

Flammability Studies of Benzene and Methanol with Various Vapor Mixing Ratios at 150 °C

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Abstract—Both benzene and methanol are important raw materials in petrochemical industries worldwide. However, with increased demand in the past few years, the fire and explosion hazards from both benzene and methanol under abnormal conditions have increased rapidly with the demand. This study investigated the flammability characteristics of a binary solution for the mixture of benzene and methanol at various vapor-mixing ratios (100/0, 75/25, 50/50, 25/75, 0/100 vol%) under 150 °C, 760 and 1,520 mmHg by using a 20 Liter Spherical Explosion Vessel. Such work leads to specific safety-related property parameters, including upper explosion limit (UEL), lower explosion limit (LEL), minimum oxygen concentration (MOC), maximum explosion pressure (P_{max}), maximum rate of explosion pressure rise (dP/dt_{max}), and gas or vapor explosion constant (K_g). Along with the results which show that the UEL, P_{max} , and K_g all increased with the pressure and oxygen concentration, a triangular flammability diagram was also established. This all serves to elucidate the potential hazards when vapors of different flammable chemicals are mixed.

Key words: Fire and Explosion Hazards, Binary Solution, Safety-Related Property Parameters, Triangular Flammability Diagram

INTRODUCTION

The history of the chemical process industries is replete with major accidents [Khan et al., 1998], and many studies place an emphasis on fire and explosion hazard evaluation and analysis [Zabetakis, 1965; O'Shaughnessey, 1995; Chad and Daniels, 1998; Jo and Kim, 2001; Park and Kim, 2001; Kim et al., 2003; Shu and Wen, 2002]. The petrochemical industry frequently uses flammable mixtures such as benzene and methanol. Inevitably, these substances may result in fires and explosions under various upset scenarios, and their hazards may also be exacerbated by the demand for chemicals in processes. Fig. 1 shows the growth of demand for benzene and methanol in recent years in Taiwan, indicating potential hazards if not operated suitably [Petrochemical Industry of Taiwan, ROC, 2005].

This study aimed at determining safety properties of benzene and methanol mixtures, in which the upper explosion limit (UEL), lower explosion limit (LEL), minimum oxygen concentration (MOC), maximum explosion pressure (P_{max}), maximum rate of explosion pressure rise (dP/dt_{max}), and gas or vapor explosion constant (K_g) have particular significance in terms of throughputs and potential hazards in the petrochemical industry. There are several methods for manufacturing benzene, including (1) the method of reforming petroleum and (2) the method of cracked gasoline [Fruscella, 1996]. In 1952, Dow Chemical Co. launched the most commonly used

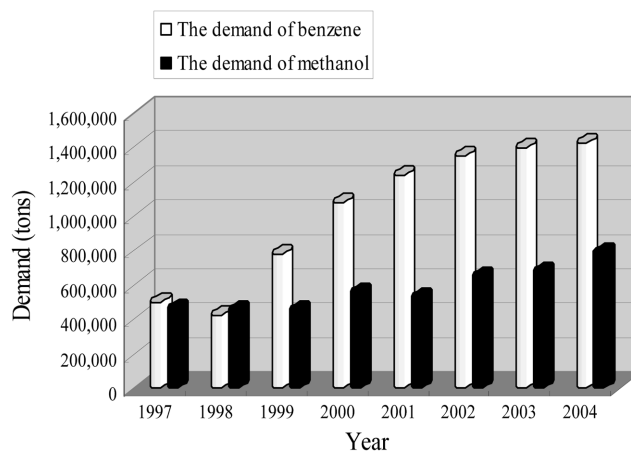


Fig. 1. The demand for benzene and methanol in Taiwan since 1997 [Petrochemical Industry of Taiwan, ROC, 2005].

extraction method of Udex; later the UOP Co. developed and received a patent for extracting benzene. In the process industries, its major application is to produce styrene, and later acrylonitrile-butadiene-styrene (ABS) copolymer.

After World War II, natural gas was the essential material for producing methanol extensively. Natural gas was reformed and CO_2 added to adjust the ratio of CO and H_2 to 1 : 2. Pressure is the key parameter for synthesizing methanol, as displayed in Table 1. After the purification process, methanol can be acquired up to almost 99 wt%. After oxidation, formaldehyde can be obtained, which is the main purpose in terms of application. Methanol and isobutylene can synthesize (methyl tertiary butyl ether, MTBE) as a petroleum

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Table 1. Classifications of pressure in methanol manufacturing process [Chen, 2004]

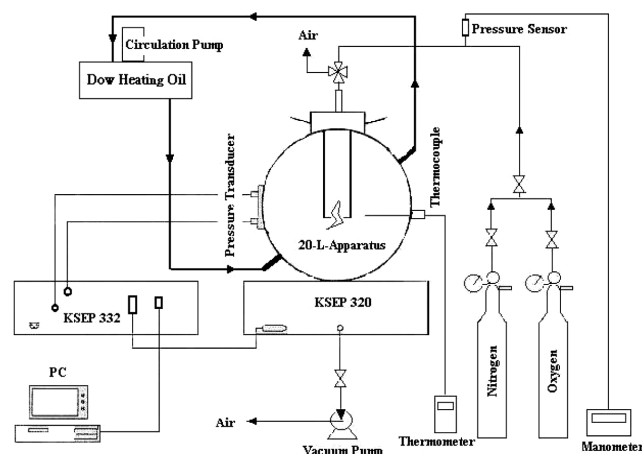
| | Pressure (atm) | Temperature (°C) | Catalysts |
|-----------------|----------------|------------------|----------------|
| High pressure | 300-600 | 320-380 | Cr, Zn |
| Middle pressure | 105-300 | 225-270 | Cu, Zn, Cr, Al |
| Low pressure | 40-60 | 200-300 | Cr, Zn |

additive [English et al., 1996]. Through further work, methanol can also be converted to acetic acid.

