

# **New Approaches for Calculating Safety Parameters and Estimating Hazard Severity for Cumene Hydroperoxide**

Deng-Jr Peng, Chi-Min Shu and Jing-Heng Wang

Process Safety and Disaster Prevention Laboratory,  
Department of Environmental and Safety Engineering,  
National Yunlin University of Science and Technology,  
Touliu, Yunlin, Taiwan 640, R.O.C.

Mei-Ling Shyu

Department of Electrical and Computer Engineering, University of Miami,  
Coral Gables, FL 33124-0640, U.S.A.

Shu-Ching Chen

Distributed Multimedia Information System Laboratory, School of Computer Science,  
Florida International University, Miami, FL 33199, U.S.A.

## **Abstract**

Commonly used chemicals number more than four billion worldwide today, but an adequate understanding of the inherent properties of these materials exists only for several hundred thousands of them. Therefore, unexpected hazards or even accidents are difficult to avoid during preparation, transportation, manufacturing, storage and even disposal periods. Among these, hazards due to hydroperoxides can occur more frequently in various stages, with enormous resulting damage. As far as safety estimation is concerned, the basic safety parameters, unknown substance hazards and their severity need to be calculated and evaluated effectively. Screening methods are presented and validated to prove that they are viable approaches. Therefore, one of the responsibilities of a process safety engineer is to combine traditional approaches with modern computer techniques to develop a more thorough and convenient safety estimation model. Examples with cumene hydroperoxide are demonstrated.

Keywords: hazards; hydroperoxides; safety parameters; severity; screening methods

## **Introduction**

Historically, chemical process industries have encountered countless hazards and unacceptable accidents. Faisal and others have categorized many disasters between 1926 and 1997 [1-4]. Among these calamities, chemical runaway reactions comprise a certain significant portion, which are selectively shown in Table 1.

In reality, such accidents can be actively prevented if information can be prudently collected and experience learned from Keller and his associates [5] classified runaway reactions via severity, and then introduced a quick and cost-effective method to estimate safety classes.

Among the estimation safety classifying processes, some safety parameters are very important, such as TMR (time to maximum rate),  $T_{NR}$  (temperature of no return), and  $T_{SADT}$  (temperature of self-accelerating decomposition temperature). Therefore, in this study, we will introduce theories of these safety parameters, along with new screening methods conducted by simulation software to calculate the same safety parameters for cumene hydroperoxide (CHP) as a typical reactive chemical. This is expected to launch a time-effective, convenient and efficient method to assist the chemical industry in comprehending various unknown hazard characteristics of hydroperoxide.

Table 1

List of Selected Major Accidents Due to Fire and/or Explosion in the Chemical Process Industries [1-4]

Year	Location	Chemical	Event	Deaths/injured
1943	Ludigshafen, Germany	Butadiene	Explosion	>100d
1944	Cleveland, OH	LNG	Fire	128/200~400
1947	Texas City, TX	Ammonium nitrate	Explosion	552/3000
1948	Ludigshafen, Germany	Dimethyl ether	Explosion	245/2,500
1956	Cali, Columbia	Dynamite, munitions	Explosion	1,200d
1958	Niagara Falls, NY	Nitromethane	Explosion	?/>200
1962	Ras Taruna, Saudi Arabia	Propane	Fire	1/111
1964	Tokyo, Japan	MEKPO	Fire/Explosion	19/114
1966	LaSallie, Quebec	Styrene	Explosion	11/10
1967	Lake Charles, LA	Isobutane	Explosion	7/14
1969	Teeside, UK	Cyclohexane	Fire	2/23
1971	Netherlands	Butadiene	Explosion	8/21
1972	Rio de Janerio, Brazil	Butane	Explosion	37/53
1973	Kingman, AZ	Propane	Fire	13/89
1974	Flixborough, UK	Cyclohexane	Explosion	28/76
1975	Beek, Netherlands	Propylene	Explosion	14/108
1976	Chalmette, LA	Ethyl benzene	Explosion	13/?
1977	Gujarat, India	Hydrogen	Explosion	5/35
1978	San Carlos, Spain	Propylene	Fire	216/200
1984	Cubatao, Brazil	Petrol	Fire	100/150
1984	Mexico City, Mexico	LPG	Fire	650/6,400
1985	Priola, Italy	Ethylene	Explosion	23/11
1986	Kennedy Space Center, FL	Hydrogen	Explosion	7/119
1987	Piper Alpha, North sea	Hydrogen	Explosion	167/55
1988	Narco, LA	Propane	Explosion	7/48
1989	Pasadena, TX	Ethylene	Explosion	23/314
1990	Tokyo, Japan	BPO	Fire/Explosion	9/17

