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Thermal explosion simulation of methyl ethyl ketone peroxide in three types of vessel under the same volume by explosion models

Kun-Yue Chen · Wei-Ting Chen · Chen-Wei Chiu · Tsung-Chih Wu · Chi-Min Shu

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Abstract Methyl ethyl ketone peroxide (MEKPO), which has highly reactive and exothermically unstable characteristics, has been extensively employed in the chemical industries. It has also caused many thermal explosions and runaway reaction accidents in manufacturing processes during the last three decades in Taiwan, Japan, Korea, and China. The goal of this study was to simulate thermal upset by MEKPO for an emergency response. Vent sizing package 2 (VSP2) was used to determine the thermokinetics of 20 mass% MEKPO. Data of thermokinetics and hazard behaviors were employed to simulate thermal explosion in three types of vessel containing 20 mass% MEKPO under various scenarios at the same volume. To compare and appraise the difference of important parameters, such as maximum temperature (T_{max}), maximum pressure (P_{max}), etc. This was necessary and useful for investigating the emergency response procedure associated with industrial applications.

Keywords Maximum temperature (T_{max}) · Methyl ethyl ketone peroxide (MEKPO) · Runaway reaction accidents · Thermal explosion · Vent sizing package 2 (VSP2)

List of symbols

E_a	Activation energy (kJ mol^{-1})
k_0	Pre-exponential factor (s^{-1})
n	Order of reaction (dimensionless)
P_{max}	Maximum pressure during overall reaction (psig)
Q	Calorific capacity (kJ mol^{-1})
q_{wall}	Time dependence of heat flux on the wall (W m^{-2})
q_e	Time dependence of heat flux on the ambient (W m^{-2})
R	Gas constant (8.314 J mol^{-1} K^{-1}); radius (m)
r	Reaction rate (s^{-1})
T_0	Exothermic onset temperature (°C)
T_e	Environmental temperature (°C)
T_{max}	Maximum temperature during overall reaction (°C)
T_{wall}	Temperature on the wall (°C)
t	Time (s)
V_{nr}	Normal component of velocity (m s^{-1})
V_{tn}	Tangential component of velocity (m s^{-1})
Z	Height (m)
α	Time dependence of the heat transfer coefficient (W m^{-2} K^{-1})
λ	Thermal conductivity (W m^{-1} K^{-1})
Φ	Thermal inertia (dimensionless)

Introduction

Methyl ethyl ketone peroxide (MEKPO) has higher oxidized reactivity, due to its applications being quite

K.-Y. Chen · W.-T. Chen
Doctoral Program, Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology (NYUST), 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan ROC

C.-W. Chiu
Department of Fire Safety, Taiwan Police College, Taipei 11696, Taiwan ROC

T.-C. Wu
Department of Safety, Health, and Environmental Engineering, Hungkuang University, 34 Chung-Chie Rd., Shalu, Taichung 49902, Taiwan ROC

C.-M. Shu (✉)
Department of Safety, Health, and Environmental Engineering, NYUST, 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan ROC
e-mail: shucm@yuntech.edu.tw

widespread in the chemical industries, where MEKPO can be applied as a catalyst, initiator, hardener, for oxidation, bleaching, and so on for polymerization. The hazardous material MEKPO is often stored, transported, and employed in polymerization in the petrochemical industries [1]. From the domestic chemical accidents, the disasters which were attributed to the peroxide hold a prominent proportion, having resulted in severely injuring and even killing personnel and creating financial losses. Among them, MEKPO is used as a catalyst and an accelerator for unsaturated polyester (UP) systems [2]. Pfaffli states that MEKPO, a "cold catalyst", while accelerated with cobalt carboxylate, could even decompose at the ambient temperature [3]. Moreover, it is practical in various industries, such as automobile, airline, boating, fabric, and paint [4]. MEKPO has been employed to have a decomposition exothermic reaction but caused runaway reactions, like the Taipei Fuyuan street explosion that killed 18 and injured 59 in 1979; Taoyuan county Lishung Co. explosion resulted in 5 deaths and 55 injured in 1984; Taichung city Chinshen road explosion, killed 7, injured 5 in 1989; and October 1986, a detonation fire happened at Taoyuan county Yongxing Resin Coating Co., that took 10 lives, and seriously wounded 8, and left 39 with minor wounds; the dead personnel included 3 fire fighters, and 3 voluntary fire fighters. Otherwise, MEKPO has caused several serious explosion accidents among Taiwan, Japan, Korea, and China [5]. Around the world, MEKPO also has been recognized as a flammable type or class III or IV by the code of NFPA 43B. The members of DIERS (Design Institute for Emergency Relief Systems) have adopted researches on the characteristics of pressure relief for organic peroxides.

