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FLAMMABILITY STUDIES OF BENZENE AND METHANOL WITH DIFFERENT VAPOR MIXING RATIOS UNDER VARIOUS INITIAL CONDITIONS

Y. M. Chang[1], *K. H. Hu*[2*], *J. K. Chen*[1] *and C. M. Shu*[1]

[1]Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology (NYUST), 123, University Rd., Sec. 3, Touliu, Yunlin, Taiwan 64002, ROC
[2]Jen-Teh Junior College of Medicine, Nursing and Management, 1, Jin-Ten Rd., Houlong, Miaoli, Taiwan 35664, ROC

This research investigated the influence of binary solutions of benzene and methanol for their vapor flammability characteristics. The different mixing ratios (100/0, 75/25, 50/50, 25/75 and 0/100 vol%) samples were injected into a 20-liter spherical explosion vessel under various initial temperatures (100, 150 and 200°C) to study their flammability behaviors. According to the experimental results, the flammability diagram of mixtures can be completely illustrated and combined with specific safety-related properties such as lower explosion limit (LEL), upper explosion limit (UEL), minimum oxygen concentration (MOC), maximum explosion overpressure (P_{max}), and gas or vapor deflagration index (K_g). The experimental results showed that the UEL, P_{max} and K_g all increased with the temperature, pressure and oxygen concentration, whereas there was no significant variation on the part of LEL. The results can provide specific information on fire and explosion hazards for related industries.

Keywords: *binary solutions, fire and explosion hazards, flammability diagram, safety-related properties*

Introduction

In recent years, much concern has arisen over the large numbers of fire and explosion accidents that have occurred in industries all over the world [1, 2]. Many studies emphasizing on flammability hazard evaluation and thermal analysis of chemical materials have been presented in the open literature [3–15]. In the petrochemical industry, flammable mixtures, such as benzene and methanol, are frequently used. These are both important middle raw materials [16, 17]. In past decades, many explosion properties of all single chemicals have been studied, but there is very little information about binary mixtures. However, when the binary mixtures are evaporated from a flammable gas, their harmful or pernicious impact could be greater than that of single solvent alone.

The purpose of this study was to investigate the flammability of benzene, methanol, and their mixture in order to understand the fire and explosion characteristics for binary solutions. It included lower explosion limit (LEL), upper explosion limit (UEL), maximum explosion overpressure (P_{max}), rate of maximum explosion pressure rise $(dP/dt)_{max}$, gas or vapor deflagration index (K_g), minimum oxygen concentration (MOC), all at 100, 150 and 200°C of initial temperatures and 101/202 kPa of initial pressures, respectively. Concerned about the hazards of various mixing ratios in this research, we studied the different ratios of benzene and methanol in 100/0, 75/25, 50/50, 25/75 and 0/100 vol% to identify the potential hazards of binary mixtures when vapors of different flammable chemicals are mixed. In conclusion, the results can help related industries prevent unexpected accidents and provide specific information on related properties for fires and explosions in mixing chemicals.

Experimental setup and method

The flammability of benzene, methanol and their mixtures was investigated in a vessel of 20 L (20-L-Apparatus or so-called 20 L Spherical Explosion Vessel) [18]. The experimental samples of benzene and methanol used for this paper were supplied from Formosa Chemicals and Fiber Corporation of Taiwan with 99.88 vol% benzene in purity and 99.99 vol% methanol from Formosa Plastics Corporation of Taiwan and then stored at 4°C.

The 20-L-Apparatus was purchased from Adolf Kühner AG as illustrated in Fig. 1. It is a standard test method for pressure and rate of pressure rise for combustible dusts [19], and Kühner AG has extended it into Combustible Gases and Vapors testing. The test chamber is a stainless steel hollow sphere with a personal computer interface. The top of the cover con-

* Author for correspondence: khhu@jente.edu.tw

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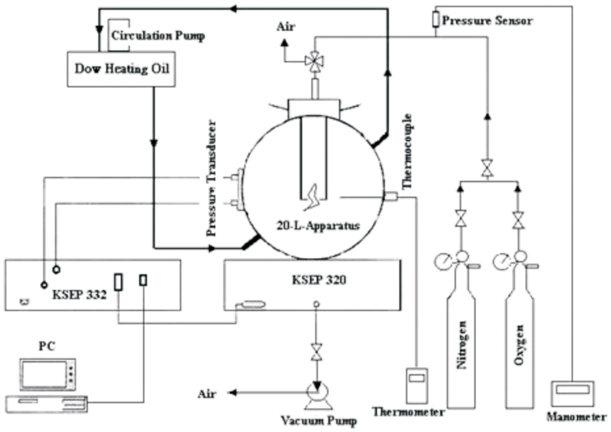

