength of 254 nm.

Ⅲ. RESULTS AND DISCUSSION

3.1 Experimental Results and Analysis for Stripping-down TNT

In order to investigate the removal efficiency of TNT from 155 mm artillery projectile by supercritical CO_2 fluid, a number of experiments have been carried out. At first, the operating pressure and temperature are set at 25 MPa and 55 ℃, respectively, and the removal percentages of TNT at residence times of 120, 90 and 60 minutes are examined. The experimental results indicate that the removal percentage of TNT can reach 100% above 90 minutes of residence time as shown in Figure 5. Further, the operating condition is set at a pressure of 25 MPa and a temperature of 60 ℃, and the removal percentages of TNT at residence times of 90, 75 and 60 minutes are explored. The results show that TNT can also be completely removed above 75 minutes of residence time as shown in Figure 6. In order to reduce the residence time effectively, the operating temperature rises to 65 ℃ under the same operating pressure condition, and the removal percentages of TNT at residence times of 60, 45 and 30 minutes are assessed. It is an expectable result that the removal percentage of TNT can reach 100% above 45 minutes of residence time as shown in Figure 7. The detailed experimental data are listed in Table 3. Therefore, it is experimentally confirmed that TNT can be completely removed from 155 mm artillery projectile by supercritical CO_2 fluid and the removal efficiency increases with increasing operating temperature under the same operating pressure condition.

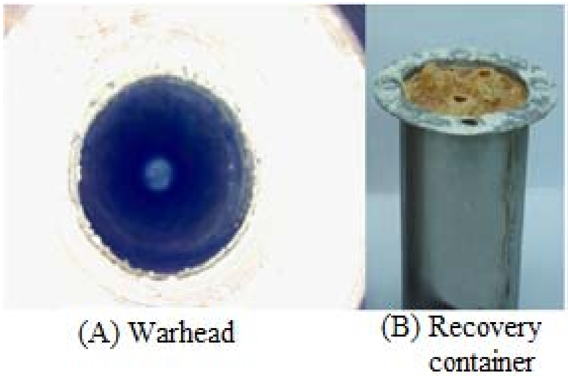


Fig. 5. The result of stripping-down TNT from 155 mm artillery projectile at pressure of 25 MPa, temperature of 55 ℃ and residence time of 90 minutes.

Fig. 6. The result of stripping-down TNT from 155 mm artillery projectile at pressure of 25 MPa, temperature of 60 ℃ and residence time of 75 minutes.

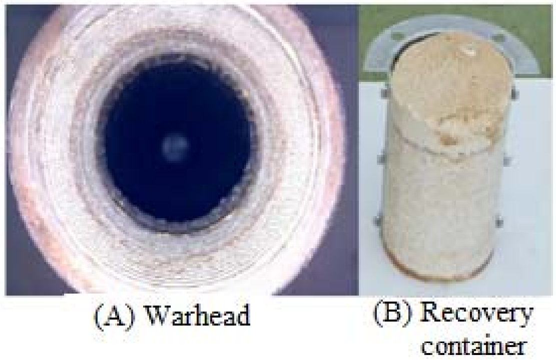


Fig. 7. The result of stripping-down TNT from 155 mm artillery projectile at pressure of 25 MPa, temperature of 65 ℃ and residence time of 45 minutes.

Considering the factors of improving industrial safety and reducing energy consumption, the lower operating pressure, lower operating temperature and shorter residence time are better operating conditions in the industrial process for stripping-down TNT from the waste munitions. In practical industrial application, the best operating condition may be located at a pressure of 25 MPa and a temperature of 65 ℃.

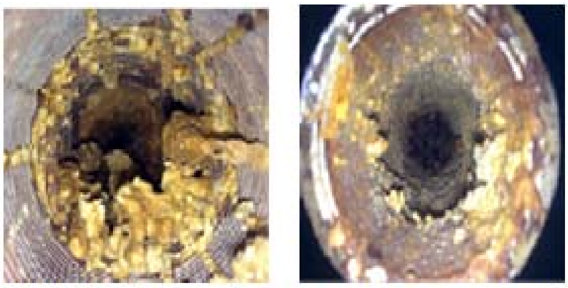
Table 3. Removal percentage of TNT at constant pressure of 25 MPa and various temperature and residence time conditions.

