Fire and explosion properties examinations of toluene-methanol mixtures approached to the minimum oxygen concentration

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Abstract The minimum oxygen concentration (MOC) is an important safety parameter of safety for fire/explosion prevention of practical processes with fuel-air-inert mixtures. In this study, the critical fire and explosion properties stand for the explosion sensitivity (lower explosion limit (LEL), upper explosion limit (UEL)), explosion maximum indices (maximum explosion pressure (P_{max}) , maximum rate of explosion pressure rise $(dP dt^{-1})_{max}$) and explosion damage degree (gas or vapor deflagration index $(K_{\sigma})/St$ Class). These imperative parameters of various toluene/ methanol mixing solvents (100/0, 75/25, 50/50, 25/75 and 0/100 vol.%) were experimentally determined within a closed spherical vessel of 20 L (20-L-Apparatus) at 101 kPa and 150 °C. Particularly, we discussed the variations both on the above characteristics and implied flammability hazard degree within different initial oxygen circumstances; the specific effects on toluene/methanol mixing solvents were to be clarified accompanied with reducing loading oxygen concentrations, gradually approaching up to the MOC in this present work. Finally, a triangle flammability diagram with the five toluene/methanol components in our testing

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Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering, NYUST, 123, University Rd., Sec. 3, Douliou, Yunlin, Taiwan 64002, ROC arrangements and conditions was established for graphically indicating the dangerous fire/explosion hazard region. It has been confirmed that this study would be very useful in relevant industrial processes for a proactive loss prevention program. The experimentally derived outcomes are recommended for the inherently safer design (ISD) for forestalling any accidents from fires and explosions.

Keywords Fire and explosion properties · Inherently safer design (ISD) · 20-L-Apparatus · Minimum oxygen concentration (MOC) · Toluene/methanol mixing solvents

List of symbols

BP	Boiling point, °C
$(\mathrm{d}P \mathrm{d}t^{-1})_{\mathrm{max}}$	Maximum rate of explosion pressure rise,
	bar s ⁻¹
FP	Flash point, °C
IE	Ignition energy, J
Kg	Gas or vapor explosion constant, m bar s^{-1}
LEL	Lower explosion limit, vol.%
MOC	Minimum oxygen concentration, vol.%
Р	Initial pressure, kPa
P _m	Corrected explosion overpressure, bar
$P_{\rm max}$	Maximum explosion pressure, bar
P _{ex}	Explosion overpressure, bar
St	Explosion class, dimensionless
UEL	Upper explosion limit, vol.%

Introduction

Although chemical materials are quite useful for necessary industrial applications, their potential toxicity and flammability risks [1, 2] might give rise to serious harm both to people and the environment. In addition, based on the rapidly increasing trend and continual development of industrial chemical processes, much concern and effort should be paid to forestall any accidents associated with chemical materials.

Generally speaking, miscible chemicals, such as organic solvents, pharmaceutical products, paint sprays etc. [1-3]are very comprehensive, even inclusive of everything following our everyday activities. Among them, organic solvents are the most common source of fires and explosions that may generate seriously contingent situations in the process industries [1, 3]. The first step in conducting process flammability hazard analysis has to involve characterizing the crucial flammability properties of chemicals that might potentially incur a fire/explosion in a plant. Further consideration must be given to the reciprocal influence of the important working conditions such as the operating temperature, pressure, or loading fuel/oxygen concentration. It is imperative to recognize the degree of danger of the used substances' explosion limits and pressure [3] under their surrounding scenarios, and then to conduct data interpretation to determine the safe operating envelope for the process, even for a large-scale one.

Comprehensive research associated with fire/explosion prevention and thermal hazard analysis has been proposed by many excellent studies lately [2-18]. In fact, toluene and methanol are grouped into "Flammable liquids (Class I liquids)" because their flash points (FP) are all less than 23 °C (73°F) (*FP*—toluene: 4.4; methanol: 12 °C) [19–23], according to the National Fire Prevention Association in the US (NFPA) regulations [24-26] summarized in Table 1. Furthermore, associated with the boiling point (BP), they are literally part of Class IB liquids since their BP is more than 38 °C (100°F) (BP-Toluene: 119.6; methanol: 64.7 °C) [19-23]. This shows toluene/methanol and their mixtures appear in a liquid state at room temperature; nevertheless, not only their liquids but also their vapors could easily burn or explode. Hence, the flammability safety properties of toluene, methanol, even their mixtures are needed and basic for the necessary operations, storage or transportation.