Fig. 1 A schematic diagram of the 20-L-Apparatus and its control system [18, 22]

Table 1 The criteria for the observed reaction behavior in the 20-L-Apparatus [18, 22]

IE[a]=10 J	P_{ex}[b]/bar	P_m[c]/bar	Decision
UEL and LEL testing	0.1	0.1	no ignition
	0.1	0.1	ignition

[a]IE – ignition energy; [b]P_{ex} – explosion overpressure; [c]P_m – corrected explosion overpressure

tains 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 [18]. A comprehensive software package KSEP 6.0 is available, which allows safe operation of the test equipment and an optimum evaluation of the explosion test results. The 20-L-Apparatus has the highest reliability because of its standard spherical shape [19–21]. The equipment is able to determine the explosion behavior of combustible materials (combustible dusts, flammable gases, or solvent vapors) in accordance with internationally recognized test procedures, as displayed in Table 1, such as ASTM 1226 (American Society for Testing and Materials, USA) and VDI 2263 (Verein Deutscher Ingenieure, Germany). Accordingly, a material's inherent safety-related flammability properties of LFL, UFL, P_{max}, $(dP/dt)_{max}$, K_g and MOC will be derived in this test system by series.

LEL and UEL for gas and solvent vapors

By definition [23], 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 homogenous mixture of the combustible and a gaseous oxidizer under the specified conditions of a 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 lower explosion limit (LEL) and the upper explosion limit (UEL), respectively. 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) [24]. In this work, the test series were 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 [18].

In this study, we could use Le Chatelier's law [25–27] to predict the explosion mixing limits: and

$$\mathrm{LEL}_{mix}=\frac{1}{\sum_{i=1}^{n}\frac{y_i}{\mathrm{LEL}_i}} \quad \text{and} \quad \mathrm{UEL}_{mix}=\frac{1}{\sum_{i=1}^{n}\frac{y_i}{\mathrm{UEL}_i}} \tag{1}$$

where $\mathrm{LEL}_i/\mathrm{UEL}_i$ are the lower/upper explosion limits for component i in vol% of component i in fuel and air.

y_i is the mole fraction of component i on a combustible basis and n is the number of combustible species. However, Le Chatelier's law is an empirically derived equation that is not universally applicable [24].

Maximum explosion overpressure (P_{max}), maximum rate of explosion pressure rise $(dP/dt)_{max}$, and gas or vapor deflagration index (K_g)

The explosion indices, P_{max}, and $(dP/dt)_{max}$ are defined as the mean values of the maximum values of all three series. Subsequently, the gas or vapor deflagration index (K_g) is calculated from $(dP/dt)_{max}$ by means of the Cubic law [21]:

$$V^{1/3}\times(dP/dt)_{max}\ K_g \tag{2}$$

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

As there are many gas products and industrial practices, it is appropriate to assign this maximum constant to one of several explosion classes (St), as given in Table 2, and to use these as a basis for sizing explosive relief according to NFPA 68 [18, 21, 22].

Table 2 K_g and explosion classes (St) [18, 21, 22]

K_g/m bar s^{-1}	Explosion classes, (St)
<1	St-0
1–200	St-1
201–300	St-2
>300	St-3

Minimum oxygen concentration (MOC)

The LEL is based on fuel in air. However, oxygen is the key ingredient, and a MOC is required to propagate a flame. When oxygen concentration is less than the MOC, the reaction cannot generate enough energy to heat the entire gas mixtures (including the inerts) to the extent required for the self-propagation of the flame.

MOC 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 [20, 24, 28].

Results and discussion

The experimental data indicated the LEL and UEL changed with different concentrations that were calculated by the ideal gas law. However, different vapor mixing ratios (75/25, 50/50 and 25/75 vol%) of benzene/methanol also affect the results of explosion parameters. Here, we specifically discuss varying concentrations and different vapor mixing ratios as follows.

Different concentrations

Table 3 shows the variation of flammability range with five different vapor mixing ratios under 100/150/200°C, 101 kPa and 21 vol% oxygen concentration.

