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Evaluations of fire and explosion hazard for the mixtures of benzene and methanol using rough set method

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Abstract The effect of initial temperatures (100, 150, and 200 °C), operating pressures (101 and 202 kPa), and various loading oxygen concentrations (21, 17, 14…oxygen vol.%) on the flammability hazard evaluations for the mixtures of benzene and methanol (100/0, 75/25, 50/50, 25/75, and 0/100 vol.%) by using rough set method, was studied. The results indicated that the most important influence factor was the operating pressure. There is no significant difference in the safety assessment for the different concentrations of mixtures. This study proposed a helpful reference for a related practical plant combined with experimentally and theoretically feasible way for flammability prevention and protection.

Keywords Benzene · Flammability hazard evaluations · Influence factor · Methanol · Rough set method

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List of symbols

A	Set of attribute in rough set method (dimensionless)
B	Set of attribute in rough set method (dimensionless)
$bn_R(A)$	Boundary of A in rough set method $bn_R(A) = \underline{R}(A) - \bar{R}(A)$ (dimensionless)
$b(x_i)$	Parameter in rough set method (dimensionless)
$b(x_j)$	Parameter in rough set method (dimensionless)
C1	Input factor of rough set method (initial temperature)
C2	Input factor of rough set method (initial pressure)
C3	Input factor of rough set method (loading oxygen concentration)
C4	Input factor of rough set method (benzene/methanol mixing ratio)
C5	Output result of rough set method (explosion class)
$(dP\ dt^{-1})_{max}$	Maximum rate of explosion pressure rise (kPa s^{-1})
f_a	Mapping in rough set method f_a: $U \rightarrow V_a$ (dimensionless)
IE	Ignition energy (J)
Ind(B)	Elementary set in B in rough set method (dimensionless)

IS	Information system in rough set method (dimensionless)
K_g	Gas or vapor explosion (m kPa sec^{-1})
LEL	Lower explosion limit (vol.%)
LFL	Lower flammable limit (vol.%)
LOC	Limiting oxygen concentration (vol.%)
MOC	Minimum oxygen concentration (vol.%)
P	Initial pressure (kPa)
P_{ex}	Explosion overpressure (kPa)
P_m	Corrected explosion overpressure (kPa)
P_{max}	Maximum explosion pressure (kPa)
$pos_R(X)$	Positive calculation manner in rough set method (dimensionless)
$neg_R(X)$	Negative calculation manner in rough set method (dimensionless)
$\bar{R}(A)$	Upper approximations in rough set method (dimensionless)
$\underline{R}(A)$	Lower approximations in rough set method (dimensionless)
St	Explosion class (dimensionless)
t	Time (s)
U	Universe finite set of object (dimensionless)
UEL	Upper explosion limit (vol.%)
UFL	Upper flammable limit (vol.%)
V	Volume of test apparatus (m^3 L)
V_a	Set of value of a (called the domain of attribute a) in rough set method (dimensionless)
x_i	Object in rough set method (dimensionless)

Introduction

Along with the rapid development of the chemical industry, numerous major accidents have occurred while utilizing chemicals [1, 2]. These substances may be inherently hazardous, as has been confirmed by a series of chemical process disasters around the world [1–3]. From the process safety and loss prevention point of view, in 1998, Marsh analyzed the types of loss for large hydrocarbon chemical plant accidents over a period of 30 years, as shown in Fig. 1 [2]. Fires and explosions occurred as high as 97% above other damage patterns. Among them, "vapor cloud explosion" is in the majority with 36%, the second is "fire" for 31%, and "explosion" has 30%. As we know, fires and explosions can cause enormous damages and potential losses of life and property. Clearly, effective prevention and protection for fire/explosion is, without question, one of the most imperative issues of serious concern in the petrifaction industry nowadays [3, 4].

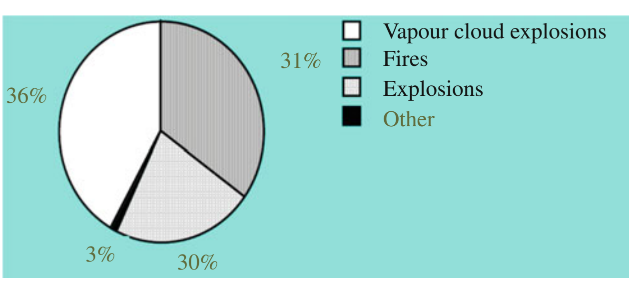


Fig. 1 Type of loss for large hydrocarbon chemical plant accidents—a 30-year review [2]

Flammable/combustion chemicals and their mixtures are commonly encountered in industrial manufacturing processes [3]. Most accidents can be traced back to unfamiliarity with these substances with potential flammability hazard [5–22]. Much concern should be paid while using flammable materials during regular operation, transportation, or storage, and even under various abnormal scenarios in a plant. In a review of previous literature and reports, we learn that for assuring fire/explosion safety of flammability substances used in process, a detailed investigation of their flammability characteristics and pertinent hazards is mandatory [12–22]. Traditionally, examinations of basic flammability characteristics have been conducted experimentally to detect the safety-related parameters of chemical substances, comprising explosion sensitivity [lower explosion limit (LEL), upper explosion limit (UEL)], explosion maximum indices (maximum explosion pressure (P_{max}), maximum rate of explosion pressure rise [(dP dt^{-1})$_{max}$], explosion hazard degree [gas or vapor deflagration index (K_g)/explosion class (St)], and minimum oxygen concentration (MOC) under setting initial temperatures and pressures. Like benzene, methanol and their various mixtures in this study [20], we first detected a series of experimental data on them by means of a traditional approach with an internationally recognized 20-L Spherical Explosion Vessel (the so-called 20-L-Apparatus). Based on previous good outcomes, we attempted to get more complete flammability hazard evaluations of benzene/methanol mixtures, and preferably provided a positive decision for fire/explosion prevention. Herein, the rough set method can be adopted for making a more specific and quantitative consideration of decision on safety assessment of benzene/methanol mixtures in this article [23–25].