1992	Sodegraura, Japan	Hydrogen	Explosion	10/7
1994	Dronka, Egypt	Aviation, Diesel Fuel	Fire	410d
1996	Tao Yuan, Taiwan	MEKPO	Fire/Explosion	10/47
1997	Kaoshiung, Taiwan	LPG	Fire	14/11
1998	Kaoshiung, Taiwan	LPG	Fire/Explosion	4/43

d: death

?: information not available

## Principles of $TMR_{ad}$ and Determination of Hazard Severity

In principle, the best way to acquire  $TMR_{ad}$  (time to maximum rate at adiabatic conditions) would be to perform an adiabatic experiment and a nonadiabatic experiment. The calculated  $TMR_{ad}$  is always longer than one from adiabatic experiments. Therefore, this study will introduce the obtained  $TMR_{ad}$  methods for both normal Arrhenius type reactions and autocatalytic reactions. For a normal reaction with  $\Delta T_{ad} > 50$  K or a typical autocatalytic reaction with self heating rate of greater than 200 J/g (or 160 kJ/mole), the process safety engineer should cautiously calculate  $TMR_{ad}$  [6] in order to avoid any unexpected events. In general, a typical industrially acceptable value of  $TMR_{ad}$  is 10-24 hours [7]. According to Frank-Kamenetskii's theory (F-K Model) [8], the relation function of the obtained Arrhenius type for nth order reaction  $TMR_{ad}$  could be written as:

$$\tau_{ad} = TMR_{ad} = \frac{RT_0^2}{AE_a \Delta T_{ad}} \exp\left(\frac{E_a}{RT_0}\right) \quad (1)$$

For an autocatalytic reaction, Grever derived a related function for the obtained method of  $TMR_{ad}$  which could be written as [9]:

$$\tau_{ad} = TMR_{ad} = k_0^{-1} \exp(\beta B) E_a (\beta B) \quad (2)$$

According to Andreas Keller, who proposed specific experimental steps, a process safety engineer could obtain safety values ( $S_a$  and  $S_i$ ) of unknown materials so as to determine hazard severity. The following are steps of the whole process to obtain safety values  $S_a$  and  $S_i$ , and the flow diagram is shown in Figure 1:

1. Run scanning experiment via dynamic DSC.
2. Check the samples' experimental values with  $\Delta T_{ad} > 50$  K.
3. Identify reaction types and unknown materials' severities by the  $E_{a,e}$  or  $\Delta H$  (estimated  $E_a$  with dynamic DSC, J/mole; reaction heat,  $\Delta H$ , J/g) plot and evaluate them separately.

4. Calculate  $TMR_{ad}$  (dyn) for the unknown material reactions by dynamic DSC.
5. Confirm the ones with  $TMR_{ad}$  (dyn) less than 24 hrs and evaluate these separately.
6. Conduct isothermal TAM experiment or search literature values to determine  $TMR_{ad}$  (iso).
7. Run adiabatic VSP2 experiment or search literature values to determine  $TMR_{ad}$  (adi).
8. Calculate  $S_a = \frac{TMR_{ad}(dyn)}{TMR_{ad}(adi)}$  or  $S_i = \frac{TMR_{ad}(dyn)}{TMR_{ad}(iso)}$

If  $S_a$  or  $S_i < 1 \Rightarrow$  safe

Otherwise  $\Rightarrow$  unsafe [5, 9-13]

### **Principles of $T_{NR}$ and $T_{SADT}$ and safety parameters determination by simulation**

Among the estimation of safety parameters,  $T_{NR}$  and  $T_{SADT}$  are two important parameters. Previously, theories mostly used methods derived by Townsend [10] and Fisher [11] to obtain these parameters; but, based on their related formulas to manually calculate safety parameters, it would be a tedious, complex, and time-consuming process; otherwise, the accuracy is doubtful. Some screening and simulated methods have been developed. Basically, process safety engineers could import raw data obtained from experiments, then acquire rapid and accurate kinetic data, along with specific safety parameters.

