Journal of Hazardous Materials 308 (2016) 120–130

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Numerical analysis of thermal decomposition for RDX, TNT, and Composition B

Shin Hyuk Kim [a], Baggie W. Nyande [a], Hyoun Soo Kim [b], Jung Su Park [b], Woo Jin Lee [c], Min Oh [a,*]

[a] Department of Chemical Engineering, Hanbat National University, 125 Dongseo-daero, Yuseong-gu, Daejeon 305-719, Republic of Korea
[b] Agency for Defence Development, 462 Jochiwon-gil, Yuseong-gu, Daejeon 305-150, Republic of Korea
[c] Hanwha corporation, 117 Yeosusandan 3-ro, Yeosu-si, Jeollanam-do, Republic of Korea

HIGHLIGHTS

- Reaction mechanism of thermal decomposition of military explosives is investigated.
- Mathematical modeling of thermal decomposition are executed.
- Commercial scale reactor is employed for demilitarization of waste explosives.
- Dynamic response of thermal decomposition is examined in a reactor.

ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form
23 December 2015
Accepted 29 December 2015
Available online 6 January 2016

Keywords:
RDX
TNT
Composition B
Thermal decomposition
Demilitarization

ABSTRACT

Demilitarization of waste explosives on a commercial scale has become an important issue in many countries, and this has created a need for research in this area. TNT, RDX and Composition B have been used as military explosives, and they are very sensitive to thermal shock. For the safe waste treatment of these high-energy and highly sensitive explosives, the most plausible candidate suggested has been thermal decomposition in a rotary kiln. This research examines the safe treatment of waste TNT, RDX and Composition B in a rotary kiln type incinerator with regard to suitable operating conditions. Thermal decomposition in this study includes melting, 3 condensed phase reactions in the liquid phase and 263 gas phase reactions. Rigorous mathematical modeling and dynamic simulation for thermal decomposition were carried out for analysis of dynamic behavior in the reactor. The results showed time transient changes of the temperature, components and mass of the explosives and comparisons were made for the 3 explosives. It was concluded that waste explosives subject to heat supplied by hot air at 523.15 K were incinerated safely without any thermal detonation.

1. Introduction

Rapid evolution of military technology coupled with sustained peace around the world has led to excess stockpiles of waste explosives and propellants, which has made demilitarization on an industrial scale a necessity in many nations such as Germany and the USA [1,2]. Demilitarization of these surplus explosives and propellants with regard to efficiency and safety can be carried out in a number of ways including (1) storage and disposal by ocean/land burial, (2) open burning/detonation, (3) closed detonation, (4) chemical conversion to higher value products and (5) combustion by fluidized beds, rotary kilns and tunnel chambers [3,4]. The enforcement of stringent environmental regulations has rendered open burning/detonation and sequestration unacceptable. Meanwhile, chemical conversion to higher value products requires advanced and sophisticated technologies; thus, it is economically strenuous [5]. Environmental and economic limitations have therefore left combustion in fluidized beds, rotary kilns and tunnel chambers as the only plausible option for demilitarization.

TNT, RDX and Composition B are widely used for military-grade explosives because of their ease of manufacture and relatively high detonation power [6–8]; however, they are very sensitive to heat and shock and could lead to highly catastrophic events if thermal decomposition is not carried out properly under the correct operating conditions [9]. This accounts for the paucity of research into this disposal technique. The mechanism of explosive decom-

* Corresponding author. Fax: +82 428211593.
E-mail address: minoh@hanbat.ac.kr (M. Oh).

http://dx.doi.org/10.1016/j.jhazmat.2015.12.061
0304-3894/

Nomenclature

A_{comp}	Heat transfer area of composite (m)
A_k	Collision factor of k^{th} CPR (s^{-1} or $m^3\,mol^{-1}\,s^{-1}$)
A_l	Collision factor of l^{th} GPR (s^{-1} or $m^3\,mol^{-1}\,s^{-1}$)
c_i	Concentration of component I ($mol\,m^{-3}$)
C_p	Heat capacity of gas ($J\,kg^{-1}\,K^{-1}$)
$C_{p,j}$	Heat capacity of explosive j ($J\,kg^{-1}\,K^{-1}$)
CPR	Condensed phase reaction
D	Diameter of reactor (m)
D_z	Diffusion coefficient ($m^2\,s^{-1}$)
E_k	Activation energy of k^{th} CPR ($J\,mol^{-1}$)
E_l	Activation energy of l^{th} GPR ($J\,mol^{-1}$)
GPR	Gas phase reaction
h_j	Heat transfer coefficient of explosive j by convection ($J\,m^{-2}\,s^{-1}$)
ΔH_r	Heat of reaction ($J\,mol^{-1}$)
ΔH_j^l	Latent heat of explosive j ($J\,mol^{-1}$)
k_k	Reaction constant of k^{th} CPR (s^{-1} or $m^3\,mol^{-1}\,s^{-1}$)
k_l	Reaction constant of l^{th} GPR (s^{-1} or $m^3\,mol^{-1}\,s^{-1}$)
K_z	Heat dispersion coefficient ($J\,m^{-1}\,s^{-1}\,K^{-1}$)
$K_{z,j}$	Thermal conductivity of explosive j ($J\,m^{-1}\,s^{-1}\,K^{-1}$)
m_j	Mass of explosive j (kg)
m_j^{ini}	Initial mass of explosive j (kg)
Nu	Nusselt number
P	Pressure of a reactor (Pa)
Pr	Prandtl number
q_j	Heat rate by heat transfer of composite ($J\,s^{-1}$)
R	Ideal gas constant ($kJ\,mol^{-1}\,s^{-1}$)
Re	Reynolds number
S_e^{gas}	Heat source by gas reaction ($J\,m^{-3}s^{-1}$)
S_e^{comp}	Heat source by composite reaction ($J\,m^{-3}s^{-1}$)
$S_{m,i}^{gas}$	Mass source of component i by gas ($mol\,m^{-3}s^{-1}$)
$S_{m,i}^{comp}$	Mass source of component i by composite ($mol\,m^{-3}s^{-1}$)
$S_{m,j}^{comp}$	Mass source of explosive j ($mol\,m^{-3}s^{-1}$)
T	Temperature of gas (K)
T_j	Temperature of explosive j (K)
u	Velocity ($m\,s^{-1}$)
V	Volume of composite (m^3)

