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FLAMMABILITY CHARACTERISTICS STUDIES ON TOLUENE AND METHANOL MIXTURES WITH DIFFERENT VAPOR MIXING RATIOS AT 1 ATM AND 150°C

Y. M. Chang[1], *J.-C. Lee*[2], *J.-R. Chen*[1], *H.-J. Liaw*[3] *and C.-M. Shu*[1*]

[1]Doctoral Program, Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology (NYUST), 123, University Rd., Sec. 3, Douliou, Yunlin, Taiwan 64002, Republic of China
[2]Department of Safety, Health, and Environmental Engineering, NYUST, 123, University Rd., Sec. 3, Douliou, Yunlin Taiwan 64002, Republic of China
[3]Department of Occupational Safety and Health, China Medical University, 91 Hsueh-Shih Rd., Taichung, Taiwan 40402 Republic of China

The flammability characteristics of chemical substances are very important for safety considerations in manufacturing processes. This study investigated the mixing of toluene and methanol mixtures with five vapor mixing ratios (100/0, 75/25, 50/50, 25/75 and 0/100 vol.%) at initial conditions of 1 atm and 150°C, and determined the flammability properties to identify their potential fire and explosion hazards. These safety-related parameters included lower explosion limit (LEL), upper explosion limit (UEL), maximum explosion overpressure (P_{max}) and rate of maximum explosion pressure rise ($(\mathrm{d}P/\mathrm{d}t)_{max}$); all of them were measured by a 20-L-Apparatus.

In terms of flammability tests for this research, the experimental results indicated that when methanol was increased, which could induce a higher range of flammability, afterwards the situation could be triggered to a dangerous level, such as fire or explosion. Based on the above-mentioned, we could obtain a series of flammability properties and provide inherently safer design in related industrial processes for preventing serious fire and explosion accidents.

Keywords: *20-L-Apparatus, explosion accidents, fire accidents, flammability characteristics, inherently safer design, methanol mixtures, toluene mixtures*

Introduction

Miscible chemical liquids are frequently used in industry or our daily lives for many purposes and products, including organic solvents, paint sprays, pharmaceutical products, and so on [1]. In general, definition and classification for flammable/combustible liquids are clearly outlined according to NFPA 30 and 321 [2–4] by the flash point (FP) and boiling point (BP), discriminated according to their flammability hazard levels. Typically, flammable liquids are viewed as Class I liquids (Class IA, Class IB and Class IC) with FP below 100°F (38°C) and vapor pressures not exceeding 40 psia at 100°F (275 kPa at 38°C) [5]; combustible liquids with FP at or above 100°F (38°C) are subdivided into Class II, Class IIIA, Class IIIB, respectively.

Such flammable and combustible liquids might burn or explode, and cause serious incidents by the flammable vapors resulting from the evaporation of liquids at temperatures above their flash point when exposed to an ignition source, such as a spark [5]. Actually, according to the historical records [6], more and more have resulted from mixing two (even more) kinds of different flammable solvents. In addition, in fact, most chemical solvents involve more than one flammability component in the liquid phase. When they are evaporated to generate the flammable vapors, their harmful or pernicious impact could be greater than one solvent alone from mixing solvents.

Evaluation and protection from chemical hazards to ensure safe operation is of much interest. To date, many concerns about thermal analysis and flammability properties investigations in accordance with particular chemical materials have been raised by many researchers [7–21]. However, most of them merely mention single chemicals; or which material's basic data could also be derived from the material safety data sheet (MSDS) only for a specific pure substance. Very little information has focused on mixing flammable liquids [22, 23], such as toluene and methanol mixtures.

Based on the fire and explosion protection idea, knowledge connected with safety-related parameters should be established beforehand, especially the flammability limits. Many fires and explosions that

* Author for correspondence: shucm@yuntech.edu.tw

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

happen in processes are caused by flammable chemicals located within their flammability limits; and because most flammable liquids are normally stored and handled above their FP, they continually give off vapors when the vapor–air mixture is within the flammable/flammability range [5]. This is from the lower flammable/flammability limit (LFL) to upper flammable/flammability limit (UFL), or what is referred to as the explosion/explosive ranges of the extent to the lower explosion limit (LEL) and upper explosion limit (UEL), respectively [11, 24].