In this study, the important influence factors of initial temperatures (100, 150, and 200 °C), operating pressures (101 and 202 kPa), and various loading oxygen concentrations (21, 17, 14…oxygen vol.%) of benzene, methanol, and their mixture (100/0, 75/25, 50/50, 25/75 and 0/100 vol.%) were discussed for flammability hazard evaluation via 20-L-Apparatus and by using a soft computing manner of rough set. According to the experimentally derived data of abovementioned flammability characteristics and corresponding fire/explosion hazard, we aimed to find the most important influence factor from above various testing conditions under systematic interacting effects upon each testing scenario. In addition, we wanted to determine whether the potential influence factors would make significant variations to the safety-related parameters, so as to further rate the degrees of influence factors for safety assessment specifically and quantitatively by means of rough set manner. The novel outcomes of this study, which first began to combine with the 20-L-Apparatus experimental measurement and rough set calculation approach for flammability hazard evaluations of mixing chemicals, can be recommended to a relevant practical plant for fire/explosion prevention and protection both experimentally and theoretically.

Experimental of 20-L-Apparatus investigations

Samples and initial conditions

Pure benzene and methanol with more than 99.8 mass% were employed for this study. They were supplied from Formosa Chemicals and Fiber Corp. of Taiwan, and Formosa Plastics Corp. of Taiwan, respectively. The primary properties of benzene and methanol are given in Table 1 [26–32]. We dispensed the pure reagents to five different mixing concentrations of benzene/methanol mixtures, 100/0, 75/25, 50/50, 25/75, and 0/100 vol.%, so as to realize the flammability potential of these mixed solvents. Each prescription represented the mixing condition of benzene and methanol, imitating the working situations within a practical process.

Table 1 Basic properties of benzene and methanol [26–32]

Product name	Benzene	Methanol
Formula	C_6H_6	CH_3OH
UN no.	1114	1230
CAS no.	00071-43-2	00067-56-1
Molecular weight	78.06 g mol^{-1}	32.04 g mol^{-1}
Boiling point (101 kPa)	80 °C	64.7 °C
Specific gravity (H_2O = 1)	0.877	0.79
Flammability limits	1.3–7.1 vol.%	6.0–36.5 vol.%
TLV-TWA	5 ppm	200 ppm
TLV-STEL	10 ppm	250 ppm

Thereby, the influence factor of various benzene/methanol mixing concentrations in this study was established.

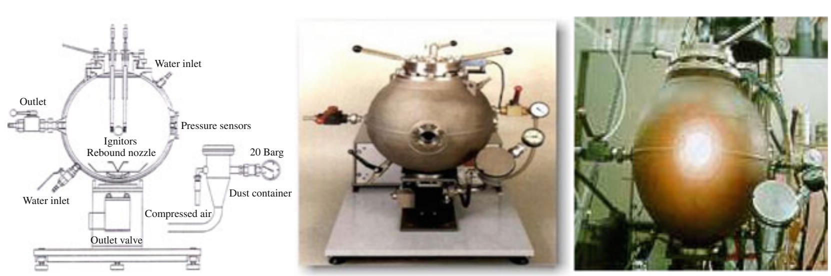
Considering the normal and elevated atmospheric pressures within a real process, 101 and 202 kPa were selected for comprising the influence of initial pressure on flammability properties. Likewise, three different initial temperatures were set to 100, 150, and 200 °C by the oil bath of our experimental device. This was driven by our desire to investigate the influence of initial temperature, also ensuring that the experimental temperature was heated at least to more than both the normal boiling point of benzene (80 °C) and methanol (64.7 °C), and would be detected in gas phase with good mixing state [4].

Regarding the loading oxygen concentration, it plays a key role for judging the occurrence of fire/explosion in a chemical process. We surveyed a series of examinations of various loading oxygen concentrations from at least normal 21 vol.% approaching each MOC (i.e., from 21, 17, 14…vol.% oxygen, etc.) to discover whether the potential influence of loading oxygen concentrations would make significant changes to flammability characteristics of interest and corresponding flammability damage before each mixing solvent's MOC. The detailed experimental procedures and results of systematic interacted testing scenarios are in the following section.