Research on the related properties of benzene and methanol has been performed for years [Lee et al., 1984; Park and Ihm, 1985; Lee and Lee, 1995; Hong et al., 2003], and there have been many investigations on flammability quality related to single chemicals, but so far very little attention has been given to binary mixing chemicals, i.e., mixing two kinds of different flammable solvents or chemicals in manufacturing processes. The flammable liquid solutions presented in a real situation usually include not less than two components; when they are evaporated to form a flammable gas, their harmful impact might be greater than one solvent alone. Prevention and elimination is one of the main concerns for various chemical processes [Chae et al., 1994]; therefore, there is a great need to study the flammability of flammable binary mixing chemicals and liquid solutions, e.g., mixtures of benzene and methanol in this work. The purpose of this study was to: (1) investigate the specific safety-related property parameters of benzene, methanol and their mixtures, including LEL, UEL, P_{max} , $(dp/dt)_{max}$, K_g , and MOC, at initial temperatures of 150 °C and between 760, 1,520 mmHg by using a 20 Liter Spherical Explosion Vessel, (2) identify the hazards of various vapor mixing ratios of benzene and methanol in 100/0, 75/25, 50/50, 25/75 and 0/100 vol%, respectively, (3) realize the fire and explosion hazards of binary mixtures when mixing vapors of different flammable chemicals and (4) provide specific information for related industries and prevent them from further unexpected accidents.

EXPERIMENTAL APPARATUS AND METHOD

In this work, specific experimental data for above-mentioned safe-

**Fig. 2. A schematic diagram of the 20-L-Apparatus and its control system [Shu and Wen, 2002].**

ty-related property parameters were obtained by using the 20-L-Apparatus which was purchased from Adolf Kühner AG. The main structure of this apparatus can be roughly separated into four parts, as illustrated in Fig. 2: spherical explosion vessel, heating and circulation device, pressure setting system, and transmission computer interface [Shu and Wen, 2002]. The test chamber is a stainless steel hollow sphere equipped with a personal computer interface; the top of the 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 piezoelectric pressure sensors to measure the pressure in operation. A comprehensive software package KSEP 6.0 is available, which ensures safe operation of the test equipment and an optimum evaluation of the explosion test results [Kühner, 2005]. We could investigate the fire and explosion safety-related property parameters by means of this equipment and set various required situations before operation.

In the past, the international standards have described the 1 m³ vessel as the standard test apparatus, but its disadvantage is its huge size [Zabetakis, 1965]. Recently, a more resourceful, convenient and less expensive 20-L-Apparatus has gained more use as the standard equipment. The explosion behavior of combustible materials (combustible dusts, flammable gases, or solvent vapors) must be in accordance with internationally recognized test procedures as well.

The purpose of the flammability testing for this study was to define the flammability concentration limits for various benzene and methanol mixing vapors (100/0, 75/25, 50/50, 25/75, 0/100 vol%) at initial temperature of 150 °C and two initial pressures of 760, 1,520 mmHg as the test vessel could not sustain at pressure exceeding 2,280 mmHg. The basic properties of benzene and methanol are shown in Table 2; the boiling point of benzene and methanol is 80 and 64.7 °C, respectively [Kirk-Othmer, Encyclopedia of Chemical Technology, 1996]. Because the combustion of liquid fuels takes place in the gas phase [Rah, 1984], we deliberately set the initial temperature as 150 °C in order to exceed their normal boiling point forming the total flammable vapor, so as to test in good mixing state in gas phase.

The test method and procedures for the fire and explosion property in this study are described as follows:

1. LEL and UEL for Gas and Solvent Vapors

The explosion limit for flammable gas or solvent vapor is from

Table 2. Basic properties of benzene and methanol [Kirk-Othmer, Encyclopedia of Chemical Technology, 1996]

| Product name | Benzene | Methanol |
|---------------------------------------|-------------------------------|--------------------|
| Formula | C ₆ H ₆ | CH ₃ OH |
| UN No. | 1114 | 1230 |
| CAS No. | 00071-43-2 | 00067-56-1 |
| Molecular weight | 78.06 g/mole | 32.04 g/mole |
| Boiling point (760 mmHg) | 80 °C | 64.7 °C |
| Vapor pressure | 75 mmHg (20 °C) | 160 mmHg (30 °C) |
| Specific gravity (H ₂ O=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 |

the LEL to the UEL. LEL means that a mixture will not burn when the composition is lower than the value, and UEL indicates that it is also not combustible when it is above this value. So, only when the composition is within the range is a mixture flammable [Crowl and Louvar, 2002].

By definition [ASTM (E681-85), 1991], the LEL/UEL of a gas/vapor is the lowest/highest concentration at which a gas/vapor explosion is not detected in three successive tests in experimental operation [Shu and Wen, 2002]. In this study, the benzene and methanol were evaporated from liquid to vapor phase by a thermo oil bath controlled at 150 °C.

We could use the Le Chatelier equation [Le Chatelier, 1891] to predict the explosion mixing limits:

$$LEL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{LEL_i}} \quad \text{and} \quad UEL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{UEL_i}} \quad (1)$$

where

LEL_i/UEL_i is the lower/upper explosion limit 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 equation is an empirically derived equation which is not universally applicable [Crowl and Louvar, 2002].

2. Maximum Explosion Overpressure (P_{max}), Maximum Rate of Explosion Pressure Rise (dP/dt)_{max}, and Gas or Vapor Deflagration index (K_g)

The peak values that accompany the explosion of a combustible vapor are the P_{max} and $(dP/dt)_{max}$. Experimentally, the peak values can be obtained from tests over a wide range of concentrations ignited by electric spark [Crowl and Louvar, 2002].

The P_{max} and $(dP/dt)_{max}$ are the mean values of the maximum values of all three series. Subsequently, the K_g is calculated from $(dP/dt)_{max}$ by means of the Cubic law [NFPA 68, 2002]:

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

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 m³), 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 indicated in Table 3 [Kühner, 2005], and to use these, after certain manipulations, as a basis for sizing explosive relief according to NFPA 68 [NFPA 68, 2002].

3. Minimum Oxygen Concentration (MOC)

Oxygen is the key ingredient, and an MOC is required to propagate a flame. When oxygen concentration is less than the MOC, the reaction cannot generate sufficient energy to heat the entire gas

mixtures (including the inerts) to the extent required for the self-propagation of the flame [Crowl and Louvar, 2002]. 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 [ASTM (E681-85), 1991; Crowl and Louvar, 2002].