Theoretically, formulas for the calculation of  $T_{NR}$  and  $T_{SADT}$  are the following [11]:

$$(T_{NR} + 273.15)^2 = \frac{m \times (E) \times \Delta H \times A \times \exp(-E / R(T_{NR} + 273.15))}{R \times (U) \times (1.8) \times S} \quad (3)$$

$$T_{SADT} = T_{NR} - \frac{R \times (T_{NR} + 273.15)^2}{E} \quad (4)$$

In this study, all  $T_{NR}$ ,  $T_{SADT}$ , and the characteristics of the vessel are determined by using Fisher's approach and under onset temperature condition.

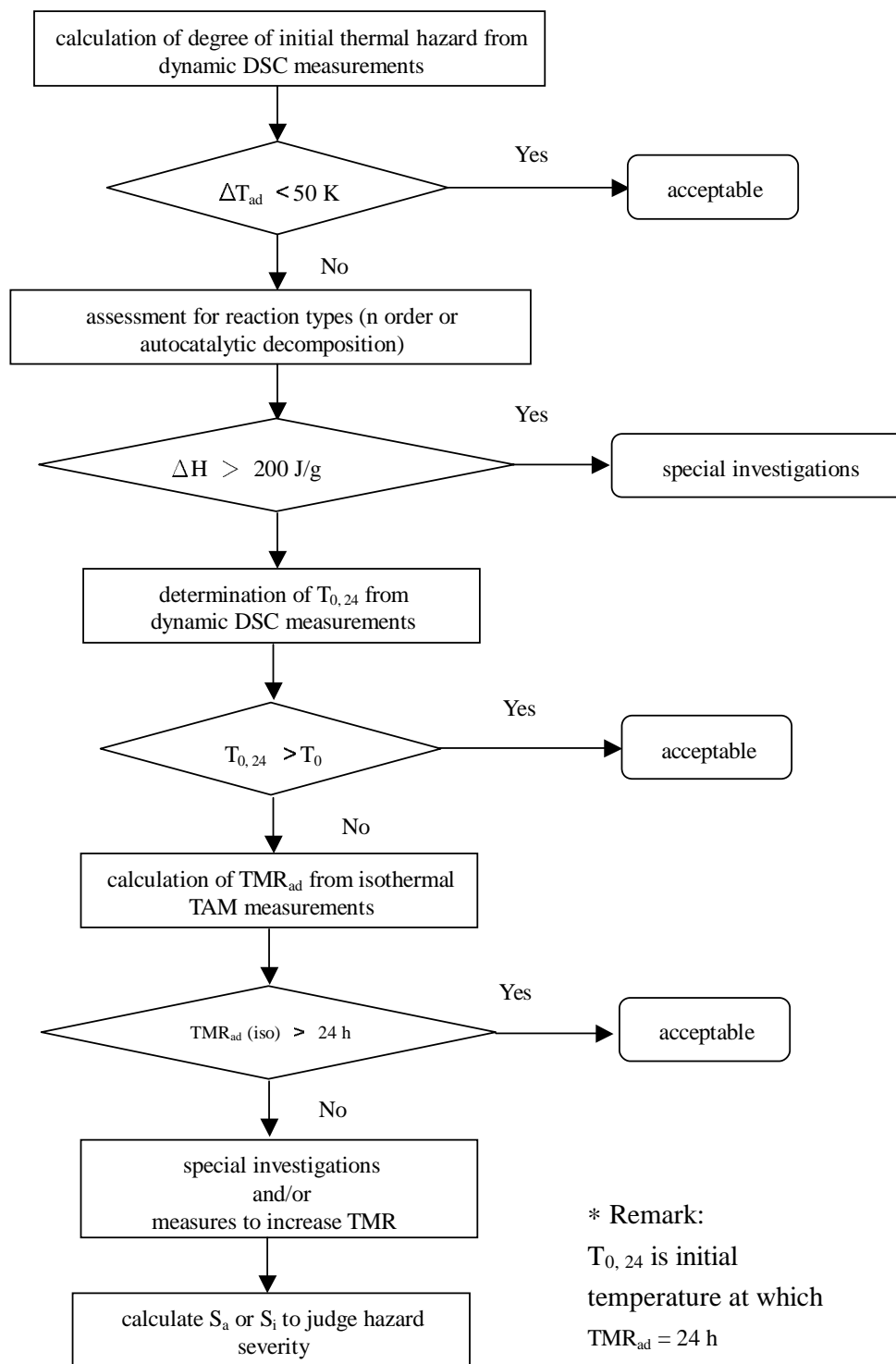


Figure 1. Description of the Thermal Risk Assessment Procedure Including the Estimation Method [5, 9-16].