Experimental setup and procedures

The evaluation of flammability hazard of benzene/methanol mixing solvents was started with the 20-L-Apparatus approach. This is a closed spherical vessel with 20 L volume purchased from Adolf Kühner AG, as shown in Fig. 2 [32]. A sight glass was bracketed in the middle of the device for observing the blinker light of combustion. From Shu and Chang et al. [12–22] previously, the 20-L-Apparatus was considered adequate for measuring explosion behaviors of combustible materials, such as solvent vapors, flammable gases, or combustible dusts, and in accordance with the standard testing criteria below. The whole device included the flammability testing chamber and its control system, which mainly consisted of four parts [33, 34]: spherical explosion vessel (for preparing homogeneous mixtures of a specified concentration and testing that involved it); heating/

Fig. 2 The 20-L spherical explosion vessel (20-L-Apparatus) employed for this study [32]



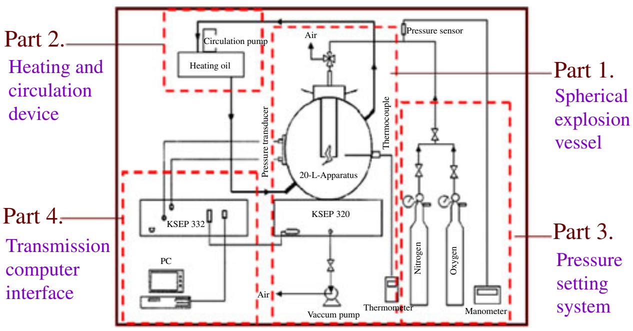


Fig. 3 Schematic diagram of the experimental setup and its control system [33, 34]

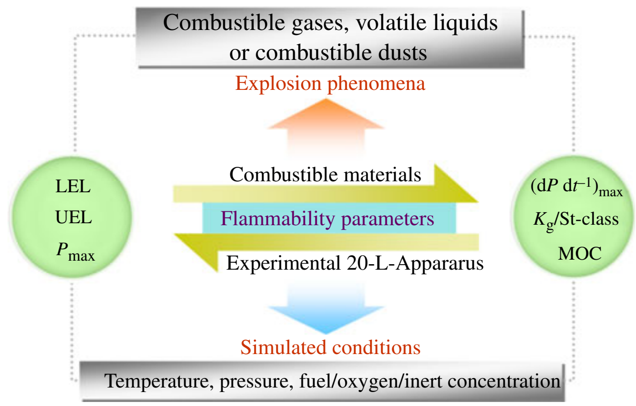


Fig. 4 Various applications of 20-L-Apparatus [34]

circulation setting (for reaching and maintaining the required setting temperature); pressure setting system (for accomplishing the required surrounding pressure conditions and vacuity); and transmission computer interface (for catching the soon-to-be explosion pressure-time corresponding recorded promptly), as demonstrated in Fig. 3 [3, 33].

Figures 1 and 2 show the 20-L-Apparatus and its control system, built and operated accompanied with NFPA (National Fire Protection Association) 68, ASTM (American Society for Testing and Materials, USA) 1226, and VDI (Verein Deutscher Ingenieure, Germany) 2263 [34]. The test system is able to determine a material's inherent safety properties in accordance with well recognized test procedures (Table 2) [12, 13, 34]. The test chamber is a stainless steel hollow sphere with a personal computer interface connected to the 20-L-Apparatus. The mixtures are ignited by a pyrotechnic igniter, which has a total of 10 J electric current used as ignition source for the gas/vapor system, and is located at the center of this vessel [34]. The top of the spherical explosion vessel cover contains holes for the lead wires to the ignition system. The opening provides for ignition by a condenser discharging with an auxiliary spark gap, which is controlled by the KSEP 320 unit of the 20-L-Apparatus. The KSEP 332 unit uses two "Kistler" piezoelectric pressure sensors on the flange to measure the pressure as function of time [34]. A comprehensive software package KSEP 6.0 was available, which allowed safe operation of the test equipment and an optimum evaluation of the explosion test results.

The 20-L-Apparatus has great reliability because of its standard spherical shape [32–34] compared with another

Table 2 Criteria for the observed reaction behavior in the 20-L-Apparatus [12, 13, 34]

IE/J	P_{ex}/kPa	P_m/kPa	Decision
10	<100	<100	No ignition
10	≥100	≥100	Ignition

IE ignition energy, P_{ex} explosion overpressure, P_m corrected explosion overpressure

measurement apparatus for fire and explosion characteristics that have been brought out. It is suitable for dictating the various flammability properties of LEL, UEL, P_{max}, $(dP\ dt^{-1})_{max}$, K_g, *St*, and MOC in the series of test procedures. Figure 4 [34] schematizes the assortments with various applications of the 20-L-Apparatus. We could use it for setting various simulation conditions for preventive measures against fire and explosion hazards by investigating the flammability safety-related properties with this equipment.

LEL and UEL for gases and solvent vapors

Vapor–air mixtures will ignite and burn only over a well-specified range of compositions [3, 4]. By definition [35], the lower limit of flammability or lower flammable limit (LFL) is the minimum concentration of a combustible substance that is capable of propagating a flame in a homogeneous mixture of a combustible and a gaseous oxidizer under a specified test. By contrast, the upper limit of flammability or upper flammable limit (UFL) is the maximum concentration. The LFL and UFL are also referred to as the LEL and UEL, respectively [3, 4, 35]. A mixture is flammable only when the composition is between LEL and UEL. Commonly used units are volume percent fuel (percentage of fuel plus air, vol.%) [3, 4, 35]. In this study, the test series was continued with a systematic increase and decrease of the sample concentration until a concentration was reached at which no ignition was observed in three successive tests [34]. Practically speaking, for a material, the lower the LEL or wider explosion range, the greater its flammability hazard degree would be [4].

