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A novel mathematical model of formulation design of emulsion explosive

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Abstract

A novel mathematical model has been developed to aid the formulation of emulsion explosives. This mathematical model calculated heat of explosion, oxygen balance and raw material cost as a function of explosive ingredients, and the solution of the mathematical model was obtained by a MS Excel program. The effects of the different content of NH_4NO_3, $NaNO_3$, H_2O, and span-80 and composite fuel oil on the heat of explosion and the specific volume of emulsion explosive were discussed based on the proposed mathematical model. The results show that (1) with the increasing of the content of NH_4NO_3, the heat of explosion and the specific volume increase. (2) The better content of $NaNO_3$, H_2O and Span-80 in the formulation of emulsion explosive are 7%~9%, 9%~10%, 1.5%~2% respectively, and this formulation results in an oxygen balance of zero or close to zero.

Keywords: Mathematical model, Emulsion explosive, Explosion, oxygen balance

1. Introduction

The commercial emulsion explosives developed in the early 1960s [1, 2] are very important blasting means because of their higher detonation parameters and better water-resistant characteristics [3, 4]. Ammonium nitrate used in the emulsion explosives is the primary oxidizer and sodium nitrate is frequently added to improve the properties of the oxidizer solution. The oil phase consists of various mineral oils, waxes, and even polymers. Explosive properties are usually primary consideration during the formulation of emulsion explosives. A non-optimum explosive formulation should result in a poor explosive performance and an increase in noxious fumes, all of which are detrimental to the overall blasting objectives. The object of the present work is to develop a novel mathematical model to improve the formulation design of emulsion explosives.

The contents of this paper are as follows: 1) a novel computer aided method for the formulation of emulsion explosives; 2) the establishment of a mathematical model for the formulation of emulsion explosives; 3) the computer aided formulation design and optimization of emulsion explosive and, 4) numerous reasonable formulations with an oxygen balance of zero or close to zero.

2. Mathematical model

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Explosive properties are usually primary consideration during the formulation of industrial explosives [5]. Because explosive properties are a function of the heat of explosion (***Qv***) of an explosive, the heat of explosion is selected as the primary figure of merit for our mathematical model. Emulsion explosives consist of Carbon (C), Hydrogen (H), Oxygen (O), Nitrogen (N) and sodium (Na). The general empirical formula of emulsion explosives is "$C_aH_bO_cN_dNa_h$". Assumed the specific empirical formula is, "$C_{ai}H_{bi}O_{ci}N_{di}Na_{hi}$", then the molar mass of component "i" is given as "m_i" and the molar number of component "i" in 1 kg explosive is $10x_i/m_i$, where "x_i" is the percent mass content of component "i". The equation for the reaction of an explosive containing C, H, O, N, Na is given in equation (1).

$$C_aH_bO_cN_dNa_h=\sum_{i=1}^{n}\frac{10x_i}{m_i}(C_{a_i}H_{b_i}O_{c_i}N_{d_i}Na_{h_i})$$
$$\rightarrow\frac{h}{2}Na_2O+\frac{b}{2}H_2O+\frac{d}{2}N_2+(c-\frac{h}{2}-\frac{b}{2}-a)CO_2$$
$$+(2a-c+\frac{b}{2}+\frac{h}{2})CO \qquad (1)$$

where a = $\Sigma 10a_ix_i/m_i$, b = $\Sigma 10b_ix_i/m_i$, c = $\Sigma 10c_ix_i/m_i$,and d = $\Sigma 10d_ix_i/m_i$, h = $\Sigma 10h_ix_i/m_i$, The mathematical formula (where the primary figure of merit is Heat of Explosion) is shown in equation (2).

$$Q_v=\frac{h}{2}\Delta H_{Na_2O}+\frac{b}{2}\Delta H_{H_2O}+\frac{d}{2}\Delta H_{N_2}+(c-\frac{b+h}{2}-a)\Delta H_{CO_2}$$
$$+(2a-c+\frac{b}{2}+\frac{h}{2})\Delta H_{CO}-\sum_{i=1}^{n}\frac{10}{m_i}x_i\cdot\Delta H_i \qquad (2)$$