Below the MOC, an ignition of a specific mixture cannot occur in three successive tests. In general, nitrogen is used as an inert gas; therefore, the following test conditions are based on nitrogen only.

After the first test series in normal air (O₂=21 vol%), the second series will be run in N₂ at about 17 vol% O₂ over a wide range of gas concentrations, for determining the P_{max} and K_g explosion indices. The tests, in turn, have to be continued by systematic reduction, say 3 to 4 vol% each time, of the oxygen concentration in nitrogen until gas explosions are no longer possible [Shu and Wen, 2002].

RESULTS AND DISCUSSION

The experimental data indicate that the UEL and LEL changed

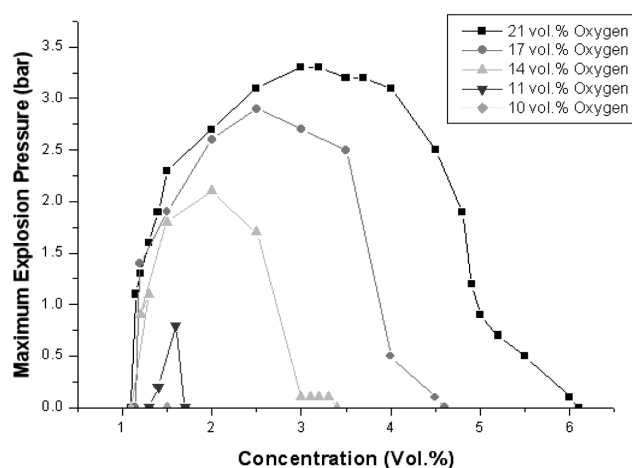


Fig. 3. Maximum explosion pressure vs. benzene/methanol (100/0 vol%) at 150 °C/760 mmHg.

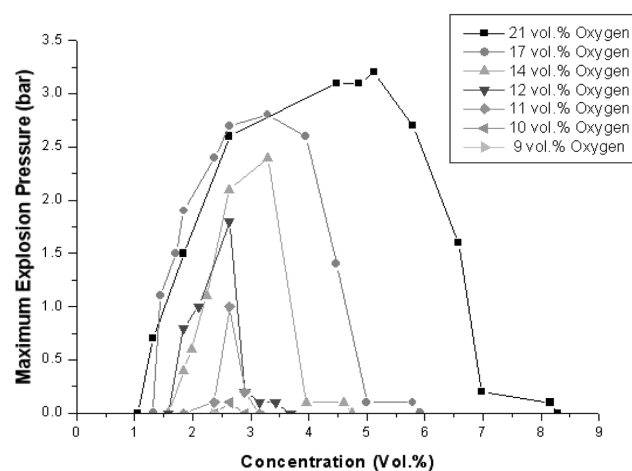


Fig. 4. Maximum explosion pressure vs. benzene/methanol (75/25 vol%) at 150 °C/760 mmHg.

Table 3. K_g and explosion classes (St) [Kühner, 2005]

| K_g (mbarsec ⁻¹) | Explosion classes (St) |
|--------------------------------|------------------------|
| <1 | St-0 |
| 1-200 | St-1 |
| 201-300 | St-2 |
| >300 | St-3 |

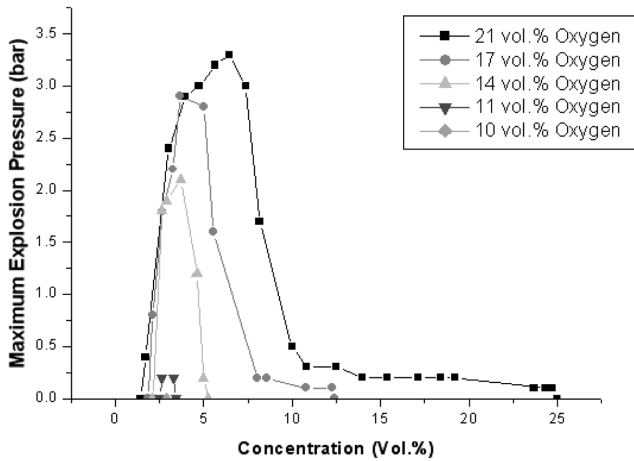


Fig. 5. Maximum explosion pressure vs. benzene/methanol (50/50 vol%) at 150 °C/760 mmHg.

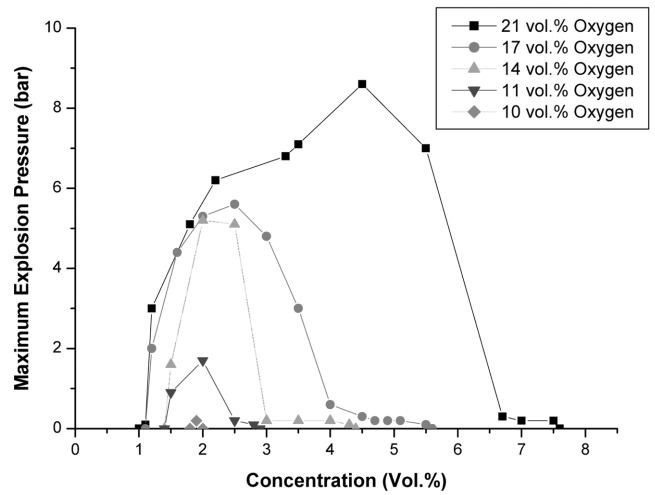


Fig. 8. Maximum explosion pressure vs. benzene/methanol (100/0 vol%) at 150 °C/1,520 mmHg.