Obviously, the results indicate that relationship under such operating conditions.

Different vapor mixing ratios

The experimental results were the P_{max} from the flammability limit tests *vs.* various ratios of benzene and methanol concentrations for the mixtures of benzene/methanol/O_2/N_2.

The above-mentioned experimental data indicate the flammability limits of benzene and methanol and their mixtures, as displayed in Tables 6–8. In the condition of 101 kPa, 150°C and 21 vol% O_2, the flammability limits of benzene and methanol are from 1.10–6.10 and 5.50–40.60 vol%, and then other flammability limits changed with the different mixing ratios, respectively. The LELs of three mixing concentrations, 75/25, 50/50 and 25/75 vol% of benzene/methanol, are 1.18, 1.40 and 2.90 vol%, respectively. The UELs of three mixing concentrations on benzene/methanol of 75/25, 50/50 and 25/75 vol%, are 8.29, 25.00 and 33.55 vol%, correspondingly.

Obviously, the tendency of flammability limits of benzene/methanol mixtures in the data (75/25, 50/50 and 25/75 vol%) tends to increase with increasing methanol. However, the mixtures' flammability limits will be between 100% benzene and 100% methanol and close to either one of the majorities. Besides, in comparison with the LEL and UEL values by experiments and predicted by Le Chatelier's law under 150°C, 101 kPa and different oxygen concentrations are listed in Table 4. Based upon the results, we compared the LEL and UEL values by experiments and Le Chatelier's law under 150°C, 101 kPa and different oxygen concentrations, as in Table 4. Le Chatelier's law could only applied to the calculated LELs, whereas the predicted UELs equation needs to be modified in the future.

Effects on initial temperatures

Practically speaking, temperature is also an important safety factor. Based upon the state notes from Vanderstraeten and Zabetakis [29, 30], the UELs of common hydrocarbons increase with enhanced temperature and LELs are alleviated. The UELs variations from the initial temperature of 100 to 200°C with five different vapor mixing ratios under 101 kPa and 21 vol% oxygen concentrations are as follows:

- UEL of benzene:methanol (100:0 vol%) from 6.00 vol% $\xrightarrow{\text{rise to}}$ 7.00 vol%
- UEL of benzene:methanol (75:25 vol%) from 7.24 vol% $\xrightarrow{\text{rise to}}$ 8.42 vol%
- UEL of benzene:methanol (50:50 vol%) from 24.10 vol% $\xrightarrow{\text{rise to}}$ 25.00 vol%
- UEL of benzene:methanol (25:75 vol%) from 31.97 vol% $\xrightarrow{\text{rise to}}$ 35.39 vol%
- UEL of benzene:methanol (0:100 vol%) from 38.70 vol% $\xrightarrow{\text{rise to}}$ 48.70 vol%

Table 3 The variation of flammability range with five different vapor mixing ratios under 100/150/200°C, 101 kPa and 21 vol% oxygen concentration

Variation of flammability range/vol%	100°C	150°C	200°C
Benzene:methanol (100:0)	4.90 vol%	5.00 vol%	6.00 vol%
Benzene:methanol (75:25)	5.40 vol%	7.11 vol%	6.84 vol%
Benzene:methanol (50:50)	21.73 vol%	23.60 vol%	23.03 vol%
Benzene:methanol (25:75)	29.21 vol%	30.65 vol%	33.02 vol%
Benzene:methanol (0:100)	32.70 vol%	35.10 vol%	43.60 vol%

Table 4 The comparison of LEL/UEL by experiments and the evaluations by Le Chatelier's law under 150°C, 101 kPa

Different vapor mixing ratios/vol%	LEL by experiment/vol%	LEL by evaluation/vol%	UEL by experiment/vol%	UEL by evaluation/vol%
O_2=21 vol%				
75 benzene/25 methanol	1.18	1.40	8.29	7.70
50 benzene/50 methanol	1.40	1.80	25.00	10.60
25 benzene/75 methanol	2.90	2.80	33.55	16.80
O_2=17 vol%				
75 benzene/25 methanol	1.32	1.40	5.92	5.80
50 benzene/50 methanol	1.80	1.90	12.30	7.90
25 benzene/75 methanol	3.30	2.90	22.47	12.50
O_2=14 vol%				
75 benzene/25 methanol	1.58	1.40	4.74	4.30
50 benzene/50 methanol	2.10	1.80	5.30	5.70
25 benzene/75 methanol	2.76	2.80	9.87	8.70
O_2=11 vol%				
75 benzene/25 methanol	1.84	1.60	3.16	2.10
50 benzene/50 methanol	2.50	2.10	3.40	2.90
25 benzene/75 methanol	3.00	3.10	4.60	4.40