## Results and discussion

Historically, there are many examples of the fearful impact of hydroperoxides, along with their inherent hazards. Therefore, this part of article will use examples, such as CHP and its contaminants, to investigate their hazards during process, storage, transportation or even disposal periods. [13]

In the past, CHP has been an important intermediate phenol process, and it is now also an important precursor among the main process of DCPO (Di-Cumene Peroxide). In practice, CHP can be used as the emulsified polymerization initiator, hardener of SBR (Styrene-Butadiene-Rubber), ABS (Acrylonitrile-Butadiene-Styrene), and unsaturated polyester resins [14]. However, CHP has generated several hazard cases in Taiwan as shown in Table 2, and its characteristics are shown in Table 3. In addition, CHP demonstrates severe dangers when it is mixed with contaminants [15].

In Tables 4 and 5, experimental results, kinetic parameters, and safety parameters are obtained from DSC (Differential Scanning Calorimetry, Mettler Toledo 821<sup>e</sup>) and VSP2 (Venting Sizing Package2) of CHP and its contaminants [16]. Changes of  $T_{onset}$  and  $E_a$  show that hazards of CHP with contaminants could be more dangerous. Therefore, process safety engineers should judge its potential hazard properties, so that the following illustrations would demonstrate whether CHP, including its various contaminants, was dangerous or not. Note too that this study also used simulation screening method to do safety assessment, which is, in turn, compared with values of empirical formulas with similar approaches, but it would be more convenient, reliable, and easier to estimate an unknown material's reactivity properties under variable mechanisms.

Typically, by using both F-K Model and Keller theories,  $TMR_{ad(adi)}$ ,  $TMR_{ad(Dyn)}$ , and safety indices,  $S_a$ , of CHP are calculated as follows:

$$S_{a,CHP} = \frac{TMR_{ad}(dyn)}{TMR_{ad}(adi)} = \frac{0.03}{0.0411} = 0.730 \quad (\text{safe})$$

Therefore, CHP safety properties are on the safe side.

If the vessel is inadvertently mixed with contaminants, the safety properties of CHP could be shown as follows:

$$\text{Ion (acid):} \quad S_{a,CHP+H_2SO_4} = \frac{TMR_{ad}(dyn)}{TMR_{ad}(adi)} = \frac{0.089}{0.0617} = 1.442 \quad (\text{unsafe})$$

$$S_{a,CHP+HCl} = \frac{TMR_{ad}(dyn)}{TMR_{ad}(adi)} = \frac{4.117}{0.1444} = 28.511 \text{ (unsafe)}$$

$$\text{Ion (base): } S_{a,CHP+NaOH} = \frac{TMR_{ad}(dyn)}{TMR_{ad}(adi)} = \frac{0.298}{0.0258} = 11.55 \text{ (unsafe)}$$

Tables acquired from experimental data for CHP with contaminants significantly demonstrate a higher degree of severity than the pure one. Therefore, from these cases, this method is proven useful for hazard evaluation, in terms of degree of severity.

Furthermore, after obtaining safety indices,  $S_a$  or  $S_i$ , process safety engineers could calculate  $T_{NR}$ , and  $T_{SADT}$  to use in conceptual design and process control, along with recommended temperature ranges during various stages. In this study, these safety parameters could also be determined by simulation, as in Tables 4 and 5, but there is no example to determine safety indices in this article.

Table 2

Selected Thermal Explosion Accidents Caused by Peroxides in Taiwan since 1979 to 1999 [15]

Year	Chemicals	Deaths/Injures	Hazard	Cause
1979	MEKPO	33/49	Explosion (Storage)	Thermal Decomposition
1981	CHP	1/3	Explosion (Condensation)	Thermal Decomposition
1984	MEKPO	5/55	Explosion (Reactor)	Thermal Decomposition
1986	CHP	0/0	Explosion (Reactor)	Thermal Decomposition
1996	MEKPO	10/47	Explosion (Storage)	Thermal Decomposition

Table 3

Basic chemical and physical characteristics of CHP [18]