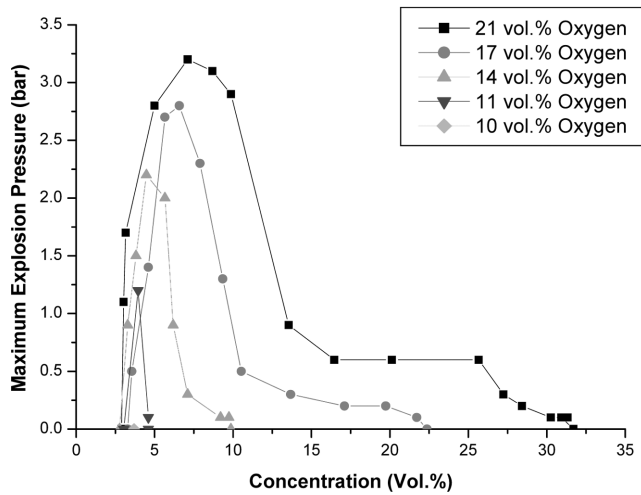


Fig. 6. Maximum explosion pressure vs. benzene/methanol (25/75 vol%) at 150 °C/760 mmHg.

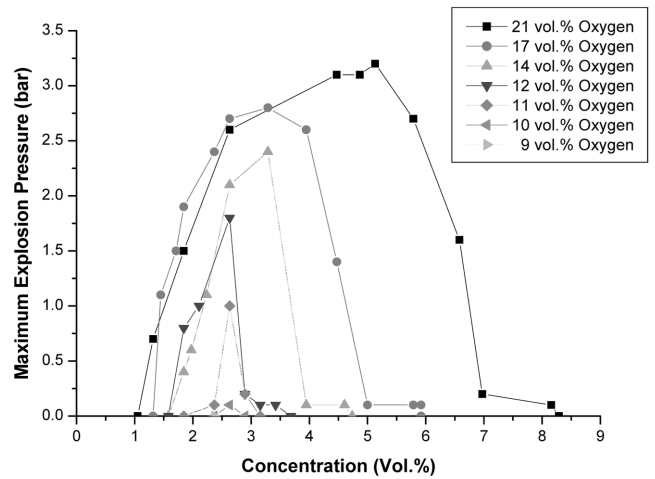


Fig. 9. Maximum explosion pressure vs. benzene/methanol (75/25 vol%) at 150 °C/1,520 mmHg.

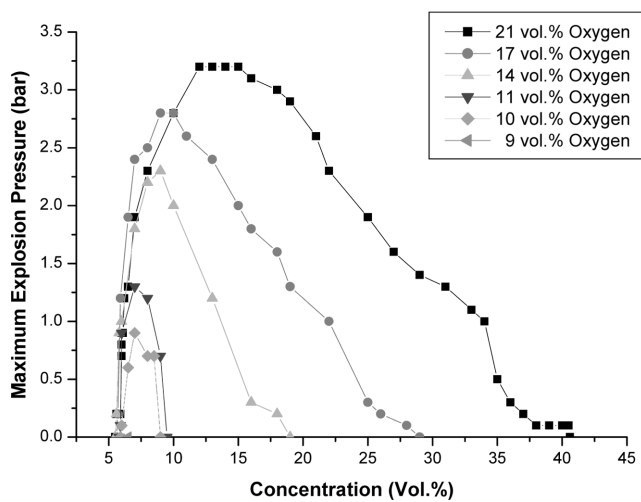


Fig. 7. Maximum explosion pressure vs. benzene/methanol (0/100 vol%) at 150 °C/760 mmHg.

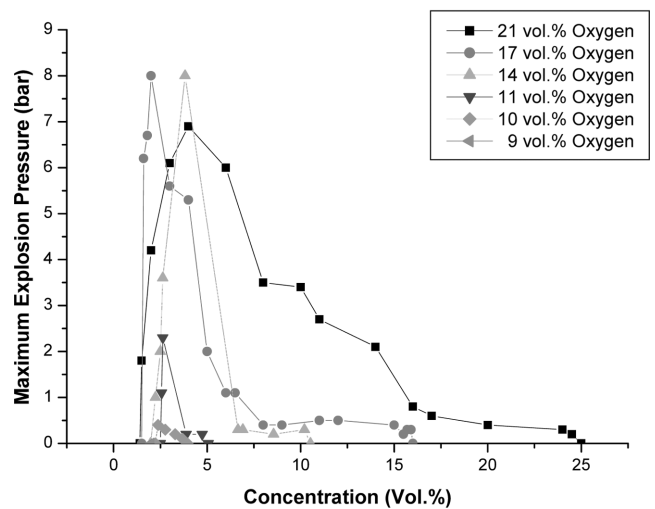


Fig. 10. Maximum explosion pressure vs. benzene/methanol (50/50 vol%) at 50 °C/1,520 mmHg.

with different concentrations 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 especially discuss varying concentrations and different vapor mixing ratios as follows:

1. Different Concentrations

Figs. 3 to 12 demonstrate the concentrations forming an expanded bell-type curve with P_{max} by enhancing oxygen concentration under 150 °C and 760 mmHg/1,520 mmHg, respectively. Obviously, the results indicate the relationship between concentrations and explosion parameters under the specific operation conditions.

2. Different Vapor Mixing Ratios

Figs. 3 to 12 illustrate the experimental results of the P_{max} from the flammability limit tests versus various ratios of benzene and methanol concentrations for the mixtures of benzene/methanol/ O_2 / N_2 , with initial pressure of 760 and 1,520 mmHg at 150 °C. In normal air ($O_2=21$ vol%), the flammability limit of benzene is from 1.10

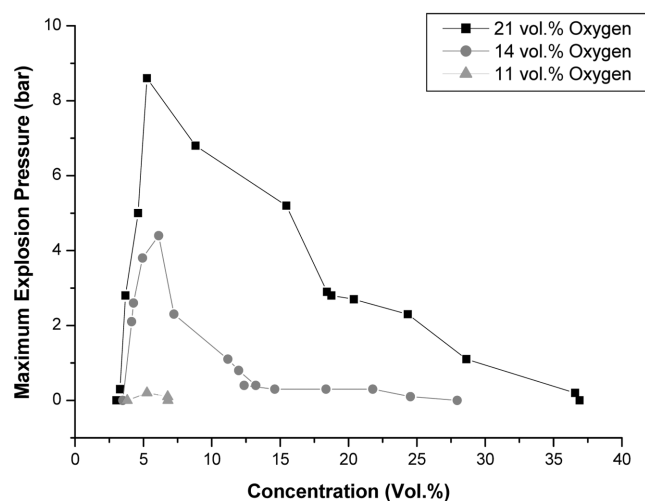


Fig. 11. Maximum explosion pressure vs. benzene/methanol (25/75 vol%) at 150 °C/1,520 mmHg.