The mathematical expressions for the other figures of merit are:
Oxygen Balance (OB) = $\Sigma a_ix_i = 100\eta$
Variable Sum (VS) = $\Sigma x_i = 100$
Cost Sum (CS) = $\Sigma p_ix_i = p/10$
Lower limits and upper limits = $s_i< x_i<t_i$, where i = 1,2,…, n.
In this mathematical model the following definitions are employed:

ΔH_f Heat of formation for the ingredients, the entire explosive or explosive products ($kJ.mol^{-1}$)
g the molar number of the explosion products;
x_i the content of component "i" of the explosive;
m_i the molar mass of component "i";
a_i the oxygen balance of component "i" (%);
η the oxygen balance of the explosive (%);
p_i raw material cost of component "i", $RMBy.t^{-1}$;
p raw material cost of explosive, $RMBy.t^{-1}$;
s_i lower limit of component "i"; (%);
t_i upper limit of component "i"; (%).

3. Mathematical expression for formulations of emulsion explosives

3.1 Ingredients of emulsion explosives and their chemical parameters

The oxidizer of emulsion explosives is usually made up of ammonium nitrate and sodium nitrate, and the fuel is a mixture of various mineral oils and waxes. The formula, molar mass, heat of formation, oxygen balance and raw material cost of these components are given in Table 1 [6-9].

3.2 Mathematical expression for formulation of emulsion explosives

Provided that the amount of AN, SN, Water, Span-80, wax and mineral oil are respectively designated as x_1, x_2, x_3, x_4, x_5 and x_6, then:

$a=0.561x_4+0.709x_5+0.70x_6$

$b=0.500x_1+1.111x_3+1.028x_4+1.496x_5+1.529x_6$

$c=0.375x_1+0.353x_2+0.556x_3+0.140x_4$

$d=0.250x_1+0.118x_2$

$h=0.118x_2$

and, Formula (3) gives the general formula for Heat of Formation of emulsion explosives.

$$\sum \frac{10x_i \cdot \Delta H_{f(i)}}{m_i} = 44.183x_1 + 45.562x_2 + 29.486x_3 + 21.970x_4 \qquad (3)$$

and then the primary figure of merit (Maximum Heat of Explosion) is given by formula (4).

$$MaxQ_v=51.08x_1+52.79x_2-23.07x_3-97.77x_4-173.05x_5-171.42x_6 \qquad (4)$$

Formula (4) is assumed as following conditions:

$$\begin{cases} 20x_1 + 47.1x_2 - 239x_4 - 346x_5 - 346x_6 = 100K \\ x_1 + x_2 + x_3 + x_4 + x_5 + x_6 = 100 \\ 1.2x_1 + 1.6x_2 + 15x_4 + 4x_5 + 3x_6 \le P/10 \\ 70 \le x_1 \le 82 \\ 5 \le x_2 \le 15 \\ 8 \le x_3 \le 13 \\ 1 \le x_4 \le 3 \\ 2 \le x_5 \le 4 \\ 1 \le x_6 \le 3 \end{cases}$$

For formula (4), the values η and P may be assumed, in general $\eta \le 0$.

Table 1
Physical chemistry parameters of the raw materials of emulsion explosives

No.	Empirical formula	Ingredient	MW (g/mole)	ΔHf (kJ/mole)	OB (%)	Cost (RMBy/t)
1	$N_2O_3H_4$	AN	80	353.46	+ 20	1400
2	O_3NNa	NA	85	462.27	+47.1	1600
3	H_2O	water	18	—	—	—
4	$C_{24}H_{44}O_6$	Span-80	428	—	239	15000
5	$C_{18}H_{36}$	Wax	254	558.03	- 346	4000
6	$C_{12}H_{26}$	mineral oil	170	392.88	-346	3000

3.3 Computer solutions

To arrive at a solution, a computer was employed. The mathematical formulas constructed previously were inputted into a MS Excel program. The mathematical solution varied with different oxygen balance values (η) and raw material costs *P*.