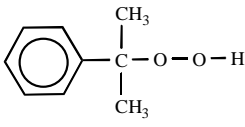
Name	Flash point	Boiling point (1 atm)	Molecular weight (g/mole)	Molecular formula
CHP	79.5°C (Closed Cup)	116°C	152.21	

Table 3 Calculated kinetic and safety parameters derived from the kinetic scanning experiments of CHP and contaminants by DSC [16]

Data CHP and contaminants	Sample mass (mg)	Scanning rate, r (°C/min)	T <sub>0</sub> (°C)	T <sub>max</sub> (°C)	E <sub>a</sub> (kJ/mol)	ΔH (J/g)	TMR <sub>dyn</sub> (min)	T <sub>NR</sub> (°C)	T <sub>SADT</sub> (°C)
35 wt% CHP	6.15	4	135	192.6	112.80	607.3	0.03	76	67.01
			<b>136</b>	<b>191.8</b>	<b>113.00</b>	<b>630.5</b>	<b>0.04</b>	<b>59.85</b>	<b>51.73</b>
35 wt% CHP + H <sub>2</sub> SO <sub>4</sub> (1N)	4.33 + 1.05	4	90	167.3	77.59	667.3	0.089	11	2.35
			<b>96</b>	<b>166.9</b>	<b>78.00</b>	<b>526.1</b>	<b>0.068</b>	<b>12.85</b>	<b>4.13</b>
35 wt% CHP + HCl (1N)	4.68 + 0.74	4	85	171.9	138.59	715.7	4.117	64	57.18
			<b>85</b>	<b>169.7</b>	<b>141.97</b>	<b>601.3</b>	<b>4.464</b>	<b>46.45</b>	<b>40.47</b>

---Calculated values based on experimental data

---Simulated values based on CISP software

\* all values of T<sub>NR</sub> and T<sub>SADT</sub> were determined by Fisher's approach with fixed conditions [11]

Table 4 Calculated kinetic and safety parameters derived from the adiabatic experiments of CHP and contaminants by VSP2 [16]

Data CHP and contaminants	Conc. & mass	Φ	T <sub>0</sub> (°C)	T <sub>max</sub> (°C)	E <sub>a</sub> (kJ/mol)	(dT/dt) <sub>0</sub> (°C/min)	TMR <sub>adi</sub> (min)	T <sub>NR</sub> (°C)	T <sub>SADT</sub> (°C)
35 wt% CHP	16 g	1.45	140.93	248.72	119.75	0.70	0.0411	92.34	83.07
			<b>146.85</b>	<b>249.85</b>	<b>120.43</b>	<b>0.65</b>	<b>0.0446</b>	<b>94.12</b>	<b>84.81</b>
35 wt% CHP + H <sub>2</sub> SO <sub>4</sub>	(0.5 M, 1 g)	1.45	121.01	241.42	118.06	0.45	0.0617	87.86	76.85
			<b>125.11</b>	<b>249.63</b>	<b>117.53</b>	<b>0.52</b>	<b>0.0563</b>	<b>82.76</b>	<b>71.99</b>
35 wt% CHP + HCl	(1 M, 1 g)	1.45	131.15	259.64	155.22	0.15	0.1444	103.40	95.81
			<b>137.56</b>	<b>256.56</b>	<b>155.21</b>	<b>0.16</b>	<b>0.1466</b>	<b>101.64</b>	<b>94.12</b>

---Calculated values based on experimental data

---Simulated values based on CISP software

\* all values of T<sub>NR</sub> and T<sub>SADT</sub> were determined by Fisher's approach with fixed conditions [11]

## Conclusion

In summary, through these new and revised methods, safety indices can be estimated by conventional empirical formulas, as well as simulation software. The advantages of this new approach could enhance the technology of process safety while determining the degree of severity.



The merits of this method could be expressed as follows:

1. This method of assessment can be used, and its accuracy accepted.
2. This procedure could be applied in initial process assessment, even as early as in the stage of conceptual design in plant.
3. It establishes concepts of safety parameters and safety indices.
4. It prevents hazards among stages, handling, storage, transportation, and disposal period.
5. It combines CPQRA (chemical process quantities of risk analysis) and TRA (transportation risk analysis) to conduct risk assessment.
6. It subsumes safety indices and contaminants of materials to MSDS of standard issues. In addition, software simulation for estimating safety properties or safety indices of unknown materials is a convenient way to do an initial assessment of process plants. Therefore, this study launches a new method, as shown in Figure 2, to establish an assessment flowchart for estimating versatile hazard conditions exclusively for reactive chemical process control and design.