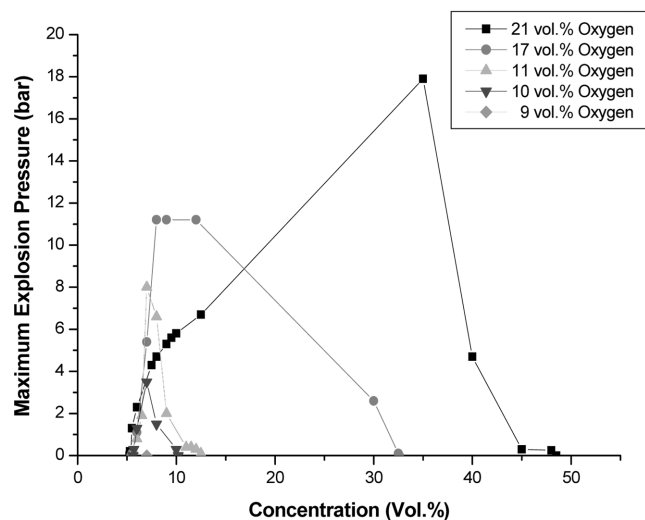


Fig. 12. Maximum explosion pressure vs. benzene/methanol (0/100 vol%) at 150 °C/1,520 mmHg.

to 6.10 vol% and the flammability limit of methanol is from 5.50 to 40.60 vol%, and then other flammability limits changed with the different mixing ratios, respectively. Here, the LELs of three mixing concentrations, 75/25, 50/50, and 25/75 of benzene/methanol, are 1.18, 1.40 and 2.90, respectively. The UELs of three mixing concentrations of benzene/methanol of 75/25, 50/50 and 25/75, are 8.29, 25 and 33.55 vol%, respectively. With more methanol dosed, its UEL and LEL also increased, whereas the limits did not exceed any flammability limit of methanol and benzene at the same conditions, as illustrated in Figs. 13 and 14. We compared the LEL and UEL values by experiments and Le Chatelier's equation under 150 °C, 760 mmHg and different oxygen concentrations in Table 4. Based upon the results, we compared the LEL and UEL values by experi-

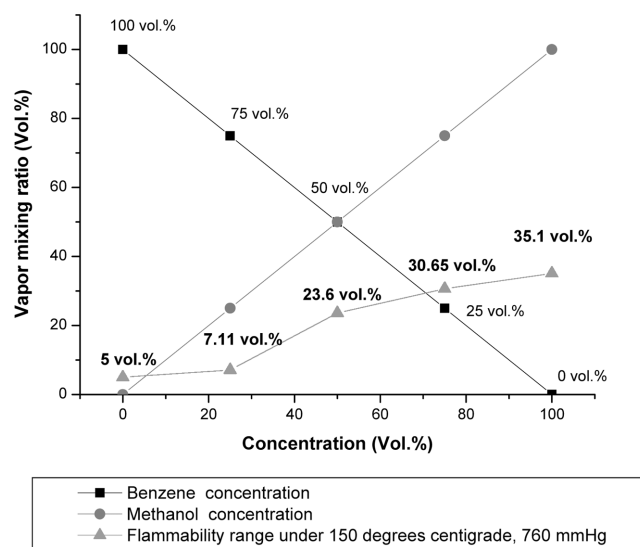


Fig. 13. The variation of flammability range with five different vapor mixing ratios under 150 °C, 760 mmHg and 21 vol% oxygen.

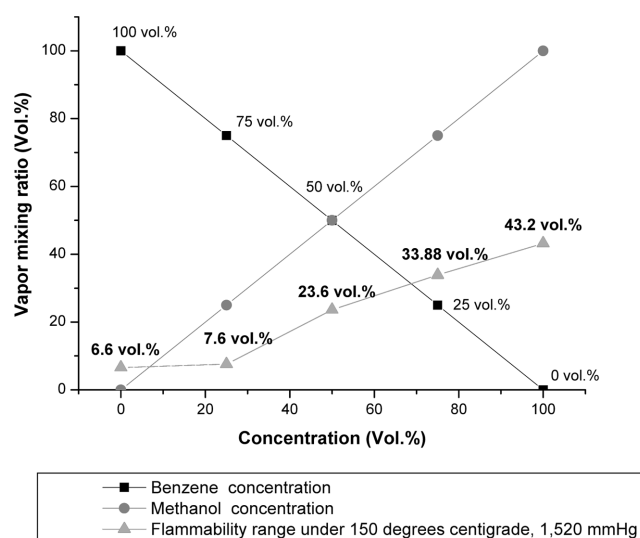


Fig. 14. The variation of flammability range with five different vapor mixing ratios under 150 °C, 1,520 mmHg and 21 vol% oxygen.

Table 4. A comparison of LEL by experiment and Le Chatelier's equation under 150 °C, 760 mmHg

| 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 |

Table 5. Fire and explosion characteristics of different ratios of benzene and methanol at 150 °C and 760 mmHg to 100/0, 75/25, 50/50, 25/75 and 0/100 vol%, respectively