Besides, the variations of LELs with five different vapor mixing ratios under 101 kPa and 21 vol% oxygen concentrations from 100 to 200°C are as follows:

- LEL of benzene:methanol (100:0 vol%) from 1.1 vol% $\xrightarrow{\text{decrease to}}$ 1.00 vol%
- LEL of benzene:methanol (75:25 vol%) from 1.84 vol% $\xrightarrow{\text{decrease to}}$ 1.58 vol%
- LEL of benzene:methanol (50:50 vol%) from 2.37 vol% $\xrightarrow{\text{decrease to}}$ 1.97 vol%
- LEL of benzene:methanol (25:75 vol%) from 2.76 vol% $\xrightarrow{\text{decrease to}}$ 2.37 vol%
- LEL of benzene:methanol (0:100 vol%) from 6.0 vol% $\xrightarrow{\text{decrease to}}$ 5.10 vol%

According to the above-mentioned experimental data, while enhancing the initial temperature from 100 to 200°C, the flammability ranges, i.e., LELs–UELs in vol%, will get enlarged. The tendency of flammability limits of benzene/methanol mixtures in the data tend to expand the flammability range with increasing temperature.

Effects on initial pressures

In the case of benzene:methanol (75:25 vol.%), the explosion parameters by raising initial pressure from 101 to 202 kPa under 150°C and 21 vol% oxygen concentration are shown in Table 5. The P_{max}, $(dP/dt)_{max}$ and K_g values will increase rapidly with pressure increased.

Table 5 Fire and explosion characteristic variations between different initial pressures of 101 and 202 kPa

Initial pressure	101 kPa	202 kPa
P_{max}	3.20 bar	8.90 bar
$(dP/dt)_{max}$	258.00 bar s^{-1}	1523.00 bar s^{-1}
K_g	69.66 bar s^{-1}	411.21 bar s^{-1}
explosion classes	St-1	St-3

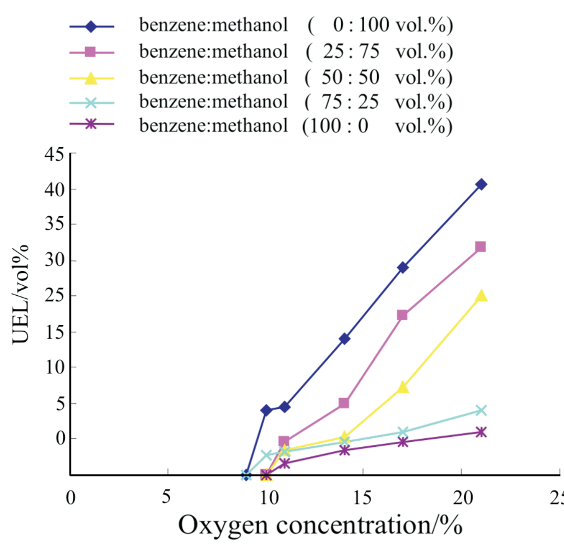

Fig. 2 UEL *vs.* oxygen concentration with benzene and methanol at 150°C and five different mixing ratios

Table 6 Fire and explosion characteristics of different ratios of benzene and methanol (100/0, 75/25, 50/50, 25/75 and 0/100 vol%) at 100°C, 101 kPa and 21 vol% oxygen concentration

Mixtures/vol%	MOC/vol%	LEL/vol%	UEL/vol%	P_{max}/bar	$(dP/dt)_{max}$/bar s^{-1}	K_g/m bar s^{-1}	St
Benzene:methanol (100:0)	12	1.10	6.00	3.60	216	58.32	St-1
Benzene:methanol (75:25)	12	1.84	7.24	3.50	211	56.97	St-1
Benzene:methanol (50:50)	11	2.37	24.10	3.60	256	69.12	St-1
Benzene:methanol (25:75)	11	2.76	31.97	3.70	287	77.49	St-1
Benzene:methanol (0:100)	11	6.00	38.70	3.60	278	75.06	St-1

St – explosion classes

Table 7 Fire and explosion characteristics of different ratios of benzene and methanol (100/0, 75/25, 50/50, 25/75 and 0/100 vol%) at 150°C, 101 kPa and 21 vol% oxygen concentration