P_{max}, $(dP\ dt^{-1})_{max}$, K_g parameters, and explosion (St) class measurements

The explosion indices, P_{max} and $(dP\ dt^{-1})_{max}$, are defined as the mean values of the maximum values of all three

Table 3 K_g and explosion classes (St) [34, 36]

K_g/m kPa s^{-1}	Explosion class/St
<1000	St-0
1000–200000	St-1
201000–300000	St-2
>300000	St-3

series. The K_g index is calculated from $(dP\,dt^{-1})_{max}$ by means of the cubic law [36]

$$V^{1/3} \times (dP\,dt^{-1})_{max} = K_g \quad (1)$$

where K_g and V are the maximum gas explosion constants specific to the gas and the volume of test apparatus (i.e., 0.02 m^3), respectively.

As there are many gaseous products and industrial practices, it is appropriate to assign this maximum constant to one of several explosion classes (or so-called *St* classes in this study), as given in Table 3 [34, 36], and to employ these as a basis for sizing explosive relief. Furthermore, the St class detected at each testing scenario most stands for each explosion damage class significantly and with quantification among the whole investigations. Here it represents an important final "output" result estimated for our rough set method.

Minimum oxygen concentration (MOC)

Minimum oxygen concentration, or the so-called limiting oxygen concentration (LOC), is an especially useful parameter because explosions and fires are preventable by reducing the oxygen concentration regardless of the concentration of the fuel. This concept is the basis for the common procedure called inerting [3]. When the oxygen concentration is less than the MOC, the reaction cannot create enough energy to heat the entire gas mixture (including the inert) to the extent required for the self-propagation of the flame [3] under this circumstance; oxygen is the key ingredient and an MOC is required to propagate a flame.

After the first test series in normal air (O_2 = 21 vol.%), the second series run in oxygen concentration will be about 17 vol.% in total $O_2 + N_2$ (which means $[O_2]/([N_2] + [O_2])$ = 17 vol.%), for determining the MOC. The tests, in turn, have to be continued by systematic reduction, say 3–4 vol.% each time of the oxygen concentration in nitrogen (which means $[O_2]/([N_2] + [O_2])$ until gas explosions are no longer possible, and this value is detected at least five series in a row [34]. In this study, at least three loading oxygen concentrations (21, 17, and 14 vol.%) were conducted for comparing the influence of different oxygen concentrations. The MOC, together with above-mentioned safety-related properties, was further employed for the following rough set approach.

Rough set method

In this section, we introduce the basic concept of rough set [23–25].

Basic relationship

- Information system (IS)
  $IS = (U,\ A)$is called information system, where $U = \{x_1, x_2, x_3, \ldots\ldots, x_n\}$ is the universe finite set of objects, and $A = \{a_1, a_2, \ldots, a_m\}$ is the set of attributes.
- Information function
  If the system has a mapping f_a: $U \rightarrow V_a$, then V_a is the set of value of a, called the domain of attribute a.
- Indiscernibility relation
  For each set of attributes B; A, an indiscernibility relation Ind(B) is defined by the following means: two objects, x_i and x_j, are indiscernible by the set of attribute B in A, if $b(x_i) = b(x_j)$for each $b \subset B$. The equivalence class of Ind(B) is called elementary set in B since it denotes the smallest discernible groups of objects. For any element x_i of U, the equivalence class of x_i in relation Ind(B) is expressed as $[x_i]_{Ind(B)}$[23].

Calculation method

- Lower approximations
  If$A \subseteq U$, then the lower approximations are defined as

$$\underline{R}(A) = \{x \in U | [x]_R \subseteq A\} = \bigcup \left\{ [x]_R \in \frac{U}{R} | [x]_R \subseteq A \right\}$$

$$\text{where } [x]_R = \{y | x\,R y\} \quad (2)$$

- Upper approximations
  If$A \subseteq U$, then the upper approximations are designated as

$$\overline{R}(A) = \{x \in U | [x]_R \cap A \neq \varphi\} = \bigcup \left\{ [x]_R \in \frac{U}{R} | [x]_R \cap A \neq \varphi \right\}, \quad (3)$$

$$\text{where } [x]_R = \{y | x\,R y\}$$

- Boundary
  The boundary of A is defined as

$$bn_R(A) = \underline{R}(A) - \overline{R}(A) \quad (4)$$

- Positive and negative

$$pos_R(X) = \underline{R}(X),\ neg_R(X) = U - \overline{R}(X) \quad (5)$$

- The dependences of attributes

$$\gamma_c(D) = \frac{|\mathrm{posc}(D)|}{U} \quad (6)$$

Indicates under $a \in C$, the ratio in the whole set [23].

- The significant value of attributes: the significant value of attributes is specified as

$$\sigma_{(C,D)}(a) = \frac{\gamma_c(D) - \gamma_{c-\{a\}}(D)}{\gamma_c(D)} \quad (7)$$

Results and discussion

Testing records of 20-L-Apparatus

The flammability characteristics of five benzene/methanol mixing solvents under various testing conditions received by the 20-L-Apparatus approach were carried out experimentally [20]. We briefly summarized the critical experimental data of LEL, UEL, P_{max}, $(dP\ dt^{-1})_{max}$, K_g, and St class under 150 °C, 101, and 202 kPa, which is representative of the experimental conditions of this study, as presented in Tables 4 and 5 [20, 31, 32], respectively. Afterward, we established a list with 60-set data of all the working scenarios against the results of explosion classes for the five mixed samples in Table 6. The "explosion class" of each set was viewed as the "output" result, and the four "input" influence factors, i.e., various interacting testing scenarios of temperatures (100, 150, and 200 °C), initial pressures (101, 202 kPa), loading oxygen concentrations (21, 17, and 14 vol.%), and different benzene/methanol mixing concentrations (100/0, 75/25, 50/50, 25/75, and 0/100 vol.%) appeared orderly and completely as well.