| O ₂ (vol%) | LEL (vol%) | UEL (vol%) | P _{max} (bar) | (dP/dt) _{max} (barsec ⁻¹) | K _g (mbarsec ⁻¹) | Explosion class (St) |
|------------------------|------------|------------|------------------------|--|---|----------------------|
| 100 Benzene/0 Methanol | | | | | | |
| 10 | - | - | - | - | - | St-0 |
| 11 | 1.30 | 1.70 | 0.80 | 2.00 | 0.54 | St-0 |
| 14 | 1.10 | 3.40 | 2.10 | 27.00 | 0.54 | St-0 |
| 17 | 1.15 | 4.60 | 2.90 | 149.00 | 40.97 | St-1 |
| 21 | 1.10 | 6.10 | 3.30 | 291.00 | 80.03 | St-1 |
| 75 Benzene/25 Methanol | | | | | | |
| 9 | - | - | - | - | - | St-0 |
| 10 | 2.37 | 2.89 | 0.10 | 2.00 | 0.54 | St-0 |
| 11 | 1.84 | 3.16 | 1.00 | 10.00 | 2.75 | St-1 |
| 14 | 1.58 | 4.74 | 2.40 | 50.00 | 13.52 | St-1 |
| 17 | 1.32 | 5.92 | 2.80 | 131.00 | 25.37 | St-1 |
| 21 | 1.18 | 8.29 | 3.20 | 258.00 | 69.66 | St-1 |
| 50 Benzene/50 Methanol | | | | | | |
| 10 | - | - | - | - | - | St-0 |
| 11 | 2.50 | 3.40 | 2.00 | 0.20 | 0.06 | St-0 |
| 14 | 2.10 | 5.30 | 2.10 | 2.40 | 0.66 | St-0 |
| 17 | 1.80 | 12.30 | 2.90 | 143.00 | 39.33 | St-1 |
| 21 | 1.40 | 25.00 | 3.30 | 298.00 | 81.95 | St-1 |

ments and Le Chatelier's equation under 150 °C, 760 mmHg and different oxygen concentrations, as displayed in Table 4. Le Chatelier's equation could only apply to the calculated LELs, whereas the predicted UEL equation needs to be modified in the future.

At a methanol concentration over 50 vol% in mixtures, a blue flame (cool flame) occurred after UEL. Here, the P_{max} could not be detected, but only weak combustion. In a confined space, to avoid

fire or explosion hazards, controlling the concentrations beyond the flammability limit may be a feasible approach. It is also necessary to make a suitable evaluation and take into account the trade-off between economy and safety during operation.

3. Effects on Initial Pressures

In the case of benzene : methanol (75 vol% : 25 vol%), the explosion parameters by raising initial pressure from 760 to 1,520 mmHg

Table 5. Continued

| O ₂ (vol%) | LEL (vol%) | UEL (vol%) | P _{max} (bar) | (dP/dt) _{max} (barsec ⁻¹) | K _g (mbarsec ⁻¹) | Explosion class (St) |
|------------------------|------------|------------|------------------------|--|---|----------------------|
| 25 Benzene/75 Methanol | | | | | | |
| 10 | - | - | - | - | - | St-0 |
| 11 | 3.00 | 4.60 | 2.00 | 1.20 | 0.33 | St-0 |
| 14 | 2.76 | 9.87 | 2.20 | 36.00 | 9.90 | St-1 |
| 17 | 3.30 | 22.47 | 2.80 | 135.00 | 37.13 | St-1 |
| 21 | 2.91 | 33.55 | 3.20 | 278.00 | 76.45 | St-1 |
| 0 Benzene/100 Methanol | | | | | | |
| 9 | - | - | - | - | - | St-0 |
| 10 | 5.90 | 8.50 | 0.90 | 2.00 | 0.54 | St-0 |
| 11 | 5.80 | 9.50 | 1.30 | 2.00 | 0.54 | St-0 |
| 14 | 5.50 | 18.00 | 2.30 | 49.00 | 13.23 | St-1 |
| 17 | 5.60 | 29.00 | 2.80 | 131.00 | 35.37 | St-1 |
| 21 | 5.50 | 40.60 | 3.20 | 279.00 | 75.33 | St-1 |

-: Not Detectable.

Table 6. Fire and explosion characteristics of different ratios of benzene and methanol at 150 °C and 1,520 mmHg to 100/0, 75/25, 50/50, 25/75 and 0/100 vol%, respectively

| O ₂ (vol%) | LEL (vol%) | UEL (vol%) | P _{max} (bar) | (dP/dt) _{max} (barsec ⁻¹) | K _g (mbarsec ⁻¹) | Explosion class (St) |
|-----------------------------|------------|------------|------------------------|--|---|----------------------|
| 100 Benzene/0 Methanol vol% | | | | | | |
| 9 | - | - | - | - | - | St-0 |
| 10 | 1.70 | 2.00 | 0.21 | 2.00 | 0.54 | St-0 |
| 11 | 1.40 | 2.90 | 1.70 | 6.00 | 1.62 | St-0 |
| 14 | 1.40 | 4.40 | 5.20 | 704.00 | 190.08 | St-1 |
| 17 | 1.10 | 5.60 | 5.60 | 791.00 | 213.57 | St-2 |
| 21 | 1.00 | 7.60 | 8.60 | 988.00 | 266.76 | St-2 |
| 75 Benzene/25 Methanol | | | | | | |
| 10 | - | - | - | - | - | St-0 |
| 11 | 1.40 | 2.50 | 2.20 | 285.00 | 76.95 | St-1 |
| 14 | 1.30 | 5.10 | 8.00 | 1,316.00 | 355.32 | St-3 |
| 17 | 1.20 | 7.00 | 8.20 | 1,499.00 | 392.04 | St-3 |
| 21 | 1.40 | 9.00 | 8.90 | 1,523.00 | 411.21 | St-3 |
| 50 Benzene/50 Methanol | | | | | | |
| 9 | - | - | - | - | - | St-0 |
| 10 | 2.24 | 3.95 | 0.40 | 6.00 | 1.62 | St-1 |
| 11 | 2.50 | 5.07 | 2.00 | 9.00 | 2.43 | St-1 |
| 14 | 1.97 | 10.53 | 8.00 | 1.07 | 290.75 | St-2 |
| 17 | 1.50 | 15.90 | 8.00 | 1.50 | 404.73 | St-3 |
| 21 | 1.40 | 25.00 | 8.80 | 1.53 | 413.30 | St-3 |
| 25 Benzene/75 Methanol | | | | | | |
| 10 | - | - | - | - | - | St-0 |
| 11 | 3.82 | 8.22 | 0.20 | 2.00 | 0.54 | St-0 |
| 14 | 3.49 | 27.96 | 4.40 | 59.00 | 15.93 | St-1 |
| 21 | 3.03 | 36.91 | 8.60 | 1,134.00 | 306.18 | St-3 |
| 0 Benzene/100 Methanol | | | | | | |
| 9 | - | - | - | - | - | St-0 |
| 10 | 5.60 | 10.50 | 3.60 | 677.00 | 182.79 | St-1 |
| 11 | 5.60 | 12.50 | 8.00 | 1,209.00 | 326.43 | St-3 |
| 17 | 5.40 | 32.50 | 11.20 | 4,460.00 | 1,204.20 | St-3 |
| 21 | 5.30 | 48.50 | 17.90 | 5,802.00 | 1,566.54 | St-3 |