We conducted a thermal hazard analysis of 20 mass% MEKPO with its thermokinetic parameters measured by vent sizing package 2 (VSP2). The results could be applied to simulate runaway reaction and thermal explosion of vessels containing 20 mass% MEKPO subjected to external fire scenarios. The simulation technique was applied to evaluate for large-scale reactive materials by means of applying a model of the calorimetric technique to evaluate the fundamental exothermic behavior of small-scale ones. The thermal safety software (TSS) package developed by ChemInform Saint Petersburg (CISP) Ltd., was employed to assess reaction kinetics and numerical curve fitting of thermal explosion excursion and to facilitate determination of critical conditions and thermal explosion of the vessel [6–10]. In addition, the TSS includes three groups of the program that correspond to a three-stage approach, and the software ConvEx (CE-FK) provides a numerical simulation of thermal explosion development [11]. Finally, CE-FK in the liquid thermal explosion (LTE) model was used to simulate thermal explosion of MEKPO which was, ultimately, aimed at guaranteeing safe storage or transportation.

Physical properties and accidents of MEKPO

MEKPO structurally contains a very sensitive O–O bond, which is a kind of oily liquid, its boiling point is below −20 °C, and its flash point is 52–93 °C. Fire or explosion may be triggered due to uncontrollable thermal source, resulting in a serious accident that promotes casualties, or even damages the environment. If the surrounding temperature exceeds 100 °C, MEKPO may decompose swiftly. The hazardous feature of the O–O bond indicates that it is a thermally unstable structure. The United Nations has suggested that an organic peroxide supplier must conduct a precise test of self-accelerating decomposition temperature (SADT) in any specific commercial package [12]. MEKPO has been recognized as a flammable type or class III or IV by the code of NFPA 43B. Numerous studies of induced hazards by organic peroxides have been performed worldwide. The exothermic threshold temperature of many organic peroxides is usually around 50–120 °C. However, for some runaway reaction accidents caused by MEKPO, the reaction or storage temperatures have even been as low as ambient temperature [13–15].

MEKPO is involved in many applications on various industrial scopes and all of the hidden risk contributes to grow its degree of hazard. Table 1 shows statistics from Major Hazard Incident Data Service (MHIDAS) incurred by MEKPO accidents [16].

Methods

Sample

Liquid MEKPO 31 mass% was purchased directly from Fluka Co. and stored in a refrigerator at 4 °C. Dimethyl phthalate (DMP 99 mass%) was used as a diluent in preparing the liquids of the 20 mass% MEKPO sample.

Adiabatic tests by VSP2

As a PC-controlled adiabatic calorimeter system, the VSP2, manufactured by Fauske Associates, Inc., (FAI) [17] was adopted to measure the thermokinetic and thermal hazard data, such as temperature and pressure traces with respect to time. In essence, the low heat capacity of the cell ensures that nearly all the reaction heat released remains within the test sample. Temperature, pressure-derived thermokinetic behaviors in the small test cell (112 mL) can therefore be extrapolated directly to the process scale due to the low thermal inertia of about 1.05 to 1.2 [18]. Under the experimental conditions, if the self-heating rate exceeds 0.2 °C min^{-1}, and the heat-wait-search mode is terminated and the instrument enters adiabatic (AK) mode.

Table 1 Selected thermal explosion accidents caused by MEKPO in among Taiwan, Japan, Korea, and China [5]

Date	Location	Fatalities	Injuries	Hazardous
1979	Taiwan, Taipei	33	49	Explosion (storage)
1996	Taiwan, Taoyuan	47	10	Explosion (tank)
1964	Japan, Tokyo	114	19	Explosion
1978	Japan, Kanagawa	0	0	Explosion
2000	Korea, Yosu	11	3	Explosion
2001	China, Jiangsu	2	4	Explosion
2003	Chian, Zhejiang	3	5	Explosion

In AK mode, the main heater directly to the test cell is switched off and merely the guard heater is operated to ensure negligible heat losses. This allows the self-heating behavior of the sample to be measured. If the runaway reaction has been induced in the test cell, the self-heating rate may be larger than 100 °C min^{-1}. To sustain the adiabatic conditions during an experiment, a guard heater has to be started completely by automatic interior function for heating to the same temperature between test cell and vessel. Adiabatic cotton was employed between test cell and heater, which also was being treated as an important unit for maintaining adiabatic conditions during VSP2 testing. To avoid violent explosion happening in regular 31 mass% MEKPO, here, VSP2 was used to evaluate the essential thermokinetics for 20 mass% MEKPO.