Discrete data of experimental results

The 60-set data in Table 6 were employed for the following procedure of rough set calculation. We further transferred the "input" and "output" records inside to a series of discrete data in Table 7. For instance, the initial temperatures (100, 150, and 200 °C) became 1, 2, and 3, sequentially. Two initial pressures (101 and 202 kPa) were recorded as 1 and 2, in turn. Different loading oxygen concentrations from 14, 17, and 21 vol.% were turned into 1, 2, 3, in order. As for the five benzene/methanol mixing samples (100/0, 75/25, 50/50, 25/75, and 0/100 vol.%), they were changed into 1, 2, 3, 4, and 5, successively. Similarly, the output results of *St* classes (*St* 1–4) should be presented in the discrete data of 1, 2, 3, and 4, correspondingly. In other words, we undertook to recombine Table 6 discretely by this way as given in Table 7, a list of discrete data of 20-L-Apparatus experimental results in this study, so as to grade the influence factors in the benzene/methanol mixing system later. Regarding the rephrased 60-set discrete data of Table 7, it was determined that the greater the value of discrete data was, the more the flammability hazard for an influence factor would be, which was adopted individually for the following procedure of analysis results by rough set to be discussed in the next section.

Analysis results by rough set method

Based on the mathematical model of rough set presented in the section of "rough set method", we further acquired the

Table 4 Experimental data of flammability properties of benzene/methanol mixed samples at 150 °C, 101 kPa, and 21 vol.% oxygen concentration [20, 31, 32]

Mixture	MOC/vol.%	LEL/vol.%	UEL/vol.%	P_{max}/kPa	$(dP\ dt^{-1})_{max}$/kPa s^{-1}	K_g/m kPa s^{-1}	St
Benzene/methanol (100/0 vol.%)	11	1.10	6.10	3300	291000	80030	St-1
Benzene/methanol (75/25 vol.%)	10	1.18	8.29	3200	258000	69660	St-1
Benzene/methanol (50/50 vol.%)	11	1.40	25.00	3300	298000	81950	St-1
Benzene/methanol (25/75 vol.%)	11	2.91	33.55	3200	278000	76450	St-1
Benzene/methanol (0/100 vol.%)	10	5.50	40.60	3200	279000	75330	St-1

St explosion class, dimensionless

Table 5 Experimental data of flammability properties of benzene/methanol mixed samples at 150 °C, 202 kPa, and 21 vol.% oxygen concentration [20, 31, 32]

Mixture	MOC/vol.%	LEL/vol.%	UEL/vol.%	P_{max}/kPa	$(dP\ dt^{-1})_{max}$/kPa s^{-1}	K_g/m kPa s^{-1}	St
Benzene/methanol (100/0 vol.%)	10	1.00	7.60	8600	988000	266760	St-2
Benzene/methanol (75/25 vol.%)	11	1.40	9.00	8900	1523000	411210	St-3
Benzene/methanol (50/50 vol.%)	10	1.40	25.00	8800	1525092	413300	St-3
Benzene/methanol (25/75 vol.%)	11	3.03	36.91	8600	1134000	306180	St-3
Benzene/methanol (0/100 vol.%)	10	5.30	48.50	17900	5802000	1566540	St-3

St explosion class, dimensionless

Table 6 List of explosion classes derived against various influence factors used in this study

Testing pattern/no.	Initial temperature/°C	Initial pressure/kPa	Loading oxygen concentration/vol.%	Benzene/methanol mixing concentration/vol.%	Explosion class/St
01	100	101	14	100/0	St-1
02	100	101	14	75/25	St-1
03	100	101	14	50/50	St-0
04	100	101	14	25/75	St-1
05	100	101	14	0/100	St-1
06	150	101	14	100/0	St-0
07	150	101	14	75/25	St-1
08	150	101	14	50/50	St-0
09	150	101	14	25/75	St-1
10	150	101	14	0/100	St-1
11	200	101	14	100/0	St-1
12	200	101	14	75/25	St-1
13	200	101	14	50/50	St-0
14	200	101	14	25/75	St-1
15	200	101	14	0/100	St-1
16	150	202	14	100/0	St-1
17	150	202	14	75/25	St-3
18	150	202	14	50/50	St-2
19	150	202	14	25/75	St-1
20	150	202	14	0/100	St-3
21	100	101	17	100/0	St-1
22	100	101	17	75/25	St-1
23	100	101	17	50/50	St-1
24	100	101	17	25/75	St-1
25	100	101	17	0/100	St-1
26	150	101	17	100/0	St-1
27	150	101	17	75/25	St-1
28	150	101	17	50/50	St-1
29	150	101	17	25/75	St-1
30	150	101	17	0/100	St-1
31	200	101	17	100/0	St-1
32	200	101	17	75/25	St-1
33	200	101	17	50/50	St-1
34	200	101	17	25/75	St-1
35	200	101	17	0/100	St-1
36	150	202	17	100/0	St-2
37	150	202	17	75/25	St-3
38	150	202	17	50/50	St-3
39	150	202	17	25/75	St-2
40	150	202	17	0/100	St-3
41	100	101	21	100/0	St-1
42	100	101	21	75/25	St-1
43	100	101	21	50/50	St-1
44	100	101	21	25/75	St-1
45	100	101	21	0/100	St-1
46	150	101	21	100/0	St-1
47	150	101	21	75/25	St-1
48	150	101	21	50/50	St-1