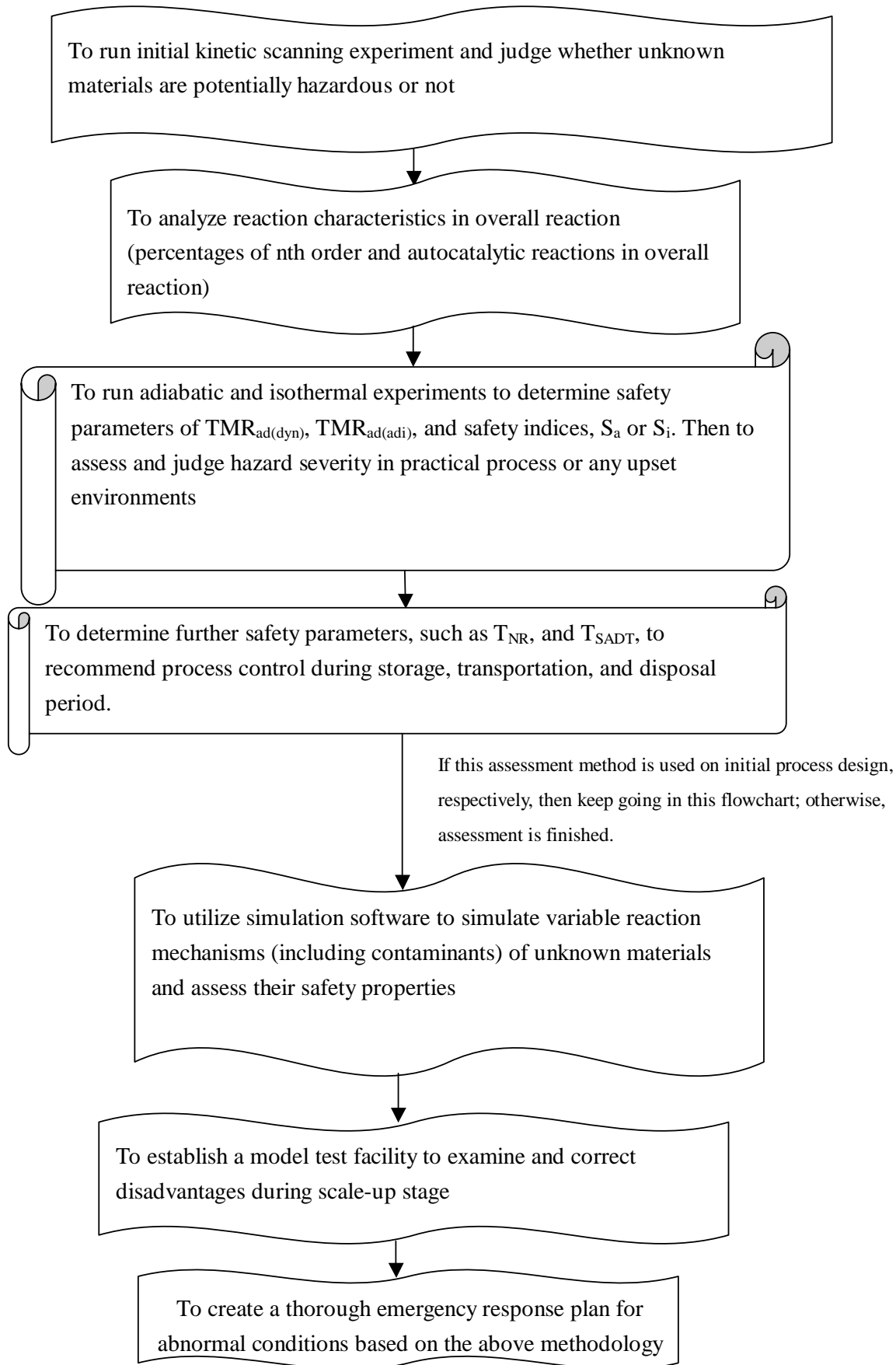


Figure 2. Flowchart of hazard assessment of specific chemical used in design or manufacturing stages