The information of flammability characteristics and fire safety assessment of different toluene/methanol mixtures

under 101 kPa, 150 °C, and normal oxygen concentration of 21 vol.% has been revealed experimentally and discussed by us in previous research [3]. However, the bulk of practical processes with fuel-air-inert mixtures are still filled with potential hazards for flammable mixtures used before the minimum oxygen concentration (MOC). In addition, MOC is an important parameter for safety recommendation and fire and explosion prevention [1]. Therefore, we further considered the influence of their safety-related parameters by loading different oxygen concentrations up to the MOCs in this present work.

In this study, we attempted to detect the fire/explosion properties of various toluene/methanol mixed solvents (100/0, 75/25, 50/50, 25/75 and 0/100 vol.%), including the explosion sensitivity (lower explosion limits (LEL), upper explosion limits (UEL)), explosion maximum indices (maximum explosion pressure (P_{max}) , maximum rate of explosion pressure rise $(dP dt^{-1})_{max}$) and explosion hazard degree (gas or vapor deflagration index $(K_{\sigma})/St$ Class) experimentally via a closed spherical vessel of 20 L (20-L-Apparatus) at 101 kPa and 150 °C. In particular, each MOC of toluene/methanol mixtures in this study was obtained by reducing different loading oxygen concentrations, in order to recognize the flammability threat of the above solvents before their MOCs. We also compared the above flammability properties by conducting different initial oxygen concentrations and toluene/methanol components in our series testing arrangements. In addition, the triangle flammability diagram was established under our testing conditions to indicate the dangerous fire/explosion hazard region graphically. The deliberate and significant experimentally derived outcomes proposed in this study could be very useful for process safety and control to prevent fire and explosion accidents.

Experimental samples and initial conditions

Samples

Toluene is methyl benzene with an irritant odor and colorless. Methanol, or so-called methyl alcohol, with achromatic appearance has a slight smell of alcohol [19–23]. They both are viewed as "flammable liquids (Class IB

 Table 1 Definition and classification of flammable/combustible liquids [24–26]

	Flammable liquids (Class I liquids)	Combustible liquids (Class II and III liquids)	
Class IA	<i>FP</i> < 73°F (23 °C); <i>BP</i> < 100°F (38 °C)	Class II	100°F (38 °C) < <i>FP</i> < 140°F (60 °C)
Class IB	$FP < 73^{\circ}F (23 \text{ °C}); BP > 100^{\circ}F (38 \text{ °C})$	Class IIIA	140°F (60 °C) $< FP < 200°F$ (93 °C)
Class IC	$FP > 73^{\circ}F (23 \text{ °C}); BP > 100^{\circ}F (38 \text{ °C})$	Class IIIB	200°F (93 °C) < <i>FP</i>

FP flash point, BP boiling point

liquids)" [24–26] with the potential flammability hazard we mentioned earlier; their primary chemical/physical properties are also delineated in other opening references [19–23].

In this study, more than 99.8 vol.%, i.e., pure toluene and methanol, was supplied directly from Formosa Chemicals and Fiber Corp. of Taiwan and Formosa Plastics Corp. of Taiwan, respectively. We deliberately chose them as samples to investigate the variations of flammability characteristics while mixing two such flammable chemical solvents with various concentrations, by preparing them for different toluene and methanol mixtures: 100/0, 75/25, 50/50, 25/75, 0/100 vol.%. The different mixing ratios chosen represented their self-components of toluene and methanol. Among those five mixing ratios by toluene/ methanol, the 100/0 vol.% mixing ratio presented pure toluene, the 0/100 vol.% as the pure methanol by contrast. In addition, the 75/25 vol.% was on behalf of the kind of high concentration situation for toluene; the 50/50 vol.% implied the equivalent mixing, and the 25/75 vol.% ratio referred to the methanol component being just more than toluene at one time.