Table 6 continued

Testing pattern/no.	Initial temperature/°C	Initial pressure/kPa	Loading oxygen concentration/vol.%	Benzene/methanol mixing concentration/vol.%	Explosion class/St
49	150	101	21	25/75	St-1
50	150	101	21	0/100	St-1
51	200	101	21	100/0	St-1
52	200	101	21	75/25	St-1
53	200	101	21	50/50	St-1
54	200	101	21	25/75	St-1
55	200	101	21	0/100	St-1
56	150	202	21	100/0	St-2
57	150	202	21	75/25	St-3
58	150	202	21	50/50	St-3
59	150	202	21	25/75	St-3
60	150	202	21	0/100	St-3

Table 7 List of discrete data of 20-L-Apparatus experimental results used in this study

Testing pattern/no.	Initial temperature/°C	Initial pressure/kPa	Loading oxygen concentration/vol.%	Benzene/methanol mixing concentration/vol.%	Explosion class/St
01	1	1	1	1	2
02	1	1	1	2	2
03	1	1	1	3	1
04	1	1	1	4	2
05	1	1	1	5	2
06	2	1	1	1	1
07	2	1	1	2	2
08	2	1	1	3	1
09	2	1	1	4	2
10	2	1	1	5	2
11	3	1	1	1	2
12	3	1	1	2	2
13	3	1	1	3	1
14	3	1	1	4	2
15	3	1	1	5	2
16	2	2	1	1	2
17	2	2	1	2	4
18	2	2	1	3	3
19	2	2	1	4	2
20	2	2	1	5	4
21	1	1	2	1	2
22	1	1	2	2	2
23	1	1	2	3	1
24	1	1	2	4	2
25	1	1	2	5	2
26	2	1	2	1	1
27	2	1	2	2	2
28	2	1	2	3	1
29	2	1	2	4	2
30	2	1	2	5	2

Table 7 continued

Testing pattern/no.	Initial temperature/°C	Initial pressure/kPa	Loading oxygen concentration/vol.%	Benzene/methanol mixing concentration/vol.%	Explosion class/St
31	3	1	2	1	2
32	3	1	2	2	2
33	3	1	2	3	1
34	3	1	2	4	2
35	3	1	2	5	2
36	2	2	2	1	2
37	2	2	2	2	4
38	2	2	2	3	3
39	2	2	2	4	2
40	2	2	2	5	4
41	1	1	3	1	2
42	1	1	3	2	2
43	1	1	3	3	1
44	1	1	3	4	2
45	1	1	3	5	2
46	2	1	3	1	1
47	2	1	3	2	2
48	2	1	3	3	1
49	2	1	3	4	2
50	2	1	3	5	2
51	3	1	3	1	2
52	3	1	3	2	2
53	3	1	3	3	1
54	3	1	3	4	2
55	3	1	3	5	2
56	2	2	3	1	2
57	2	2	3	2	4
58	2	2	3	3	3
59	2	2	3	4	2
60	2	2	3	5	4

rating of importance within the four influence factors which we were interested in (initial temperature/operating pressure/loading oxygen concentration/benzene and methanol mixing concentration) by the computer calculation approach. The 60-set importance analysis values of rough set method in this study are in Fig. 5.

In Fig. 5, the items from C1 to C4 at the top row both in the "Data Input" and "Discrete Results" regions stand for four "input" influence factors in turn, which were initial temperature (C1), initial pressure (C2), loading oxygen concentration (C3), and benzene/methanol mixing ratio (C4). Reversely, the C5 represents the corresponding "output" result of explosion class (C5). In addition, at the bottom corner, it exhibits the "Significant Results" results quantitatively, which were obtained from our rough set method indicating the importance analysis values for the

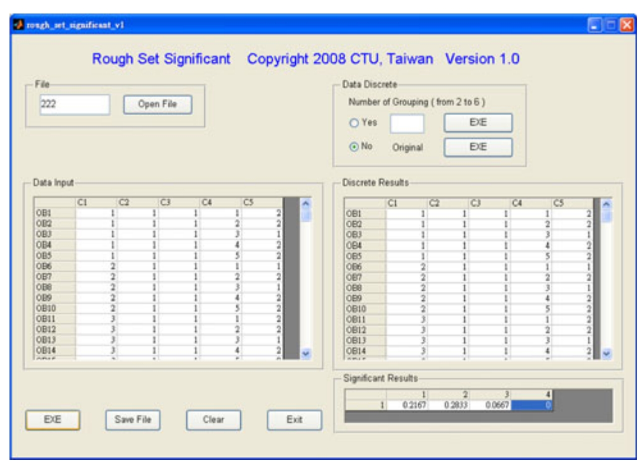


Fig. 5 Sixty-set importance analysis values of rough set method used in this study

four influence factors herein and can be compared with their specific importance degree. Preliminarily, we acquired the four corresponding values of significant results for the influence factors: C1: 0.2167, C2: 0.2833, C3: 0.0667, and C4: 0. However, we found that significant result of C4 (benzene/methanol mixing ratio) was 0, indicating it had no prominent influence on this testing system and could be eliminated.