-: Not Detectable.

under 150 °C and 21 vol% oxygen concentration are as follows:

P_{max} from 3.2 bar $\xrightarrow{r_{be-to}}$ 8.9 bar

$(dP/dt)_{max}$ from 258 barsec⁻¹ $\xrightarrow{r_{be-to}}$ 1,523 barsec⁻¹

K_g from 69.66 mbarsec⁻¹ $\xrightarrow{r_{be-to}}$ 411.21 mbarsec⁻¹

Explosion class from St-1 $\xrightarrow{r_{be-to}}$ St-3

The results indicated that the UEL, P_{max} , K_g , $(dP/dt)_{max}$, and explosion class all increased with the pressure. According to the experimentally derived data above, the obvious variations are observed between initial pressures of 760 and 1,520 mmHg, as disclosed in Tables 5 and 6. In addition, Figs. 15 and 16 also reveal the differ-

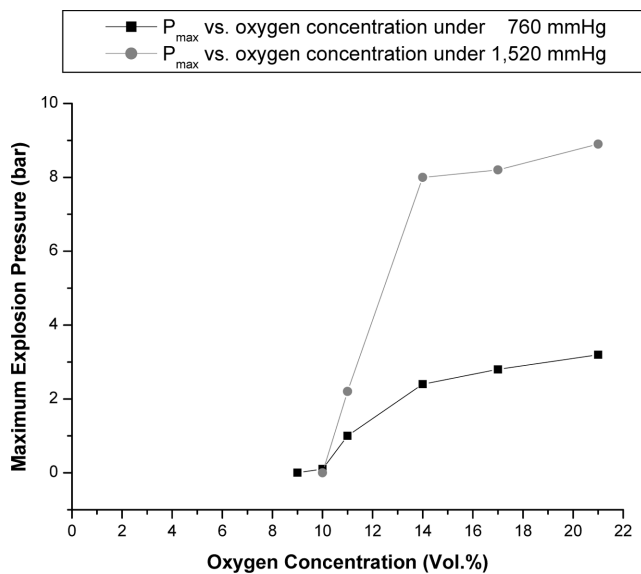


Fig. 15. The variation of P_{max} at 150 °C between 760 mmHg and 1,520 mmHg with various oxygen concentrations.

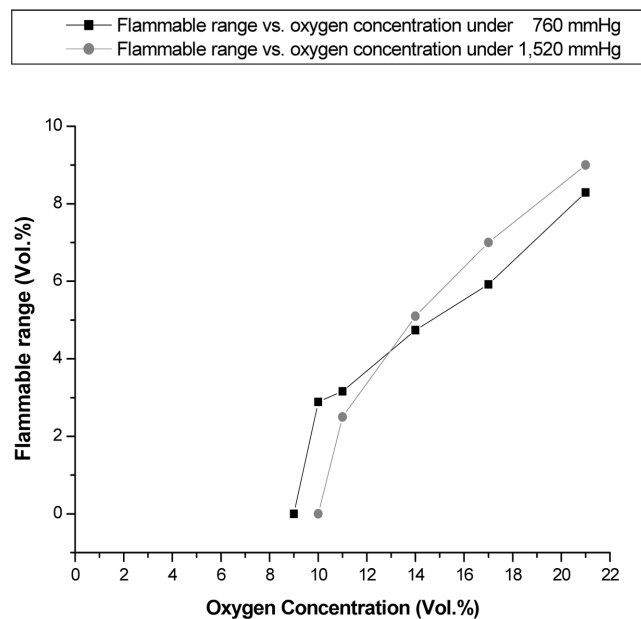


Fig. 16. The variation of flammable range at 150 °C between 760 mmHg and 1,520 mmHg with various oxygen concentrations.

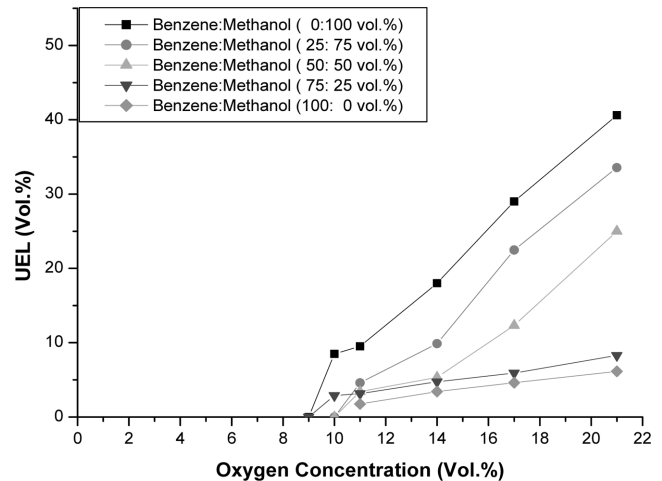


Fig. 17. UEL vs. oxygen concentration with benzene and methanol at 150 °C, 760 mmHg and five different mixing ratios.