Initial conditions

Industrially, operating conditions are the important factors not only for the quantity of output but also for process safety and control in a plant. In this present work, flammability experiments were detected in an initial pressure of 101 kPa, which presented conducting them within a normal atmospheric pressure surrounded with 21 vol.% oxygen inside. Regarding the initial temperature of 150 °C, which was selected in order to ensure exceeding both the normal *BP* of toluene (119.6 °C) and methanol (64.7 °C) by our thermo oil bath, a series of examinations were carried out at a good mixing state in the vapor phase [3].

Furthermore, we were more interested in discovering the potential hazard of toluene/methanol mixed solvents with various loading oxygen concentrations. Systematic examinations of decreasing the working oxygen concentration from the normal 21 vol.% approached to the MOCs (i.e., from 21, 17, 14, 11 vol.% oxygen, etc.) under each scenario associated with the required initial conditions. The detailed experimental procedures and outcomes are presented herein.

Experimental set-up and procedures

20 Liter spherical explosion vessel (20-L-Apparatus)

Experiments were carried out in a closed spherical vessel with 20 L volume, the 20 L spherical explosion vessel

(or so-called 20-L-Apparatus). By the opening references of Shu and Chang et al. [2, 3, 27–32] in the past, the 20-L-Apparatus was viewed as an ideal device for measuring explosion behaviors of combustible materials, such as solvent vapors, flammable gases, or combustible dusts. It was purchased from Adolf Kühner AG and available for this study as shown in Fig. 1 [33, 34]; a sight glass was bracketed in the middle of the device for observing the blinker light of combustion.

The whole device includes the flammability testing chamber and its control system, which mainly consists of four parts: spherical explosion vessel (for preparing homogeneous mixtures of a specified concentration and testing that involved it); heating/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 appearing in Fig. 2 [34, 35].

Figure 2 shows the 20-L-Apparatus and its control system, built and operated accompanied with NFPA 68 and ASTM 1226 (American Society for Testing and Materials, USA) and VDI 2263 (Verein Deutscher Ingenieure, Germany) [27–30, 35]. The test system is able to determine a material's inherent safety properties in accordance with internationally recognized test procedures, as displayed in Table 2 [34, 35]. The test chamber is a stainless steel hollow sphere with a general acceptance of the personal computer interface connected with 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, 35]. 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



Fig. 1 20-L-Apparatus for determining flammability characteristics of toluene and methanol mixtures [33, 34]



Fig. 2 Schematic diagram of the 20-L-Apparatus and its control system sections [34, 35]

Table 2 The criteria for the observed reaction behavior in the 20-L-Apparatus $\left[34,\,35\right]$

I.E = 10 J	P _{ex} (bar)	$P_{\rm m}$ (bar)	Decision
	<0.1	<0.1	No ignition
	≧0.1	≧0.1	Ignition

 $I\!E$ ignition energy, $P_{\rm ex}$ explosion overpressure, $P_{\rm m}$ corrected explosion overpressure

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 [34, 35].

The 20-L-Apparatus has the highest reliability because of its standard spherical shape [34, 35] compared with another measurement apparatus for fire and explosion characteristics that have been brought out [35]. It is suitable for detecting the various flammability properties of LEL, UEL, P_{max} , $(dP dt^{-1})_{\text{max}}$, K_g , and MOC in the series of test procedures.

LEL and UEL for gas and solvent vapors

Vapor–air mixtures will ignite and burn only over a wellspecified range of compositions [1]. By definition [36], 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 [36]. A mixture is flammable only when the composition is between the LEL and the UEL. Commonly used units are volume percent fuel (percentage of fuel plus air, vol.%) [1]. In this work, 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, 35].

Generally speaking, for a material the lower the LEL or wider explosion range, the greater its flammability hazard degree would be [37, 38].