4. Results and discussion

4.1. Effect of formulation design on the heat of explosion and the specific volume

Te heat of explosion is the energetic sources to release the explosive power and the specific volume is the medium to transfer the power. The heat of explosion calculated based on the aforementioned mathematical model and here the specific volume was equal to the total volume produced by all gaseous materials after explosion in standard state. The effects of the different contents of NH_4NO_3, $NaNO_3$, H_2O, and Span-80 and composite fuel oil on the heat of explosion and specific volume were discussed by the mathematical model as follows.

4.2. Effect of oxidant

4.2.1. Comparison ammonium nitrate with sodium nitrate

Ammonium nitrate (AN) is used as the basic oxidant in the emulsion explosives and sodium or calcium nitrate is often added to improve the properties of the oxidizer solution. Oxidant is an important ingredient in the emulsion explosives that supplies oxygen in the explosion reaction and its oxygen balance values is higher than zero. For an oxidant, the oxygen balance value only indicates that how much oxygen it can supply in the explosion reaction, but does not demonstrate how much energy it can offer. Furthermore, the higher oxygen balance value can not explain the higher energy was released in the explosion reaction. For example, 1 mol ammonium nitrate can supply 0.5 mol oxygen in the explosion reaction, at the same time, can offer 127.24 kJ energy. However, 1mol sodium nitrate can supply 1.25 mol oxygen but absorb 254.99 kJ energy in the explosion reaction. Therefore the release or absorption of energy for an oxidant is an important characteristic parameter which is related with the energetic contribution of an oxidant and ammonium nitrate is a good oxidant for the energetic contribution of industrial explosives.

4.2.2. Effect of ammonium nitrate

The effects of the different contents of AN on the heat of explosion and the specific volume are shown in Fig. 1. As seen from Fig. 1, the heat of explosion and the specific volume would be improved when the content of AN was increased. This was attributed to hydrogen, oxygen and nitrogen in AN molecule. After explosion hydrogen and oxygen were transformed into water having high heat of formation which was useful to improve the heat of explosion, and nitrogen became N_2 which was, however, help to improve the specific volume. Therefore, the AN content may be increased reasonably in the formulation design of emulsion explosives.

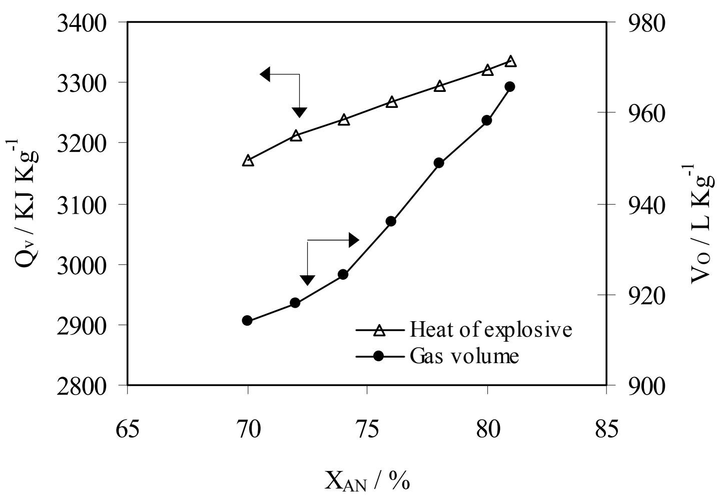

Fig. 1 The effect of AN content on the heat of explosion and specific volume

4.2.3. Effect of sodium nitrate

Generally, in order to lower the crystalloid point of oxidant, $NaNO_3$ was used as another oxidant in emulsion explosives. The effects of the different contents of $NaNO_3$ on the heat of explosion and specific volume are shown in Fig. 2.