For safety concerns and fire defense motives, we deliberately chose toluene and methanol mixtures as examples for investigating the flammability characteristics experimentally while mixing two such flammable chemical liquids with various concentrations. Both toluene and methanol are important, comprehensive and in great demand solvents for many purposes in petrochemical industries today. Their chemical formulas and structures are displayed in Fig. 1 [25, 26]. Table 1 lists basic chemical/physical properties of toluene and methanol [25, 26], indicating that both they belong to flammable liquids. According to NFPA regulations [3, 4], each of them is grouped into 'flammable liquids (Class I liquids)', liquids and vapors of not only toluene and methanol, but also their mixtures which could easily burn or explode. However, to date, references in the open literature indicating toluene/methanol mixture's essential flammability information are simply limited data available for processes. Much is still unknown, particularly their mixture's flammability limits and degree of flammable hazard. Since no adequate or sufficient awareness of referable flammability limit data yet has been proposed, experiments still have to be performed. Furthermore, explosion limits are easily measured; experimental determination is always recommended [2].

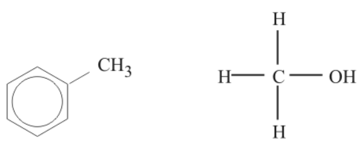

Fig. 1 Individual chemical formula and structure of toluene and methanol [25, 26]

Therefore, we made efforts to survey the fire and explosion characteristics of flammable chemical mixtures, taking various mixing ratios of toluene and methanol mixtures as an example. The aim of this present work is (1) to determine experimental fire and explosion characteristics like the explosion limits (LEL, UEL), maximum explosion overpressure (P_{max}) and rate of maximum explosion pressure rise ($(dP/dt)_{max}$) of toluene/methanol mixtures with five diverse mixing ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 vol.% at initial pressure of 1 atm, and temperature up to 150°C; (2) to identify the miscible liquid chemical's potential flammability hazards when different flammable solvent vapors components are mixed; and (3) to judge the St-class according to our experimentally derived data. In conclusion, we could obtain a series of flammability properties and recommend such useful information for inherently safer design in industrial processes in advance. Our hope is that this work will provide the knowledge to prevent, even avoid, serious fire and explosion accidents resulting from mixing chemical solvents.

Experimental

Samples

In this study, 99.8 vol.% toluene and 99.8 vol.% methanol were supplied directly from Formosa Chemicals and Fiber Co. of Taiwan and Formosa Plastics Co. of Taiwan, respectively. We deliberately allocated them into various toluene and methanol mixtures as 100/0, 75/25, 50/50, 25/75,

Table 1 Basic properties of toluene and methanol [25, 26]

Characteristics	Toluene	Methanol
Formula	C_7H_8	CH_3OH
UN No.	00108-88-3	00067-56-1
CAS No.	1294	1230
Molecular mass/g mol^{-1}	92.13	32.04
Specific gravity (H_2O=1)	0.866	0.79
Vapor density	3.1	1.1
Flash point/°C	4.4	12
Boiling point (1 atm/°C)	119.6	64.7
Melting point/°C	–95	–97.8
Vapor pressure/mmHg	22 (20°C)	160 (30°C)
Explosion limits	1.2–7.1 vol.%	6.0–36.5 vol.%

0/100 vol.%, measured for the study. Different mixing ratios chosen represented their self-components of toluene and methanol.

Experimental initial conditions

Initial pressure and temperature of 1 atm and 150°C, along with five setting samples and various oxygen concentrations were studied to evaluate the fire and explosion hazards under various required scenarios. As for the initial temperature, 150°C was chosen experimentally. We set the initial temperature as 150°C in order to exceed both the normal BP of toluene (119.6°C) and methanol (64.7°C) by a thermo oil bath, in order to ensure forming total flammable vapors so that flammability tests were carried out in a good mixing state in the vapor phase.

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

The experiments were performed in a closed spherical system with a 20 L vessel, the so-called 20 L spherical explosion vessel (20-L-Apparatus). It was purchased from Adolf Kühner AG and available for this study as shown in Fig. 2 [27]. Typically speaking, this equipment and its control system mainly consist of four parts: spherical explosion vessel, heating/circulation setting, pressure setting system, and transmission computer interface, as illustrated in Fig. 3 [28].