Results and discussion

The fire and explosion properties of toluene, methanol and their mixtures were given in our previous paper [3], under 101 kPa, 150 °C and 21 vol.% (normal oxygen concentration). In such a working scenario, we determined that the explosion limits of pure toluene (100 vol.%) were 1.1 (LEL) and 5.3 vol.% (UEL); pure methanol (100 vol.%)'s were 5.8 (LEL) and 38.0 vol.% (UEL), respectively. Obviously, their mixtures were located at the foregoing explosion range from pure toluene and methanol; and we found that while enhancing the methanol proportion from 25 to 75 vol.% in turn, the toluene/methanol mixture's explosion limits was getting correspondingly extensive. This tendency can be observed in Fig. 3, indicating the variation of explosion range with five different vapor mixing ratios. Experimentally, the 0/100 vol.% toluene/ methanol mixture (pure methanol) was recognized not only with the widest explosion range (from 5.8 to 38.0 vol.%), but also had the greatest P_{max} (3.2 bar) and $(dP dt^{-1})_{\text{max}}$ (299.0 bar s^{-1}). It was concluded that for a relevant process or plant, most types of equipment and construction might be severely damaged at such a high pressure. Therefore, a relevant process or plant has to consider supplementing explosion-proofing equipment, or adopting other methods for fire/explosion prevention and protection.

Effects on reducing oxygen concentrations

The explosion ranges and flammability hazard degree indices such as P_{max} , $(dP \ dt^{-1})_{\text{max}}$, K_g value and explosion (St) class of various toluene/methanol mixtures were all narrowed down clearly with the decrease of oxygen concentrations from O₂ 21 to about 9 vol.%. For this finding, we selected the 50/50 toluene/methanol vapor mixing ratio to compare and illustrate the inerting effect of reducing loading oxygen from 21 and 11 O₂ vol.% in Table 3. This indicates that all the parameters were decreased greatly more than 50%, particularly the explosion range, $(dP \ dt^{-1})_{\text{max}}$ and K_g values shrank suddenly, so did the implied fire and explosion hazard in our testing surroundings.

In addition, Tables 4, 5, 6, 7, 8 and Figs. 4, 5, 6, 7, 8 also demonstrate the effect of oxygen concentration on most flammability characteristics. Figures 4, 5, 6, 7, 8 indicate individual relationships between the explosion range against fitting $P_{\rm max}$ in five different toluene/methanol vapor mixing ratios from pure (100/0 vol.%) toluene to pure methanol (0/100 vol.%), under 150 °C, 101 kPa and various oxygen concentrations conditions. Originally, each relationship was approximately distributed in a normalized expanded bell-shape curve, of which one, the highest concentration was UEL, the lowest one was LEL, and the largest explosion pressure was named the $P_{\rm max}$. We found that while decreasing the oxygen concentration



Fig. 3 The variation of explosion range with five different vapor mixing ratios under 150 °C, 101 kPa and 21 vol.% oxygen

Table 3 Comparisons of flammability characteristics of 50/50 vol.% toluene/methanol mixing ratio at 150 °C, 101 kPa, 21 and 11 vol.%

Initial pressure	21 vol.%	11 vol.%	Effect
Explosion range	7.50	2.30 vol.%	Decrease by 69.33%
UEL	8.80	4.10 vol.%	Decrease by 53.41%
$P_{\rm max}$	3.20	1.60 bar	Decrease by 50.00%
$(\mathrm{d}P \mathrm{dt}^{-1})_{\mathrm{max}}$	245.0	8.0 bar s^{-1}	Decrease by 96.73%
Kg	67.0	2.0	Decrease by 97.01%
Explosion class (St)	St-1	St-1	Without change

systematically in those tests, each curve was getting cramped from a normalized one to a shrunken one. Finally, the fire/explosion was no longer possible. In other words, the UEL and $P_{\rm max}$ dropped off significantly and the explosion range became narrower, no matter what the mixing concentration was.