Thermal explosion simulation

The simulation of MEKPO thermal explosion in CE-FK is comprised of four main parts [6, 19, 20]: the geometry and dimension of a vessel, physical properties of MEKPO and material of the vessel's shell, and initial temperatures of shell and liquid: under the same volume (500 m^3), thickness (0.006 m), material (stainless steel) and initial temperature conditions, a vessel designed by following API from Formosa Plastics Group No. 6 Naphtha Cracking plant in Mailiao, Yunlin county, Taiwan. In total, three types of geometry, infinite cylinder with radius 2.52 m, vertical barrel with radius 3.98 m and height 10.1 m, sphere with radius 4.92 m, were used as shown in Fig. 1. It was chosen for simulation, because such a vessel is suitable for use in practice. Tables 2 and 3 list the descriptions of geometry [21] and shell [22] of MEKPO vessel. Initial conditions:

- CE-FK assumes that at the beginning ($t = 0$) the liquid is motionless.
- The initial temperatures and initial conversions for all the components. Initial conversions are always assumed to be zero.

Boundary conditions that define the type of heat exchange between the vessel and the environment are as follows: CE-FK allows specifying boundary conditions of the first, second, and third type, which are assumed to be uniform over each vessel surface and can be specified for each surface, individually.

The first type (1st): $T_{wall} = T_{e,}$ where T_e denotes a function that gives the time dependence of ambient temperature on the wall. The second type (2nd): $q_{wall} = -\lambda (\partial T/\partial x)_{wall} = q_e$, where q_e represents a function that gives the time dependence of heat flux on the wall. The third type (3rd): $q_{wall} = -\lambda \ (\partial T/\partial x)_{wall} = \alpha(T_e - T_{wall})$, where α and T_e are functions that give the time dependence of the heat transfer coefficient and of the ambient temperature. The vessel can be divided into three surfaces: top, side, and bottom. The boundary conditions on the side and top surfaces were assumed to be of the first type. In practice, the vessel is constructed on the ground; therefore, the bottom is in close contact with the ground, which is reasonable for taking its temperature to equal the ambient one. This study merely simulated the first-type boundary conditions for the vessel, i.e., fire conditions. If we analyzed accidental fire conditions, the ambient temperature would be much higher than the cooling failure, because, in this case, air is moved

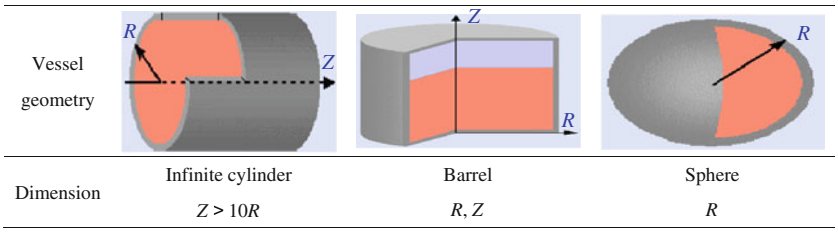

Fig. 1 Three types of vessel geometry and their dimensions [8]

Table 2 Geometry description of MEKPO vessels

Geometry	Barrel/m		Sphere/m	Infinite cylinder/m
Type method	112 mL test cell experiment	500 m^3 simulation	500 m^3 simulation	500 m^3 simulation
Radius	0.0254	3.98	4.92	2.52
Height	0.0635	10.1	NA	NA
Thickness	0.0002032	0.006	0.006	0.006

Table 3 Description of shell properties of MEKPO vessels [19]

Parameter	Units	Stainless steel
Density	kg m^{-3}	8,000
Specific heat	J kg^{-1} K^{-1}	500
Thermal conductivity	W m^{-1} K^{-1}	16
Initial temperature	°C	30

Table 4 Boundary conditions of MEKPO vessel

Boundary conditions		1st kind
Time/s	Part	Environment temperature/°C
0	Top	100
0	Side	100
0	Bottom	30

around the vessel. We took a temperature of about 100 °C to simulate the fire conditions. The boundary conditions are given in Table 4. Other boundary conditions for velocity are conventional: no-slip, and no penetration conditions on walls and symmetry conditions on the symmetry axes. Mathematically, it means that normal (V_{nr}) and tangential (V_{tn}) components of velocity are equal to zero. Here, nr and tn indicate normal direction and tangential direction [19].