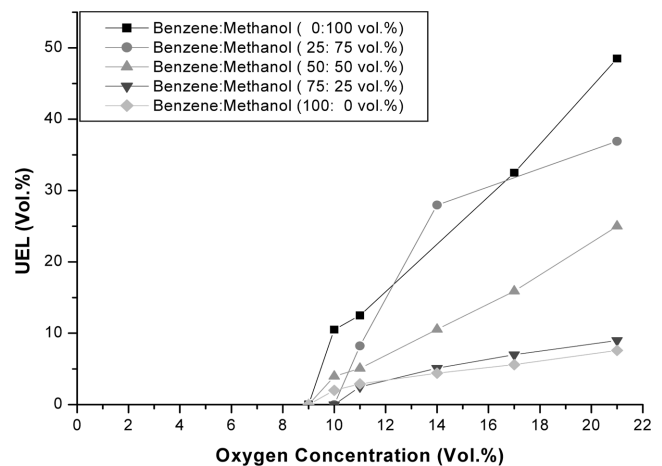


Fig. 18. UEL vs. oxygen concentration with benzene and methanol at 150 °C, 1,520 mmHg and five different mixing ratios.

ence in the initial pressures by comparing the P_{max} and flammable range (LEL-UEL) with different oxygen concentrations (10 to 21 vol%). This demonstrates again that the safety-related property parameters increased with the pressure in the case of benzene: methanol (75 vol% : 25 vol%). However, no significant variations were found.

4. Effects on Oxygen Concentrations

UEL increased with increasing oxygen concentration at the same initial pressure, and so did the UEL with the amount of methanol. Figs. 17 and 18 show the effect of oxygen concentration on UEL under two kinds of initial pressure. The flammability limits decreased as the oxygen concentration was reduced. When oxygen concentration is below the MOC, an explosion is no longer possible [Shu and Wen, 2002].

5. 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 [O'Shaughnessey and Power, 1995; Chad and Daniels, 1998]. The flammability diagram of a benzene/methanol/O₂/N₂ mixture represents the three compo-

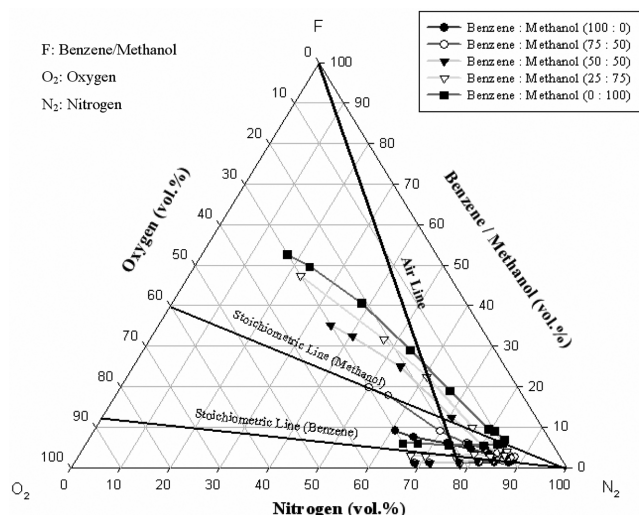


Fig. 19. Overall triangular flammability diagram illustrating the change in flammability zone with different ratios of benzene and methanol at 150 °C and 760 mmHg.

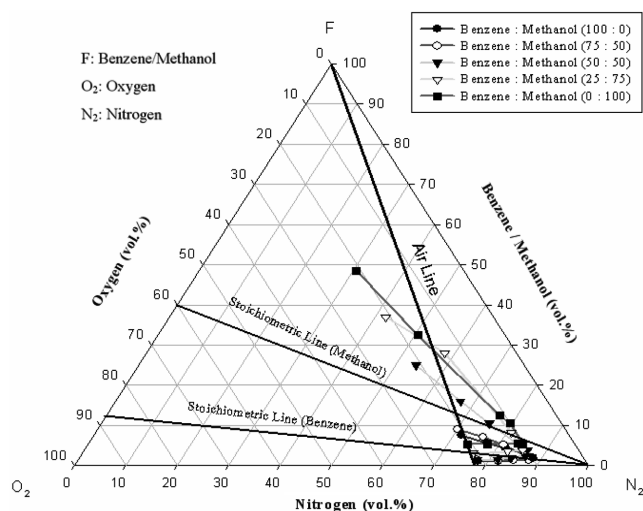


Fig. 20. Overall triangular flammability diagram illustrating the change in flammability zone with different ratios of benzene and methanol at 150 °C and 1,520 mmHg.

nents as X, O, N, under 150 °C, 760 mmHg/1,520 mmHg, as delineated in Figs. 19 and 20, respectively. It also clearly points out the MOC of every mixing concentration. The flammability diagram is mainly used to mention and provide specific information for related industries, and keep mixtures from falling into the dangerous flammable zones to prevent accidents [Shu and Wen, 2002].

CONCLUSIONS

UEL and LEL of benzene and methanol of 75/25, 50/50, 25/75 increase with increasing methanol. The flammability limits of benzene and methanol in 75/25, 50/50, 25/75 vol% are between 100 vol% benzene and 100 vol% methanol. With adding benzene or methanol, the properties close to either one of the majority. However, providing a safety margin is recommended. MOC is an im-

portant safety property in that explosions will never occur below the MOC. The results showed that MOC would not be changed with different mixing ratios of binary solutions. In the benzene and methanol mixing procedure, we can calculate the benzene and methanol vapor concentration ratios in different operating conditions. Consequently, the vapor condenses into liquid and causes a liquid-vapor co-existing phase, which may demonstrate a higher degree of hazard and unexpected conditions under higher pressure.

RECOMMENDATIONS

Temperature and pressure are important factors, so these two parameters should be varied for future study, along with an increase of oxygen concentration. Further recommendations include maintaining the initial temperature below or between the boiling point of benzene and methanol to study its explosion phenomenon, and improving the apparatus to confirm the composition before or after ignition by utilizing GC/MS. From testing results, the hazards of operating conditions could be readily identified and the safety procedure determined in such a case.

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NOMENCLATURE

| | |
|-----------------|---|
| K_g | : gas or vapor explosion constant [mbarsec ⁻¹] |
| LEL | : lower explosion limit [vol%] |
| MOC | : minimum oxygen concentration [vol%] |
| P_{max} | : maximum explosion pressure [bar] |
| P | : initial pressure [mmHg; atm] |
| St | : explosion class, dimensionless |
| T | : initial temperature [°C] |
| UEL | : upper explosion limit [vol%] |
| V | : the volume of test apparatus [m ³ ; L] |
| $(dP/dt)_{max}$ | : maximum rate of explosion pressure rise [barsec ⁻¹] |

Subscript

max : maximum value of experimental property

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