Greek letters

ρ	Density of gas ($kg\,m^{-3}$)
ρ_j	Density of explosive j ($kg\,m^{-3}$)
ϕ_j	Porosity of explosive j
μ	Viscosity of gas ($kg\,m^{-1}\,s^{-1}$)
μ_s	Viscosity of composite ($kg\,m^{-1}\,s^{-1}$)

position has been the subject of many researchers such as the investigation of convection and non-convective effects on the ignition of confined TNT [10,11]. The thermal decomposition of TNT with the cook-off process was simulated using FLUENT with condensed phase reactions (CPRs) as well as with gas phase reactions (GPRs) based on global kinetics [12]. Brill et al. [13] found discrepancies in reported global Arrhenius parameters for the thermal decomposition of nitramines based on which kinetic compensation relationships have been developed. Modeling of RDX combustion wave structure based on detailed kinetic mechanisms over a wide range of pressures was carried, and good agreement between calculated and experimental burning rates was obtained except at low pressures [14]. Theoretical studies carried out on RDX reveal four low-lying energy channels due to N-NO2 cleavage and HONO elimination pathways and corroborate experimental findings of the most abundant products [15]. Advanced analytical techniques such as the Temperature-Jump-Fourier Transform Infrared Spectroscopy (T-Jump-FTIR), UV–vis absorption have greatly improved the reliability of kinetic parameters arising from detailed reaction mechanisms [16] and the determination of species concentration profiles [17]. Numerous elementary reactions accompany the thermal decomposition of propellants and explosives. Ermolin and Zarko [18,19] considered 43 chemical species and 263 elementary reactions in their investigations. Simulation of RDX ignition by laser with a CPR and 9 main GPRs was also reported [20,21]. Kim et al. [22], considering these elementary reactions, investigated the decomposition characteristics of RDX. However, these researches have mainly focused on detonation and ignition and, to the best of the authors' knowledge, research on the thermal decomposition of Composition B has yet to be executed.

This research is aimed at investigating the key operating conditions under which the safe treatment of waste explosives can be carried out to avoid detonations. In this study, a dynamic simulation of the thermal decomposition of TNT, RDX and Composition B in a reactor was carried out using the gPROMS software package [23]. Chemical and physical changes occurring within the reactor were predicted based on the conservation equations of mass, momentum and energy coupled with heterogeneous reaction mechanisms in the reactor. The decomposition reaction mechanism considered in this study consists of 3CPRs and 263 GPRs.

2. Formulation of problem

2.1. Reaction mechanism for thermal decomposition

The high-energy material employed in this study consists of solid TNT, RDX and Composition B. In the reactor, a set of reactions including CPRs in liquid phase and GPRs takes place. The details of the reaction mechanism are illustrated in Fig. 1.

The solid RDX and TNT were heated with hot flowing air in the reactor. At 353 K, TNT underwent a phase change from solid to liquid. From this point, the temperature of TNT remained constant, while the temperature of RDX continued to increase until it attained its melting temperature (478 K). The phase change from solid to liquid was immediately followed by mutual CPRs and evaporation of the volatile components of both TNT and RDX to produce the gas phase. The physical properties of TNT and RDX are shown in Table 1 [2,7,8,24].

2.2. Condensed phase reaction in liquid phase

In the liquid phase of TNT and RDX, CPRs take place as described in Eqs. (1)–(3) [10,20]. One CPR occurs in the liquid phase of TNT and is highly exothermic. Also, CPRs take place for RDX one is mildly exothermic and the other is endothermic. The reaction mechanism and the heat of reactions indicate that the CPR of TNT causes an increase in temperature, while the CPRs of RDX may instigate the

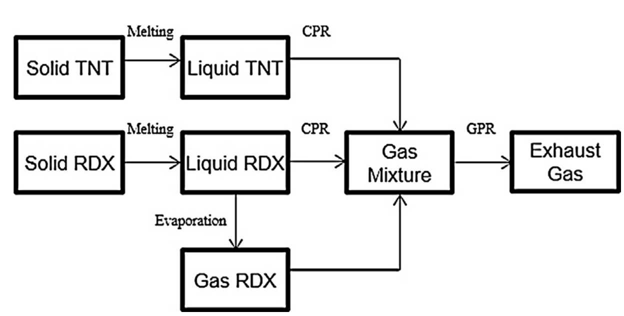

Fig. 1. Overview of thermal decomposition of RDX and TNT.