The reaction of MEKPO could be represented by the following kinetic model:

Rate equation:

$$r = k_0 e^{-E_a/RT}[\text{MEKPO}]^n$$

The kinetic parameters of a single reaction can be evaluated from the equation derived by Townsend and Tou for an adiabatic process [23] or by curve fitting method in CISP [19]. The kinetic parameters of 20 mass% MEKPO were measured by the latter one. Its values of $\ln(k_o)$, E_a, n, Q parameters are listed in Table 5.

Two important aspects of simulation should be emphasized.

1. When simulating the horizontal cylindrical tank, the model of an infinite cylinder was used. This simplification can be applied for simulation for the following reason. It is known that when the length to diameter ratio exceeds 2–3 the impact of the cylinder butts is negligible. In the case under consideration this ratio is more than 5.
2. At the moment CE-FK allows simulation of thermal explosion in a liquid taking into account laminar convection only [24]. As a matter of fact, significant impact of turbulent convection can be expected for big tanks. Therefore, the predictions of simulation are conservative.

Table 5 Thermokinetic parameters of 20 mass% MEKPO tested by VSP2

Parameter	Units	Value
$\ln(k_o)$	s^{-1}	27.18
E_a	kJ mol^{-1}	116.69
n	–	1.00
Q	kJ mol^{-1}	1297.82

Results and discussion

Since the CE-FK has not provided to run the pressure function, the pressure of MEKPO thermal explosion will wait the MEKPO response mechanism to successfully

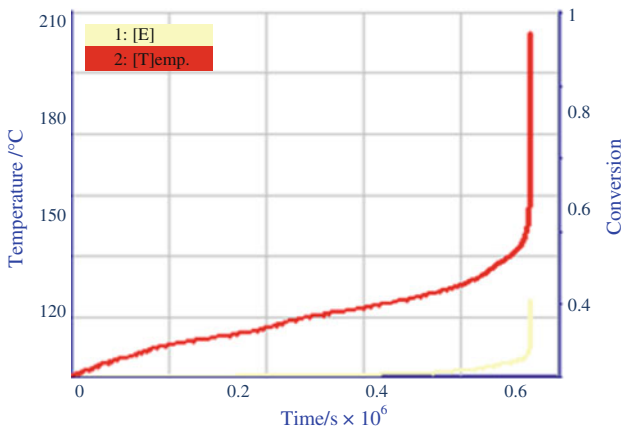

Fig. 2 Temperature, conversion versus time of sphere vessel traced with process time

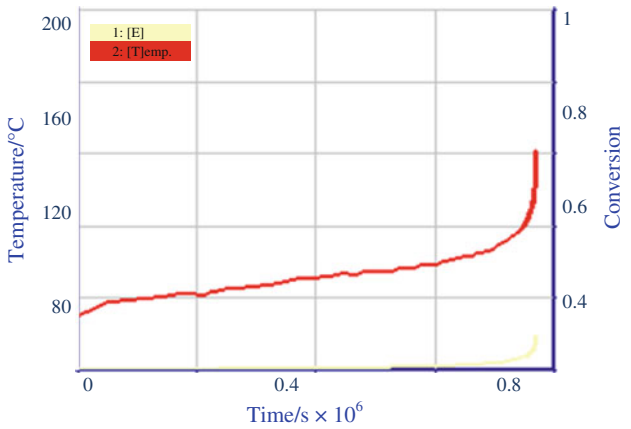

Fig. 3 Temperature, conversion versus time of barrel vessel traced with process time