Operating pressure (MPa)	Operating temperature (℃)	Residence time (min)	removal percentage (%)
25	55	120	100
		90	100
		60	76
	60	90	100
		75	100
		60	85
	65	60	100
		45	100
		30	96

3.2 Experimental results and analysis for stripping-down Composition B explosive

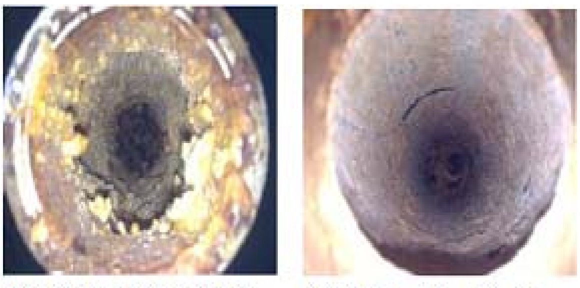
A number of experiments have been carried out in order to evaluate the feasibility of removing Composition B explosive from 105 mm artillery projectile by supercritical CO_2 fluid. At first, the operating conditions are set at constant pressure of 25 MPa, residence time of 120 minutes and temperature ranging from 55 to 65 ℃. It is found that the removal percentage of

Composition B explosive is lower than 30% at one stripping-down stage within 120 minutes of residence time as shown in Figure 8. Therefore, the process consisted of two consecutive stripping-down stages is tried in order to increase the removal percentage of Composition B explosive from 105 mm artillery projectile. A series of experiments have been conducted at various residence times under the operating pressure and temperature conditions of 25 MPa and 65 ℃. The experimental results indicate that the removal percentage of Composition B explosive can reach 100% when the residence time of the second stage is set at 60 minutes and the residence time of the first stage is longer than 45 minutes as shown in Figure 9. The detailed experimental data are listed in Table 4.



(A) Warhead by stripping-down at 55 ℃ (B) Warhead by stripping-down at 65 ℃

Fig. 8. The results of stripping-down Composition B explosive from 105 mm artillery projectile at temperature of 55 and 65 ℃ under the constant pressure and residence time conditions of 25 MPa and 120 minutes.



(A) Warhead by stripping-down at first stage (B) Warhead by stripping-down at second stage

Fig. 9. The result of stripping-down Composition B explosive from 105 mm artillery projectile using the two-stage stripping-down process at the residence times of 45 and 60 minutes under the operating pressure and temperature conditions of 25 MPa and 65 ℃.

Table 4. Removal percentage of Composition B explosive at constant pressure of 25MPa and various temperature and residence time conditions.

Operating pressure (MPa)	Operating temperature (℃)	Residence time(min) 1st	2nd	Removal percentage (%)
25	55	120	-	9
	60	120	-	22
	65	120	-	28
	65	60	60	100
		60	45	93
		60	30	81
		45	60	100
		45	45	80
		30	60	96

Therefore, it is also experimentally confirmed that Composition B explosive can be completely removed from 105 mm artillery projectile by supercritical CO2 fluid in the two-stage stripping-down process. The removal efficiency of Composition B explosive increases with increasing residence time under the same operating pressure and temperature conditions. The results also show that the residence time of the second stage is more important than that of the first stage for increasing removal percentage. Furthermore, the samples are taken out in sequence at five different sampling locations on the recovering Composition B explosive and then the weight percentages of TNT and RDX in Composition B explosive are determined by means of HPLC as shown in Figure 10. It is found that every sample includes TNT and RDX. Therefore, the Composition B explosive can be stripped down from waste munitions, but TNT and RDX cannot be separated simultaneously.

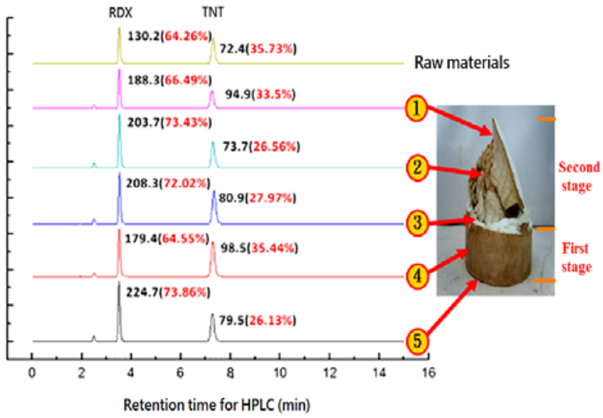


Fig. 10. The result of stripping-down Composition B explosive from 105 mm artillery projectile using the two-stage stripping-down process at the residence times of 45 and 60 minutes under the operating pressure and temperature conditions of 25 MPa and 65 ℃.

Ⅳ. CONCLUSIONS

The feasibility of industrial application for stripping-down TNT and Composition B explosive from waste munitions by supercritical CO_2 fluid under low temperature condition has been experimentally confirmed in this study, and the following conclusions are obtained:

(1) The TNT can be completely removed from 155 mm artillery projectile by supercritical CO_2 fluid and the removal efficiency increases with increasing operating temperature under the same operating pressure condition. In practical industrial application, the best operating condition may be located at a pressure of 25 MPa and a temperature of 65 ℃.

(2) The Composition B explosive can also be completely removed from 105 mm artillery projectile by supercritical CO_2 fluid in the two-stage stripping-down process. The removal efficiency of Composition B explosive increases with increasing residence time under the same operating pressure and temperature and the residence time of the second stage act as more important role.

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