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 top of the spherical explosion vessel cover contains holes for the lead wires to the ignition system. An exploding fuse wire ignition source comprised of a spiked needle is use, providing ignition energy of about 10 J [29]. 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 [23]. A sight glass was

Fig. 2 20-L-Apparatus for determining flammability characteristics of toluene and methanol mixtures [27]

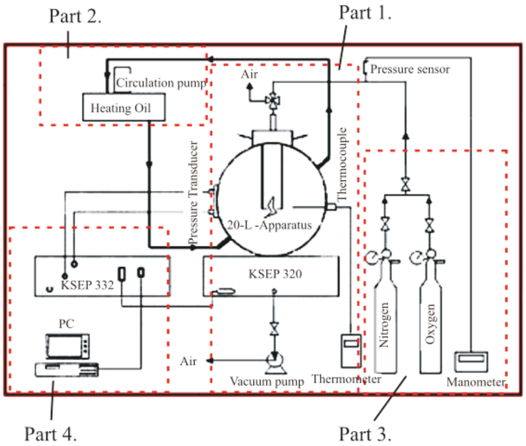

Fig. 3 Schematic diagram of the experimental set-up and its control system [28]

bracketed in the middle of the device for observing the blinker light of combustion. The KSEP 332 unit uses two 'Kistler' piezoelectric pressure sensors on the flange to measure the pressure as a function of time [23, 29]. 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 [11, 22].

The 20-L-Apparatus has the highest reliability because of its standard spherical shape [30, 31] compared with other measurement apparatus for fire and explosion characteristics that have been brought out [29]. The test system is able to determine a material's 'inherent safety' properties in accordance with internationally recognized test procedures, e.g., ASTM 1226 (American Society for Testing and Materials, USA) and VDI 2263 (Verein Deutscher Ingenieure, Germany) [11], and decide the flammability behavior as displayed in Table 2 [29]. Essentially, it is suitable for measuring explosion behaviors of combustible materials, such as solvent vapors, flammable gases, or combustible dusts and deriving the flammability properties of LEL, UEL, P_{max}, $(dP/dt)_{max}$, gas or vapor deflagration index (K_g) and minimum oxygen concentration (MOC) in a series of test procedures [29]. In this study, we focused on investigating the flammability features of toluene/ methanol solvent vapors, complying with the regular operating procedures from Adolf Kühner AG [29]; and the experimental method also followed our previously proposed study aimed at solvent/vapor testing [10]. For example, for combustible gases or vapors, the test is generally accomplished in a quiescent state (ignition delay time, t_v=0 s) [9]. We deliberately calculated the mole fraction component within the total flammable vapor from each specified experimental toluene/ methanol mixing ratio.

Table 2 The criteria for the observed reaction behavior in the 20-L-Apparatus [29]

IE=10 J	P_{ex}/bar	P_m/bar	Decision
UEL and LEL testing	<0.1	<0.1	No ignition
	≥0.1	≥0.1	Ignition

IE: ignition energy; P_{ex}: explosion overpressure; P_m: corrected explosion overpressure

Explosion limits (LEL/UEL) and explosion indices (P_{max} and $(dP/dt)_{max}$) for gas and solvent vapors

By definition [24], the lower limit of flammability or LFL is the minimum concentration of a combustible substance that is capable of propagating a flame in a homogeneous mixture of the combustible and a gaseous oxidizer under the specified conditions of a test. By contrast, the upper limit of flammability or UFL is the maximum concentration. The LFL and UFL are also referred to as the LEL and the UEL, respectively. So explosion limits include the LEL and UEL; the explosion range is exactly from LEL to UEL of a specific substance [23]. 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 [11, 29].

Generally speaking, for a material the lower the LEL or wider explosion range, the greater its flammability hazard degree would be [32]. Furthermore, the explosion indices, P_{max} and $(dP/dt)_{max}$, are defined as the mean values of the maximum values of all three series.