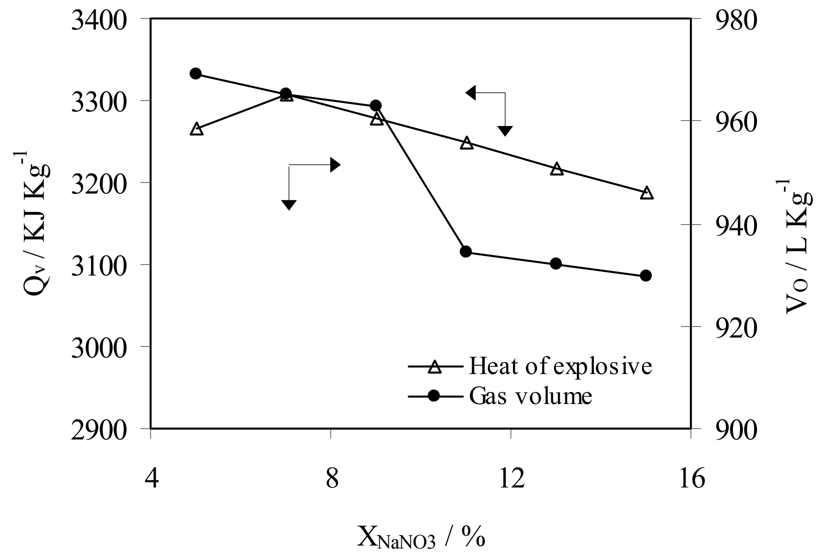

Fig. 2 The effect of $NaNO_3$ content on heat of explosion and specific volume

The heat of explosion and the specific volume were optimal when the $NaNO_3$ content was 7% as shown in Fig. 2. Considering that increasing the content of $NaNO_3$ would lower the crystalloid point of the mixture of ammonium nitrate and sodium nitrate, which is beneficial to the safety of the production process of emulsion matrix, the best theoretical formulation of emulsion explosive consists of 7% ~ 9% $NaNO_3$.

4.2.4. Effect of water

Water was used as a solvent of oxidant in emulsion explosive, which made fuel oil mix with oxidant fully, and the explosion efficiency reach to maximum. Water was changed into vapor after the explosion, evaporative heat was needed in this process and so the heat of explosion of emulsion explosive was lower than that of powder AN explosive. The effects of the different contents of H_2O on the heat of explosion and specific volume were discussed by the mathematical model. As seen from Fig. 3, the best theoretical formulation of emulsion explosive consists of 9% ~ 10% H_2O.

4.2.5. Effect of Span-80

The effects of the different emulsifier (Span-80) contents on the heat of explosion and specific volume were discussed by the mathematical model. The results are shown in Fig.4. The best theoretical formulation of emulsion explosive consists of 1.5% ~ 2.0% Span-80.

4.2.6. Effect of oxygen balance

The oxygen balance was influenced by the contents of composite fuel oil in emulsion explosive. The more the composite fuel oil used was, the more negative the oxygen balance was. With the increasing of the weight percent of the composite fuel oil, the heat of explosion decreased and the volume of toxic gases (i.e., CO) produced after the explosion increased.