The LEL values of toluene/methanol mixtures (100/0, 75/25, 50/50, 25/75 and 0/100 vol.%) measured at individual "minimum oxygen concentration" initial condition were 1.1, 1.6, 1.8, 2.7 and 5.6 vol.% in turn, varying by 1.1, 1.3, 1.3, 3.0 and 5.8 vol.% from the "normal oxygen 21 O₂ vol.%" condition, respectively. Comparatively, the UEL parameters were 2.6, 2.4, 4.1, 4.5 and 7.1 vol.% (in "minimum oxygen concentration" initial condition) changed from 5.3, 5.6, 8.8, 31.7 and 38.0 vol.% (under "normal oxygen 21 O₂ vol.%"). By comparing Figs. 4, 5, 6, 7, 8 and above experimentally derived data, we discovered that, in every curve, the UEL reduced more quickly than the LEL. We believed this was so because the UEL is affected by the limitation of oxygen directly, whereas the fuel is consistent with the LEL. Therefore, the LELs were moved slightly and UELs were reduced greatly, instead, demonstrating the inerting effect of losing oxygen, because it is well-known that for a material, the lower the LEL or wider explosion range, the greater its flammability hazard degree would be [37].

For an industrial process, if the explosion limits of the combustible/flammable material could be limited to a safe range by controlling the working oxygen concentration, the fire and explosion hazards would be reduced to an acceptable level.

MOCs of various toluene/methanol mixtures

Tables 4, 5, 6, 7, 8 not only show the safety-related parameters of toluene/methanol mixtures, but also their MOC values investigated in this study. The MOCs were 11, 11, 11, 9 and 7 vol.% associated with the toluene/methanol mixing ratios of 100/0, 75/25, 50/50, 25/75 and 0/100 vol.%, respectively. Comparatively, the pure methanol had the lowest MOC among them. It is also well known that the less the MOC, the more the fire/explosion potential

Table 4 Fire and explosion characteristics of mixing ratio of toluene and methanol 100/0 vol.% (pure toluene) at 150 °C and 101 kPa

LEL (vol.%)	UEL (vol.%)	$P_{\rm max}$ (bar)	$(dP dt^{-1})_{max}$ (bar s ⁻¹)	$K_{\rm g} \ ({\rm m \ bar \ s}^{-1})$	Explosion class (St)
methanol					
0.0	0.0	0.0	0.0	0.0	St-0
1.1	2.6	0.8	2.0	1.0	St-1
1.3	3.3	1.6	6.0	2.0	St-1
1.1	4.3	2.9	156.0	42.0	St-1
1.1	5.3	3.3	231.0	63.0	St-1
	LEL (vol.%) methanol 0.0 1.1 1.3 1.1 1.1	LEL (vol.%) UEL (vol.%) methanol 0.0 1.1 2.6 1.3 3.3 1.1 4.3 1.1 5.3	LEL (vol.%) UEL (vol.%) P _{max} (bar) methanol 0.0 0.0 0.0 1.1 2.6 0.8 1.3 3.3 1.6 1.1 4.3 2.9 1.1 5.3 3.3	LEL (vol.%) UEL (vol.%) P_{max} (bar) $(dP dt^{-1})_{max}$ (bar s ⁻¹) methanol 0.0 0.0 0.0 1.1 2.6 0.8 2.0 1.3 3.3 1.6 6.0 1.1 4.3 2.9 156.0 1.1 5.3 3.3 231.0	LEL (vol.%)UEL (vol.%) P_{max} (bar) $(dP dt^{-1})_{max}$ (bar s^{-1}) K_g (m bar s^{-1})methanol0.00.00.00.00.01.12.60.82.01.01.33.31.66.02.01.14.32.9156.042.01.15.33.3231.063.0

$O_{\rm r}$ (vol %)	IEL (vol %)	UEL (vol %)	P (bar)	$(dP dt^{-1})$ (bar s ⁻¹)	$K_{\rm g} \ ({\rm m \ bar \ s}^{-1})$	Explosion class (St)
$O_2(V01.70)$	LEL (VOI. 70)	UEL (VOI. //)	I_{max} (Dai)	$(ur ur)_{max} (bar s)$		
75 toluene/25	methanol					
9	0.0	0.0	0.0	0.0	0.0	St-0
11 (MOC)	1.6	2.4	1.2	4.0	1.0	St-1
13	1.7	3.8	2.1	24.0	7.0	St-1
17	1.0	4.7	2.8	99.0	27.0	St-1
21	1.3	5.6	3.3	244.0	66.0	St-1

Table 5 Fire and explosion characteristics of mixing ratio of toluene and methanol 75/25 vol.% at 150 °C and 101 kPa