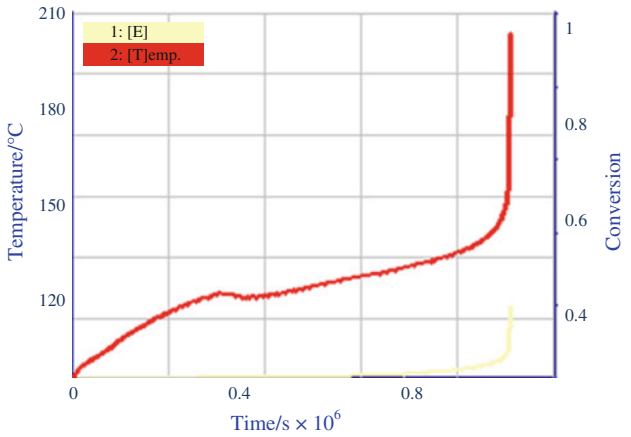

Fig. 4 Temperature, conversion versus time of infinite vessel traced with process time

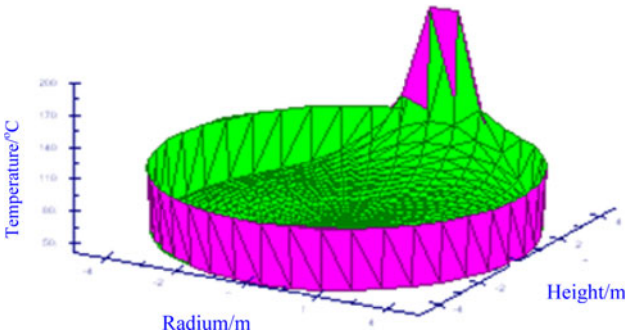

Fig. 5 Temperature field of sphere vessel traced with process time

establish the formula at CE-Pro in CISP to run out the pressure. For the experiment, to avoid bursting the test cell and losing all the exothermic data, the VSP2 tests should be careful with 20 mass% MEKPO when testing, especially in pressure. Figures 2, 3, 4, 5, 6 and 7 show the temperature, conversion versus time and temperature field in sphere, barrel, and infinite shape, respectively.

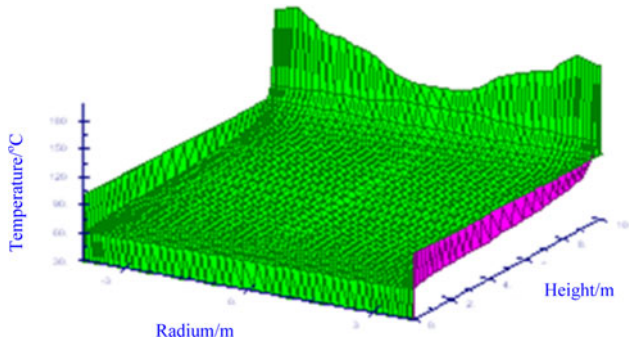

Fig. 6 Temperature field of barrel vessel traced with process time

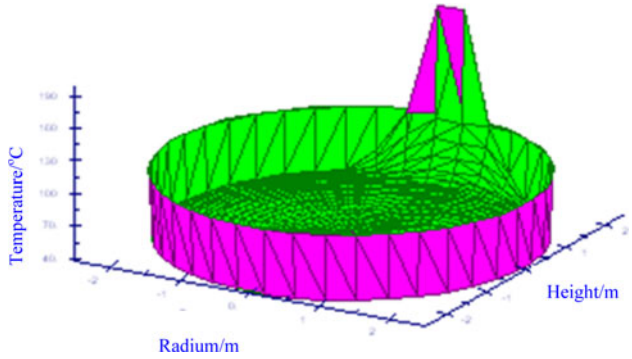

Fig. 7 Temperature field of infinite vessel traced with process time

From the simulated results the vessel was exposed to first kind fire conditions: the simulated T_{max}, would be 200.1, 121.5, and 200.0 °C, respectively, at sphere, barrel, and infinite cylinder geometry, as given in Table 6. Figures 8, 9, and 10 are the temperature versus time curves for the thermal decomposition simulation of MEKPO vessel at infinite cylinder, barrel, and sphere geometry under the first kind boundary conditions. From outcome, the simulated results compared with VSP2 tests, a slight distance still existed by the same aspect. Nevertheless, thermal explosion simulation possessed the following advantage of solving real problems for commercial scale that definitely could not be finished by the laboratory test.