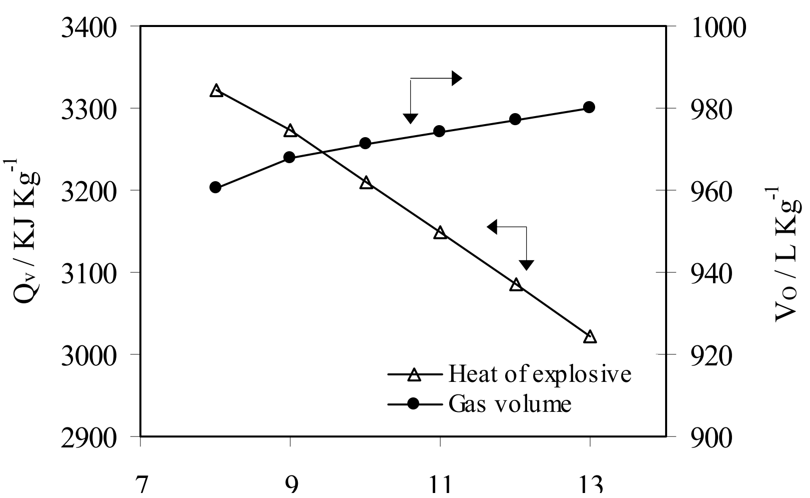

Fig. 3 The effect of water content on heat of explosion and specific volume

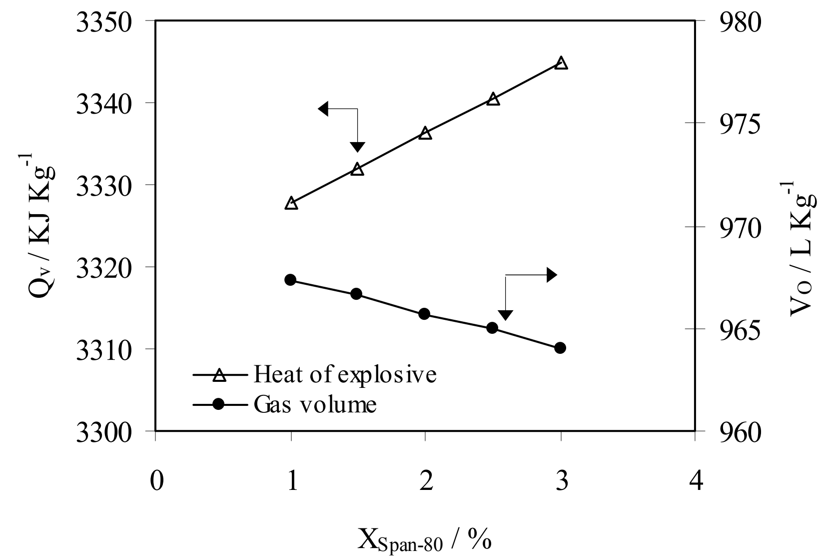

Fig. 4 The effect of Span-80 content on heat of explosion and specific volume

However, when oxygen balance value was higher than zero ($\eta>0$)) the volume of toxic gases i.e. NO produced after the explosion increased. Therefore, it was very important that oxygen balance value be zero (or close to zero) in order that formulations should have higher heat of explosion and lower toxic gas volumes. The effects of the different oxygen balance values on the heat of explosion and the specific volume are shown in Fig.5.

The best theoretical formulation of emulsion explosive consists of 7%~9%$NaNO_3$, 9%~10%H_2O, 1.5%~2%Span-80 respectively for higher heat of explosion, specific volume and lower toxic gas volume.

4.3. Validating the model

Some performance of a number of emulsion explosives containing glass micro-balloons were studied experimentally and theoretically. For each of the explosives, detonation velocity and power of explosive were measured, and oxygen balance and heat of explosion were calculated. The influence of the content of NH_4NO_3 $NaNO_3$, H_2O, and Span-80 in the emulsion matrix respectively on detonation velocity and power of explosive was examined.