Table 6 Fire and explosion characteristics of mixing ratio of toluene and methanol 50/50 vol.% at 150 °C and 101 kPa

O2 (vol.%)	LEL (vol.%)	UEL (vol.%)	$P_{\rm max}$ (bar)	$(dP dt^{-1})_{max}$ (bar s ⁻¹)	$K_{\rm g} \ ({\rm m \ bar \ s}^{-1})$	Explosion class (St)
50 toluene/50	methanol					
9	0.0	0.0	0.0	0.0	0.0	St-0
11 (MOC)	1.8	4.1	1.6	8.0	2.0	St-1
13	1.8	5.6	2.1	28.0	8.0	St-1
17	1.4	7.6	2.8	135.0	37.0	St-1
21	1.3	8.8	3.2	245.0	67.0	St-1

Table 7 Fire and explosion characteristics of mixing ratio of toluene and methanol 25/75 vol.% at 150 °C and 101 kPa

O2 (vol.%)	LEL (vol.%)	UEL (vol.%)	$P_{\rm max}$ (bar)	$(dP dt^{-1})_{max}$ (bar s ⁻¹)	$K_{\rm g} \ ({\rm m \ bar \ s}^{-1})$	Explosion class (St)
25 toluene/75	methanol					
7	0.0	0.0	0.0	0.0	0.0	St-0
9 (MOC)	2.7	4.5	0.2	2.0	1.0	St-1
11	3.2	6.2	1.6	8.0	2.0	St-1
13	2.9	8.3	2.1	28.0	8.0	St-1
17	2.7	15.7	2.9	117.0	32.0	St-1
21	3.0	31.7	3.2	235.0	64.0	St-1

Table 8 Fire and explosion characteristics of mixing ratio of toluene and methanol 0/100 vol.% (pure methanol) at 150 °C and 101 kPa

O2 (vol.%)	LEL (vol.%)	UEL (vol.%)	$P_{\rm max}$ (bar)	$(dP dt^{-1})_{max}$ (bar s ⁻¹)	$K_{\rm g} \ ({\rm m \ bar \ s}^{-1})$	Explosion class (St)
0 Toluene/100) Methanol					
6	0.0	0.0	0.0	0.0	0.0	St-0
7 (MOC)	5.6	7.1	0.2	2.0	1.0	St-1
9	5.2	9.2	0.9	2.0	1.0	St-1
11	5.3	14.6	1.8	16.0	4.0	St-1
13	5.7	21.3	2.1	34.0	9.0	St-1
17	5.9	31.8	3.0	161.0	44.0	St-1
21	5.8	38.0	3.2	299.0	81.0	St-1

danger for a substance would be. When the "methanol" composition in those five mixing ratios was raised, the MOC values became less and less, showing that both the inherent flammability feature and potential fire explosion hazard of methanol are higher than toluene's. Hence, much concern should be paid by engineers or operators if the two

chemicals are mixed for necessary operations, transportation or storage.

In addition, each MOC stood for examining at per "minimum oxygen concentration" initial condition, as just mentioned above, of those five mixing samples under $150 \,^{\circ}$ C and $101 \,$ kPa. Once the oxygen concentration is



Fig. 4 P_{max} versus toluene and methanol 100/0 vol.% mixing ratio with various oxygen concentrations under 150 °C, 101 kPa



Fig. 5 P_{max} versus toluene and methanol 75/25 vol.% mixing ratio with various oxygen concentrations under 150 °C, 101 kPa



Fig. 6 P_{max} versus toluene and methanol 50/50 vol.% mixing ratio with various oxygen concentrations under 150 °C, 101 kPa



Fig. 7 P_{max} versus toluene and methanol 25/75 vol.% mixing ratio with various oxygen concentrations under 150 °C, 101 kPa



Fig. 8 P_{max} versus toluene and methanol 0/100 vol.% mixing ratio with various oxygen concentrations under 150 °C, 101 kPa

below the MOC, an explosion is no longer possible. The degree of fire/explosion danger would be alleviated gradually as long as the oxygen concentration is reduced. Therefore, we could practically control the oxygen concentration directly to forestall fires or explosions among the operating processes with fuel-air-inert mixtures. This responds to the term called inerting [1] as we just stated in the experimental set-up and procedure section.