Table 6 Results of VSP2 test and simulation of 20 mass% MEKPO

Method and sample	T_{max}/°C	P_{max}/bar
Infinite cylinder (500 m^3, MEKPO 125 m^3 filled)	200.0	Under simulation
Barrel (500 m^3, MEKPO 125 m^3 filled)	121.5	Under simulation
Sphere (500 m^3, MEKPO 125 m^3 filled)	200.1	Under simulation

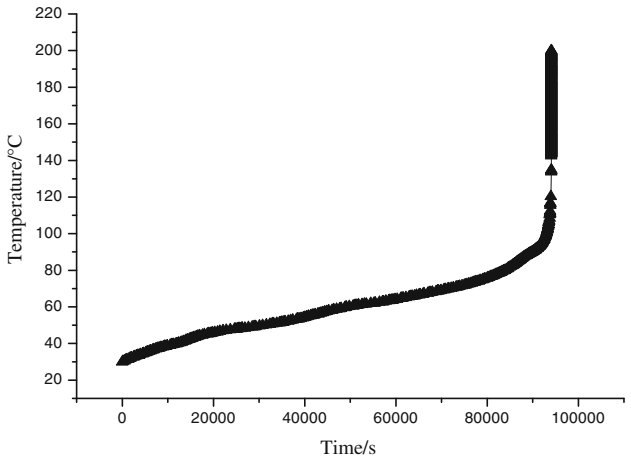

Fig. 8 Temperature versus time for thermal decomposition of 20 mass% MEKPO by VSP2 compared with thermal explosion simulation at sphere vessel

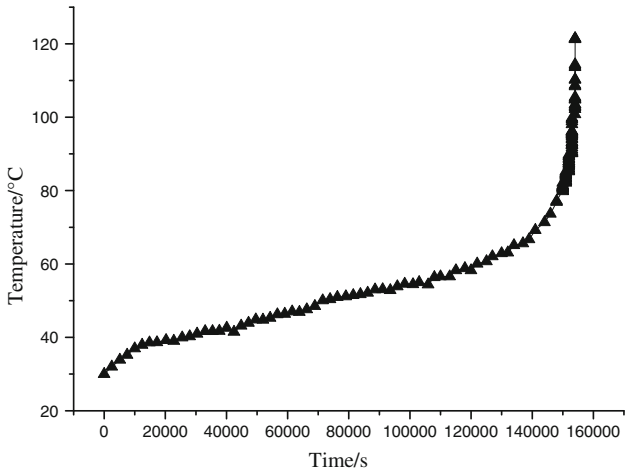

Fig. 9 Temperature versus time for thermal decomposition of 20 mass% MEKPO by VSP2 compared with thermal explosion simulation at barrel vessel

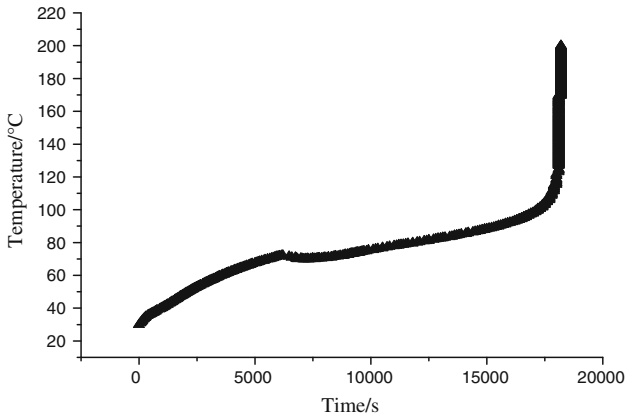

Fig. 10 Temperature versus time for thermal decomposition of 20 mass% MEKPO by VSP2 compared with thermal explosion simulation at infinite vessel

Conclusions

Through this study, four conclusions were reached and summarized as follows:

1. The trend of the simulated curves of temperature and pressure tended to follow the VSP2 tests. From Figs. 8, 9, and 10, the simulated T_{max} showed a better approach, whereas the simulated P_{max} should still be further researched.
2. The kinetics-based simulation is a very efficient method for responding to complex reacting system-multi-stage reactions, complex geometry, various types of boundary condition challenges as an assessment of thermal explosion hazards.
3. In brief, numerical simulation provides detailed results when modeling thermal explosions without essential simplifications. It is applicable to a wide variety of practical problems in many cases; the approach coupled with the appropriate software is the only way to obtain the necessary answers, for which even a laboratory test may not be feasible.
4. As far as the degree of difficulty is concerned, the simulation method requires more accurate and clear knowledge of reaction kinetics, chemical properties, and mathematical complexity, to name a few.

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