Mixtures/vol%	MOC/vol%	LEL/vol%	UEL/vol%	P_{max}/bar	$(dP/dt)_{max}$/bar s^{-1}	K_g/m bar s^{-1}	St
Benzene:methanol (100:0)	11	1.10	6.10	3.30	291	80.03	St-1
Benzene:methanol (75:25)	10	1.18	8.29	3.20	258	69.66	St-1
Benzene:methanol (50:50)	11	1.40	25.00	3.30	256	69.12	St-1
Benzene:methanol (25:75)	11	2.90	33.55	3.20	287	77.49	St-1
Benzene:methanol (0:100)	10	5.50	40.60	3.20	279	75.33	St-1

St – explosion classes

Table 8 Fire and explosion characteristics of different ratios of benzene and methanol (100/0, 75/25, 50/50, 25/75 and 0/100 vol%) at 200°C, 101 kPa and 21 vol% oxygen concentration

Mixtures/vol%	MOC/vol%	LEL/vol%	UEL/vol%	P_{max}/bar	$(dP/dt)_{max}$/bar s^{-1}	K_g/m bar s^{-1}	St
Benzene:methanol (100:0)	12	1.00	7.00	2.90	288	77.76	St-1
Benzene:methanol (75:25)	10	1.58	8.42	2.90	279	75.33	St-1
Benzene:methanol (50:50)	11	1.97	25.00	2.90	279	75.33	St-1
Benzene:methanol (25:75)	9	2.37	35.39	2.80	276	74.52	St-1
Benzene:methanol (0:100)	8	5.10	48.70	2.80	262	70.47	St-1

St – explosion classes

Effects on oxygen concentrations

UEL increased with increasing oxygen concentrations at the same initial pressure, and the UEL also increased with the amount of methanol. The results demonstrate the effect of oxygen concentration on upper flammability limit as depicted in Fig. 2. The flammability limits decreased with reducing the oxygen concentration with benzene and methanol. When oxygen concentration is below the MOC, an explosion is no longer possible [22].

Flammability diagram

In practice, 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. The flammability diagram of a fuel/O_2 /N_2 mixture represents the three components as F, O_2, N_2, respectively, as delineated in Fig. 3. It also clearly points out the MOC of every mixing concentration.

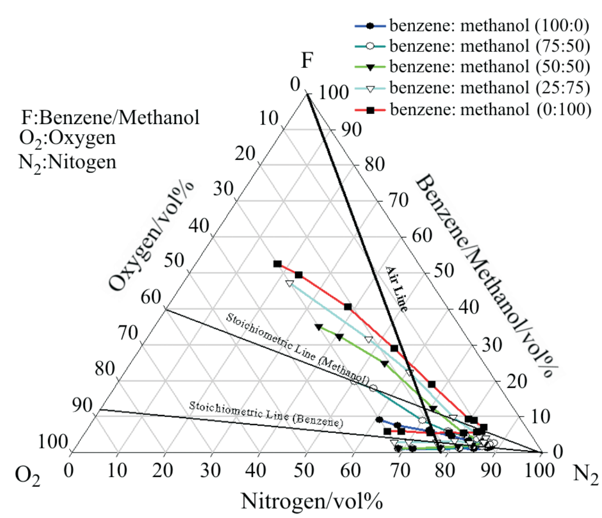

Fig. 3 Overall triangular flammability diagram illustrating the change in flammability zone with different ratios of benzene and methanol at 150°C and 101 kPa

Conclusions

Because the UEL and LEL of methanol are the maximum and the minimum of all compositions, by mixing different ratios of benzene and methanol in 100/0, 75/25, 50/50, 25/75 and 0/100 vol%, respectively, the UEL and LEL of benzene and methanol of 75/25, 50/50 and 25/75 vol% increase with increasing methanol. The flammability limits of benzene and methanol in 75/25, 50/50 and 25/75 vol% are between 100 vol% benzene and methanol. With addition of benzene or methanol, the properties close to either one of the majorities. However, providing a safety margin is recommended. In the benzene and methanol mixing procedure, we can calculate the benzene and methanol vapor concentration ratios in different operating conditions.

Consequently, the vapor condensed into liquid and caused a liquid-vapor co-existing phase, which may demonstrate higher degree of hazard and unexpected conditions under higher pressure.

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