Flammability diagram

A general way to represent the flammability of a gas or vapor is by a triangle diagram [1]. The use of triangular coordinates often makes examination of a three-component system easier because all three constants are presented on the graph at one time [17, 39, 40]. The flammability diagram of a Fuel/ O_2/N_2 mixture represents the three components as F, O_2 , N_2 , respectively; each axis of the triangle represents either 100 vol.% fuel,



Fig. 9 Overall triangular flammability diagram illustrating the changes in flammability zone with different ratios of toluene and methanol at 150 °C 101 kPa and various oxygen concentrations

oxygen, or nitrogen. In this study, the fuel part means toluene/methanol mixtures by various vapor mixing ratios (100/0, 75/25, 50/50, 25/75 and 0/100 vol.%, and the tick marks on the scales show the direction in which the scale moves across the picture [1], as delineated in Fig. 9.

Conclusions

The flammability characteristics, LEL, UEL, P_{max}, $(dP dt^{-1})_{max}$, K_g , and MOC, of toluene/methanol mixtures (100/0 (pure toluene), 75/25, 50/50, 25/75 and 0/100 (pure methanol) vol.%) were detected via systematic experiments under 150 °C, 101 kPa and various oxygen concentration initial conditions. In our investigations, the pure methanol not only had the widest explosion range (from 5.8 to 38.0 vol.%), but also the greatest P_{max} (3.2 bar), $(dP dt^{-1})_{\text{max}}$ (299.0 bar s^{-1}) and MOC (7 vol.%). In addition, we found that while enhancing the methanol proportion among the five toluene/methanol mixtures from 25 to 75 vol.% in turn, the flammability hazard degree was gradually increasing. It has been confirmed experimentally that the pure methanol sample could give rise to more serious fire/explosion damage than toluene. Therefore, a relevant process or plant has to consider supplementing sufficient explosion-proof equipment, or adopting other methods for fire/explosion prevention and protection in a process that operates with the two flammable solvents.

As for finding the effects on reducing oxygen concentrations, the explosion range, P_{max} , $(dP dt^{-1})_{\text{max}}$, K_g value and explosion (St) class were all narrowed down clearly from O₂ 21 to about 9 vol.%, illustrated in corresponding tables and figures in this paper. Especially, we discovered that the UEL is affected by reducing the oxygen directly

and more rapidly than the LEL. The MOCs detected herein were 11, 11, 11, 9 and 7 vol.% of the toluene/methanol mixing ratios of 100/0, 75/25, 50/50, 25/75 and 0/100 vol.%, respectively. Finally, the triangle flammability diagram within all testing scenarios presented on the graph simultaneously was also established for indicating the dangerous fire/explosion hazard region.

Engineers and researchers associated with process safety for characterizing the flammability properties and mitigating fire/explosion hazard have to consider both prevention and protection. Protective surveys are the primary concern of this paper. Our carefully derived experimental results demonstrate that the UEL and flammability hazard degrees would clearly be lessened with a reduced oxygen concentration, and the explosion range also got significantly narrower. It has been concluded that the damage of explosion pressure and flames to equipment and people would be alleviated definitely as long as the loading oxygen concentration was reduced under the MOC. Controlling the oxygen concentration directly in order to avoid fire or explosion accidents would be suggested as a practical concern for the operating processes with fuel-air-inert mixtures.

Recommendations

Our recommendations for future work are as follows:

- (1) Test the flammability properties of toluene/methanol with different initial temperatures, say 100, 200 and 300 °C.
- (2) Change inert gases, such as CO₂, N₂..., and enhance initial pressure to draw a complete triangular flammability diagram.
- (3) Create a comprehensive model for the explosion limits and MOC in this system; or, if not, predicted.

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References

- 1. Crowl DA, Louvar JF. Chemical process safety: fundamentals with applications. 2nd ed. NJ: Prentice-Hall; 2002. p. 252–89.
- Chang YM, Shu CM. Flammability properties analysis of methylphenolcarbonate in diphenylcarbonate production process. J Therm Anal Calorim. 2008;93(1):135–41.