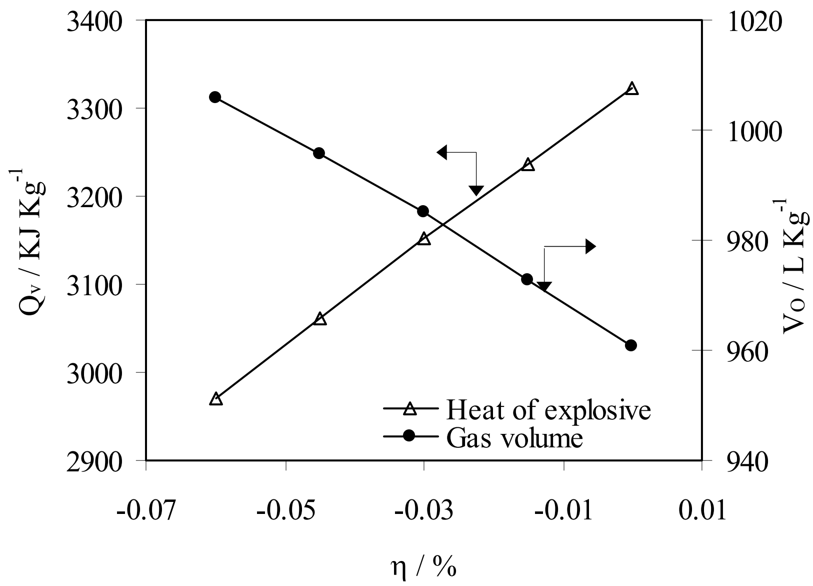

Fig. 5 The effect of oxygen balance on theoretic explosion heat and specific volume

The emulsion matrix was prepared using aqueous solutions of the mixture of ammonium nitrate with sodium nitrate. The contents of other ingredients were unchanged nearly in order to maintain the oxygen balance within the range of ±0.5%. The compositions of the emulsion matrices are given in Table 2. The emulsions were prepared using a simple facility consisting of a thermostat and a container equipped with a stirrer. The solution of oxidant was heated to 120℃ and then slowly added into the container, in which a preheated (100℃) mixture of fuels (oil and span-80) with the emulsifier was agitated with the stirrer at a speed of 1440 rpm. After adding the entire amount of the oxidizer, the agitation was continued for about two minutes to obtain fine emulsion particles. The final explosive mixtures were prepared by mixing the emulsion matrices with glass micro-spheres (produced by 3M; mean size about 80 μm). Mixing was performed carefully (using the same stirrer but at lower speed) until the distribution of the micro-spheres in the emulsion matrix became uniform. The mass fraction of micro-spheres was 2%~ 3% (above 100%) in all experiments.

For each explosive, the detonation velocity and power of explosive were measured. The results obtained enabled a comparison of the efficiency for testing explosive performance. They were also used to analyze the effect of formulation on the performance of the explosives and to choose the formulations characterized by the best detonation and performance characteristics. A more quantity of ammonium nitrate, a certain extent of water and an oxygen balance of zero or close to zero are favorable for higher heat of explosion and explosion strength.

Table 2
Formulations and performance of emulsion explosives

Mass fraction of components, %					Oxygen balance / %	Calculated heat of explosion / $kJ \cdot kg^{-1}$	Power of explosive / mL	Detonation velocity / $m \cdot s^{-1}$
AN	SN	H_2O	Span	Fuel oil				
77.0	7.0	10	2.0	4.0	0.08	3187.5	321.5	4720
77.0	7.5	9.3	2.0	4.2	-0.38	3195.6	320.3	4610
76.0	7.8	10	2.0	4.2	-0.44	3144.2	314.8	4700
75.3	9.0	9.5	1.7	4.5	-0.33	3161.0	314.7	4680

5. Conclusion

According to thermochemistry of explosion reaction, the mathematical model for formulation design of emulsion explosive was established. The computer was used to aid the formulation design and optimization of emulsion explosive by a MS Excel program. The effects of the different content of NH_4NO_3, $NaNO_3$, H_2O and Span-80 and composite fuel oil on the heat of explosion and the specific volume were discussed based on the mathematical model. The results show that with the increasing of the content of NH_4NO_3, the heat of explosion and the specific volume were increased. The best theoretical formulation of emulsion explosive consists of 7%~9%$NaNO_3$, 9%~10%H_2O, 1.5%~2%Span-80 respectively, and an oxygen balance of zero or close to zero for higher heat of explosion, specific volume and lower toxic gas volume.

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