## Nomenclatures

A	frequency factor, $\text{min}^{-1}$
$\beta$	rate coefficient of autocatalytic reaction
B	thermal reaction parameter = $\frac{E_a \Delta T}{RT_0}$ , dimensionless
$(dT/dt)_0$	self-heating rate, $^{\circ}\text{C min}^{-1}$
$E_a$	activity energy, $\text{kJmole}^{-1}$
$E_{a,e}$	estimated $E_a$
$\Delta H$	heat of reaction, $\text{kJ mol}^{-1}$
$k_0$	rate constant at $T = T_0$
m	mass of reactant, g
R	gas constant, $8.314 \text{ J/mole}^{\circ}\text{C}$
S	vessel wetted surface area, $\text{m}^2$
$T_0, T_{\text{onset}}$	onset temperature, $^{\circ}\text{C}$
$T_{0,24}$	initial temperature at which $\text{TMR}_{\text{ad}} = 24 \text{ h}$
$T_{\text{max}}$	maximum temperature during overall reaction
TMR	time to maximum, min
$\text{TMR}_{\text{ad}}$	time to maximum rate at adiabatic conditions
$\text{TMR}_{\text{ad(adi)}}$	$\text{TMR}_{\text{ad}}$ from adiabatic measurement
$\text{TMR}_{\text{ad(dyn)}}$	$\text{TMR}_{\text{ad}}$ from dynamic estimation
$\text{TMR}_{\text{ad(iso)}}$	$\text{TMR}_{\text{ad}}$ from isothermal measurement
$T_{\text{NR}}$	temperature of no return, $^{\circ}\text{C}$
$T_{\text{SADT}}$	self-accelerating decomposition temperature, $^{\circ}\text{C}$
$\Delta T_{\text{ad}}$	adiabatic temperature raise, $^{\circ}\text{C}$
U	overall heat transfer coefficient, $\text{kJmin}^{-1}\text{m}^{-2}\text{K}^{-1}$
$\Phi$	thermal inertial

## Acknowledgements

The authors gratefully acknowledge Dr. Arcady Kossoy at Saint-Petersburg, Russia; Mr. Yue-Lou Hsu at Coin Chemical Industrial Company; and Mr. Yih-Wen Wang at National Yunlin University of Science and Technology for their helpful discussions and comments.

## References

1. F. I. Khan and S. A. Abbasi, *J. Loss Prev. Process Ind.*, 12, (1999), pp. 361-378.
2. F. P. Lees, *Loss Prevention in the Process Industries (Hazard Identification, Assessment and Control)*, 2<sup>nd</sup> ed., Oxford, UK, Vol.3, (1996), pp. A 1/9-1/23.
3. Maboney, D. G. *Large Property Damage Losses in the Hydrocarbon-Chemical Industries A Thirty Year Review*, M & MPC Headquarters, (1997).
4. Center for Environmental, Safety and Health Technology Development, <http://www.e-safety.com.tw>, (2001).
5. A. Keller, *J. Loss Prev. Process Ind.*, 1, (1997), pp. 31-41.
6. J. Steinbach, *J. Chemische Sicherheitstechnik VCH*, (1995).
7. F. Stoessel, *J. Loss Prev. Process Ind.*, 6, (1993), Page 79.
8. D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics*, Plenum, 2nd ed., (1969), pp. 349-357.
9. T. Grever, *Thermal Hazards of Chemical Reactions*, Elsevier, (1994), pp. 23-27.
10. D. I. Townsend and J. C. Tou, *Thermochimica Acta*, 37, (1980) pp. 1-30.
11. H. G. Fisher and D. D. Geotz, *J. Loss Prev. Process Ind.*, 6, (1993), pp. 183-194.
12. J. Barton and Richard Rogers, *Chemical Reaction Hazards*, 2nd ed, (1997), pp. 3-19.
13. H. Y. Hou, C. M. Shu, and Y. S. Duh, *AIChE Journal (R&D Note)*, (2001)(Accepted).
14. Y. L. Hsu, Personal Communication, (2001).
15. C. M. Shu, Y. W. Wang, Y. S. Dhu, and C. S. Kao, *The Annual EDUG Meeting Papers*, (1999), pp. 1-15-1-28.
16. Y. W. Wang, C. M. Shu, Y. S. Dhu, and C. S. Kao, *I&EC Research*, 40, (2001), pp. 1125-1132.
17. Center for Industrial Safety and Health Technology, *Industrial Technology Research Institute, Technology Report*, (1994).

18. Search Engine of Vermont SIRI MSDS on Line Database,  
<http://hazard.com/msds/mf/cards/file/0761.html>, (2001).