- 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.
- 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.
- Chen YL, Chou YP, Hou HY, I YP, Shu CM. Reaction hazard analysis for cumene hydroperoxide with sodium hydroxide or sulfuric acid. J Therm Anal Calorim. 2009;95(2):535–9.
- 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.
- 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.
- 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.
- 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.
- 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. Petrochemical Industry of Taiwan, ROC, Pertichemical Industry Association of Taiwan, Taipei, Taiwan, ROC; 2002.
- Yang RK, Yang CM. Practical undergraduate thesis. Department of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology (NYUST), Yunlin, Taiwan, ROC; 2003.
- 14. Website of Occupational Safety and Health Administration (OSHA), US Department of Labor, USA. www.osha.gov.
- Disasters Information in the Internet, the Website of ICIS Global Chemical Suppliers Search. http://www.icis.com/Search/new/ PROFILE.htm.
- Chen JK. Master thesis. Institute of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology (NYUST), Yunlin, Taiwan, ROC; 2004.
- 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.
- 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.
- Poling BE, Prausnitz JM, O'Connell JP. The properties of gases and liquids, 5th ed. McGraw-Hill International Education (Chemical Engineering Series), Appendix A, Property Data Bank, A5, A12, A 20, A27; 2001.
- Howard WL. Encyclopedia of chemical technology, "methanol", 4th ed., vol 16. Kirk-Othmer, New York; 1991. p. 537–57.

- Howard WL. Encyclopedia of chemical technology, "toluene", 4th ed., vol 24. Kirk-Othmer, New York; 1991. p. 350–89.
- 22. Material Safety Data Sheet (MSDS), Methanol (Methyl Alcohol), Industrial Technical Research Institute, Hsinchu, ROC; 2009.
- 23. Material Safety Data Sheet (MSDS), Toluene (Methyl Benzene), Industrial Technical Research Institute, Hsinchu, ROC; 2009.
- Flammable/Combustible Liquid, NFPA 30, National Fire Protection Association (NFPA), Quincy, MA, USA; 2002.
- Standard on Basic Classification of Flammable and Combustible Liquids, NFPA 321, National Fire Protection Association (NFPA), Quincy, MA, USA; 1991.
- Arthur PE, Cote E, Linville JL. Fire protection handbook. 17th ed. National Fire Protection Association (NFPA), Quincy, MA, USA; 1992.
- Shu CM, Wen PJ. Investigation of the flammability zone of o-xylene under various pressures and oxygen concentration at 150°C. J Loss Prev Process Ind. 2002;15(4):253–63.
- 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;392–3:271–87.
- 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.
- Yun RL, Wan TJ, Lin CH, Chang YM, Shu CM. Fire and explosion characteristics of 3-methyl pyridine at 270°C with high oxygen concentrations. Process Saf Environ Prot. 2007;85(3): 251–5.
- 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.
- 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.
- Process Safety News, Laboratory Testing and Consulting for Process Safety Management, Fauske & Associates, Burr Ridge, Illinois, USA, LLC (Spring), 14, 2; 2007.
- Kühner B. Operating instructions for the 20-L-Apparatus. Switzerland; 200(9).
- Chang YM. Master thesis. Institute of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology (NYUST), Yunlin, Taiwan, ROC; 2006.
- 36. Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases), ASTM E 681-04, American Society for Testing and Materials (ASTM), 2004, Philadelphia, PA, USA.
- 37. Teaching Materials, Proceeding of the Safety and Health Research and Study, Center of Environmental Protection and Safety, Ministry of Education, National Taiwan University, Taipei, Taiwan, ROC; July 2004.
- Guide for Venting of Deflagrations, NFPA 68, National Fire Protection Association (NFPA), Quincy, MA, USA; 2002.
- Chad VM, Crowl DA. Application of the flammability diagram for evaluation of fire and explosion hazards of flammable vapors. Process Saf Prog. 1998;17(3):176–83.
- O'Shaughnessey D, Power B. Simulating flammability under process conditions. Process Saf Prog. 1995;14(1):22–5.