Results and discussion

Flammability characteristics analysis for toluene and methanol mixtures

According to our experimental results at 1 atm, 150°C and normal oxygen concentration 21 vol.%, the explosion limits of pure toluene (100 vol.%) were 1.1 (LEL) and 5.3 vol.% (UEL); pure methanol's were 5.8 (LEL) and 38.0 vol.% (UEL), respectively. In other previous references, Goethals *et al.* have studied the flammability limits of methane/air, toluene/air mixtures at elevated pressure and temperature, experimentally [7, 8], in different testing systems and conditions. However, the flammability properties of toluene/methanol mixtures were first proposed in the present work. When adding methanol into pure toluene for mixing them by different ratios (100/0, 75/25, 50/50, 25/75 and 0/100 vol.% toluene/methanol$_{(aq)}$), we found that while the methanol ratio was enhanced from 25 to 75 vol.% in turn, the toluene/methanol mixtures' explosion limits grew correspondingly. Figure 4 displays the relationship between P_{max} and explosion range with five different vapor mixing ratios, it clearly shows that explosion limits got wider and wider to approach 100 vol.% methanol. Table 3 enumerates their fire and explosion characteristics; their upper explosion limit, P_{max} and $(dP/dt)_{max}$ become greater obviously. Just taking the 50/50 vol.% toluene/methanol ratio, for instance, LEL becomes 1.3 vol.%, and UEL changes into 8.8 vol.%.

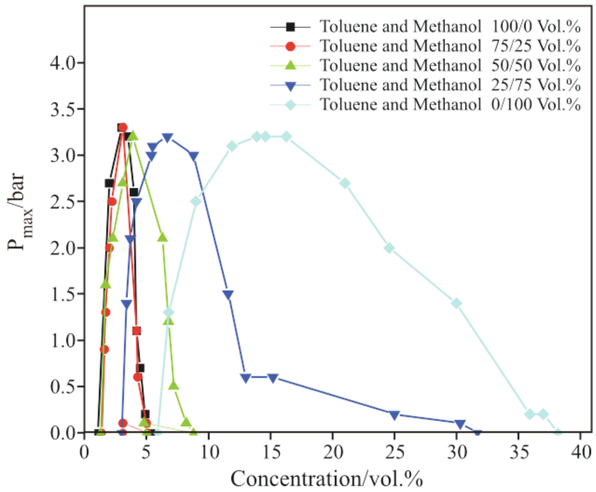

Fig. 4 Variations of maximum explosion pressure and explosion range with five different vapor mixing ratios under 150°C, 1 atm and 21 vol.% oxygen

Table 3 Fire and explosion characteristics of different ratios of toluene and methanol mixtures 100/0, 75/25, 50/50, 25/75 and 0/100 vol.% at 150°C and 1 atm

O_2/ vol.%	LEL/ vol.%	UEL/ vol.%	P_{max}/ bar	$(dP/dt)_{max}$/ bar s^{-1}
21	1.1	5.3	3.3	231.0
21	1.3	5.6	3.3	244.0
21	1.3	8.8	3.2	245.0
21	3.0	31.7	3.2	235.0
21	5.8	38.0	3.2	299.0

The LELs of three mixing concentrations, 75/25, 50/50, and 25/75 vol.% of toluene/methanol, were 1.3, 1.3 and 3.0 vol.%; the UELs were 5.6, 8.8 and 31.7 vol.%, individually.

In addition, those experimental results of explosion limits for toluene/methanol mixtures could be applied to the related industrial process. Accordingly, if miscible flammable mixtures of toluene/methanol act as the loading solvents for a specific practical application, as long as their mixing concentration is accepted, toluene could presumably be viewed as an inhibitor, reducing the flammability hazards of methanol only in this toluene/methanol mixture system. That is what we expected from the helpful fire and explosion safety information through this study.

Conclusions

In this study, flammability characteristics of toluene/methanol mixtures were proposed via a series of fire investigations by mixing different ratios of 100/0, 75/25, 50/50, 25/75 and 0/100 vol.%, respectively, all under 150°C, 1 atm conditions. The explosion limits of pure toluene and methanol were from 1.1–5.3 and 5.8–38.0 vol.%, and then other mixtures explosion limits changed with the different mixing ratios, individually. The LELs of three mixing concentrations, 75/25, 50/50 and 25/75 vol.% of toluene/methanol, were 1.3, 1.3 and 3.0 vol.%; the UELs were 75/25, 50/50 and 25/75 vol.%, were 5.6, 8.8 and 31.7 vol.%, respectively. In other words, the flammability limits of toluene and methanol in 75/25, 50/50, 25/75 were between 100 vol.% toluene and methanol. The explosion range rose with increasing methanol proportion. Toluene also acted as an inhibitor, reducing the flammability hazards of methanol only in this toluene/methanol mixture system.

From our practical survey we were able to identify, compare the flammability hazard simply in such cases, and then find safe procedures for protection. This will be able one to identify the hazardous combustible features for diverse toluene and methanol mixing concentrations.

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