After deleting the C4 column and withdrawing the repeated data in Table 7, we set up a new list of adjusted discrete data of the 20-L-Apparatus experimental results in Table 8 with the rest of the 19-set data. Likewise, the adjusted 19-set importance analysis values of the rough set method are in Fig. 6. There, can be clearly seen the revised four corresponding values of significant results for the influence factors: C1: 0.3158, C2: 0.4737, and C3: 0.1579. We concluded that the initial pressure (C2) was the most important factor among the four influence factors with 0.4737 significant result, the second factor happened to be initial temperature (C1/0.3158), and the third one was the loading oxygen concentration (C3/0.1579).

Table 8 List of adjusted discrete data of 20-L-Apparatus experimental results used in this study

Testing pattern/no.	Initial temperature/°C	Initial pressure/kPa	Loading oxygen concentration/vol.%	Explosion class/St
01	1	1	1	2
02	1	1	1	1
03	2	1	1	1
04	2	1	1	2
05	3	1	1	2
06	3	1	1	1
07	2	2	1	2
08	2	2	1	4
09	2	2	1	3
10	1	1	2	2
11	2	1	2	2
12	3	1	2	2
13	2	2	2	3
14	2	2	2	4
15	1	1	3	2
16	2	1	3	2
17	3	1	3	2
18	2	2	3	3
19	2	2	3	4

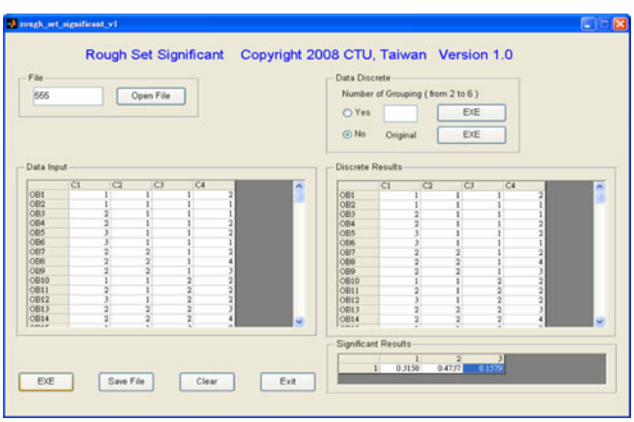


Fig. 6 Adjusted 19-set importance analysis values of rough set method used in this study

Conclusions

Based on our calculation with the important component of the influence factors through the rough set method, the most critical influence factor was operating pressure (C2), the second one was initial temperature (C1), and the third was loading oxygen concentration (C3). Their individual significant results obtained by rough set were 0.4337, 0.3158, and 0.1579, respectively. Furthermore, as for the influence factor of benzene/methanol mixing ratio (C4), due to its significant results calculated by rough set was 0, meaning that there is no significant difference in the safety assessment for the different concentrations of benzene/methanol mixtures. Therefore, through this study, the operators or engineers in chemical processes must pay more attention to the effect of working pressure.

In this study, the conventional means for investigating and evaluating the flammability characteristics and related hazard were further corroborated by the rough set approach, both specifically and quantitatively. The results of this study, which first began to combine with the 20-L-Apparatus experimental measurement and rough set computation approach for flammability hazard evaluations of mixing chemicals, can be recommended to a relevant practical plant for fire/explosion prevention and protection both experimentally and theoretically.

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References

1. Disasters information in the internet, the Website of ICIS Global Chemical Suppliers Search. http://www.icis.com/Search/new/PROFILE.htm.

2. Teaching Materials, Proceeding of the safety/health research and study, Center of Environmental Protection and Safety at National Taiwan University, Ministry of Education, Taipei, Taiwan, ROC; July 2004.
3. Crowl DA, Louvar JF. Chemical process safety: fundamentals with applications. 2nd ed. NJ, USA: Prentice-Hall; 2002. p. 252–89.
4. Arthur PE, Cote E, Linville JL. Fire protection handbook. 17th ed. National Fire Protection Association (NFPA), Quincy, MA, USA; 1992.
5. Chen YL, Chou YP, Hou HY, YP I, Shu CM. Reaction hazard analysis for cumene hydroperoxide with sodium hydroxide or sulfuric acid. J Therm Anal Calorim. 2009;95(2):535–9.
6. Hou HY, Duh YS, Lee WL, Shu CM. Hazard evaluation for redox system of cumene hydroperoxide mixed with inorganic alkaline solutions. J Therm Anal Calorim. 2009;95(2):541–5.
7. Lin CP, Shu CM. A comparison of thermal decomposition energy and nitrogen content of nitrocellulose in non-fat process of linters by DSC and EA. J Therm Anal Calorim. 2009;95(2): 547–52.
8. Wang YW, Duh YS, Shu CM. Thermal runaway hazards of tert-butyl hydroperoxide by calorimetric studies. J Therm Anal Calorim. 2009;95(2):553–7.
9. Lin SY, Tseng JM, Lee MK, Wu TC, Shu CM. Thermal runaway evaluation of α-methylstyrene and trans-β-methylstyrene with benzaldehyde. J Therm Anal Calorim. 2009;95(2):559–63.
10. Chang CW, Chou YC, Tseng JM, Liu MY, Shu CM. Thermal hazard evaluation of carbon nanotubes with sulfuric acid by DSC. J Therm Anal Calorim. 2009;95(2):639–43.
11. Lin WH, Wu SH, Shiu GY, Shieh SS, Shu CM. Self-accelerating decomposition temperature (SADT) calculation of methyl ethyl ketone peroxide using an adiabatic calorimeter and model. J Therm Anal Calorim. 2009;95(2):645–51.
12. Shu CM, Wen PJ. Investigation of the flammability zone of o-xylene under various pressures and oxygen concentrations at 150 °C. J Loss Prev Process Ind. 2002;15(4):253–63.
13. Shu CM, Wen PJ, Chang RH. Investigations on flammability models and zones for o-xylene under various initial pressures, temperatures and oxygen concentrations. Thermochim Acta. 2002;392–393:271–87.
14. Yun RL, Chang YM, Lin CH, Hu KH, Shu CM. Flammability studies of 3-methyl pyridine/water system. J Therm Anal Calorim. 2006;85(1):107–13.
15. Yun RL, Wan TJ, Lin CH, Chang YM, Shu CM. Fire and explosion characteristics of 3-methyl pyridine at 270 °C with high oxygen consequences. Process Saf Environ Prot. 2007;85(3):251–5.
16. Chang YM, Yun RL, Wan TJ, Shu CM. Experimental study of flammability characteristics of 3-picoline/water under various initial conditions. Chem Eng Res Des. 2007;85(7):1020–6.
17. Chang YM, Shu CM. Flammability properties analysis of methylphenolcarbonate in diphenylcarbonate production process. J Therm Anal Calorim. 2008;93(1):135–41.
18. Chang YM, Lee JC, Chen JR, Liaw HJ, Shu CM. Flammability characteristics studies on toluene and methanol mixtures with different vapor mixing ratios at 1 atm and 150 °C. J Therm Anal Calorim. 2008;93(1):183–8.
19. Chang YM, Lee JC, Wu SY, Chen CC, Shu CM. Elevated pressure and temperature effects on flammability hazard assessment for acetone and water solutions. J Therm Anal Calorim. 2009;95(2):525–34.
20. Chang YM, Tseng JM, Shu CM, Hu KH. Flammability studies of benzene and methanol with various vapor mixing ratios at 150 °C. Korean J Chem Eng. 2005;22(6):803–12.
21. Chang YM, Hu KH, Chen JK, Shu CM. Flammability studies of benzene and methanol with different vapor mixing ratios under various initial conditions. J Therm Anal Calorim. 2006;83(1):107–12.
22. Lin CH, Chang YM, Lee JC, Lin SY, Shu CM. Effects of flammability characteristics of steam inerting to solution of acetone in water. J Therm Anal Calorim. 2008;93(1):195–200.
23. Wen KL, Masatake Nagai M, Chang TC, Wen HC. An introduction to rough set theory and applications. Taiwan, ROC: Wu-Nan Publication; 2008.
24. Chen DG, Wang CZ, Hu QH. A new approach to attribute reduction of consistent and inconsistent covering decision systems with covering rough sets. Inf Sci. 2007;177(17):3500–18.
25. Liu JF, Hu QH, Yu DR. A weighted rough set based method developed for class imbalance learning. Inf Sci. 2008;178(4):1235–56.
26. Poling BE, Prausnitz JM, O'Connell JP. The properties of gases and liquids, 5th ed. New York, NY, USA: McGraw-Hill International Education (Chemical Engineering Series); 2001. Appendix A, Property Data Bank, A5, A12, A 20, A27.
27. Fruscella W. "Benzene" in Encyclopedia of chemical technology, 4th ed., Vol 73. Kirk-Othmer, New York, NY, USA; 1996. pp. 73–103.
28. English A, Rovner J, Brown J, Davies S. "Methanol" in Encyclopedia of chemical technology, 4th ed., Vol 16. Kirk-Othmer, New York, NY, USA; 1991. pp. 537–56.
29. Material Safety Data Sheet (MSDS), Methanol (Methyl Alcohol), Industrial Technology Research Institute, Hsinchu, Taiwan, ROC; 2010.
30. MSDS, Benzene, Industrial Technology Research Institute, Hsinchu, Taiwan, ROC; 2010.
31. Shu MJ, Lin SL. Practical undergraduate thesis. Experimental study on explosion properties of benzene, methanol and their mixtures. Department of Safety, Health, and Environmental Engineering, NYUST, Yunlin, Taiwan, ROC; 2004.
32. Chen JK. Master thesis. Fire and explosion hazard analysis on flammable binary solutions—an example on benzene/methanol mixtures. Institute of Safety, Health, and Environmental Engineering, NYUST, Yunlin, Taiwan, ROC; 2004.
33. Chang YM. Master thesis. Flammability and influential studies for fire and explosion characteristics of 3-methyl pyridine/water process. Institute of Safety, Health, and Environmental Engineering, NYUST, Yunlin, Taiwan, ROC; 2006.
34. Kühner B. Operating instructions for the 20-L-Apparatus. Switzerland; 2010.
35. Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases), ASTM E 681-04, American Society for Testing and Materials (ASTM), Philadelphia, PA, USA; 2004.
36. Guide for Venting of Deflagrations, NFPA 68, National Fire Protection Association (NFPA), Quincy, MA, USA; 2008.