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Inert effects on the flammability characteristics of methanol by nitrogen or carbon dioxide

C.-C. Chiang · J.-C. Lee · Y.-M. Chang · C.-F. Chuang · C.-M. Shu

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Abstract Knowledge of material safety properties is critical for safe handing in the chemical process industries, especially for flammable chemicals that might result in serious fires and explosions. This study investigated the flammability characteristics of methanol under working conditions during the process. The targeted fire and explosion properties, like explosion limits (UEL and LEL), vapor deflagration index (K_g), maximum explosion pressure (P_{max}), and maximum explosion pressure rise [$(dP\ dt^{-1})_{max}$], were deliberately obtained via a 20-L-Apparatus in 101 kPa (i.e., 760 mmHg/1 atm), 150 and 200 °C, along with various experimental arrangements containing nitrogen (N_2) or carbon dioxide (CO_2) as inert component. Particularly, this study discussed and elucidated the inert influence on the above safety-related parameters by two different inerting gases of N_2 and CO_2. The results indicated that adding an inert component to fuel–inert gas mixtures determined the decrease of explosion range and flammability hazard degree. The results also demonstrated that CO_2 possessed higher inerting capability than N_2 in this study.

Keywords Flammability characteristics · Flammable chemicals · Inert component · 20-L-Apparatus · Methanol

List of symbols

$(dP\ dt^{-1})_{max}$	Maximum rate of explosion pressure rise, bar s^{-1}
K_g	Gas or vapor explosion constant, m bar s^{-1}
LEL	Lower explosion limit, vol.%
MOC	Minimum oxygen concentration, vol.%
P	Initial pressure, kPa
P_{max}	Maximum explosion pressure, bar
T_b	Boiling point, °C
T_f	Flash point, °C
UEL	Upper explosion limit, vol.%
V	The volume of test apparatus, m^3; L

Introduction

Generally speaking, chemicals prevailingly present inherent and substantial hazards in form of fires and explosions. The potential hazards of fires and explosions occurring in a process are quite huge. Obviously, it is imperative to know the basic fire and explosion characteristics of chemical materials which are used in working conditions during operations. From the open literature, methanol is one of the

C.-C. Chiang
Doctoral Program, Department of Industrial Education and Technology, National Changhua University of Education (NCUE), Bao-Shan Campus, 1, Jin-De Rd., Changhua, Changhua, Taiwan 50074, ROC

C.-C. Chiang
Department of Electrical Engineering, Hsiuping Institute of Technology, 11, Gong-Ye Rd., Dali, Taichung, Taiwan 41280, ROC

J.-C. Lee · Y.-M. Chang · C.-M. Shu (✉)
Doctoral Program, Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology, 123, University Rd., Sec. 3, Douliou, Yunlin, Taiwan 64002, ROC
e-mail: shucm@yuntech.edu.tw

C.-F. Chuang
Department of Industrial Education and Technology, National Changhua University of Education (NCUE), Bao-Shan Campus, 1, Jin-De Rd., Changhua, Changhua, Taiwan 50074, ROC

substantial demand chemicals in the world [1]. It is a main substance for producing polyoxymethylene, resin, and also is an important chemical for various acetic acid sources [2]. However, according to the historical records, there are many accidents related to methanol, as illustrated in Table 1 [3]. With the use of methanol in petrochemical industries, natural gas will continue to be an important source of energy and chemical feedstock, which largely applies to the methyl tert-butyl ether (MTBE) process in industry.

To date, many studies which emphasize fire and explosion hazard evaluation and thermal hazard analysis have been presented [4–18], and their topic on flammability hazard problems can often be traced to an unsatisfactory knowledge of the dangerous properties of the substances being used. Under this fire/explosion prevention concern, as for blending, each inert gas has a specific ability to reduce the explosive range for a material [19, 20]. Therefore, in this study, we selected nitrogen (N_2) and carbon dioxide (CO_2) as testing inert gases, investigating the inert gases' effect on various flammability characteristics of methanol experimentally, under the working conditions of 101 kPa, 150 and 200 °C.

The purpose of this study was to establish the flammability properties of methanol including (1) upper explosion limit (UEL), (2) lower explosion limit (LEL), (3) maximum explosion overpressure (P_{max}), (4) maximum explosion pressure rise [$(dP\ dt^{-1})_{max}$] and (5) minimum oxygen concentration (MOC). Furthermore, we attempted to compare the influence and affected consequence for the above safety-related parameters of methanol with different inert gases employed in this study. We hope that this work could provide the knowledge for the process safety control system, and help to prevent serious fire and explosion accidents resulting from methanol among related operations, storage or transportation.

Table 1 Methanol-related accidents in the world since 2001 [3]

Date	Location	Fatalities	Injures
08/08/2005	Michigan, USA	0	32
28/02/2005	Lancashire, UK	0	3
17/02/2005	Louisiana, USA	0	0
04/02/2005	New South Wales, USA	0	0
15/11/2004	Brazil	4	0
26/10/2004	Michigan, USA	0	0
08/10/2004	Texas, USA	0	0
06/01/2004	Arkansas, USA	0	2
22/03/2003	Italy	0	9
21/02/2003	Texas, USA	0	1
30/11/2001	Mexico	0	17

Experimental

Samples

Methanol, or so-called wood alcohol, has the chemical formula of CH_3OH. Figure 1 [21] displays its chemical structure. The basic physical and chemical properties of methanol are also given in Table 2 [22, 23]. In this study, 99.99 mass%, approximate 100 mass% (pure) methanol was supplied directly from Burdick & Jackson that used an N_2, CO_2, and oxygen concentration of at least 99.99 mass%, respectively.

Experimental procedures and conditions

Flammability investigations were carried out by the following four procedures in turn. First, the testing chamber was purged with N_2 or CO_2, and then the pressure inside was reduced to less than 13 kPa to ensure the removal of all combustion residual samples from previous runs. Second, the sample of methanol was injected into the explosion vessel with the initial temperature of 150 or 200 °C to assure the complete vaporization status of methanol. Third, the inert gas of N_2 or CO_2, and the O_2 was loaded into the testing vessel. The concentrations of all components were deliberately determined from calculating their partial pressures. Fourth, the mixing vapors were ignited and the results were obtained and stored directly by our personal computer system. All of the experimental series were run at normal atmospheric pressure of 101 kPa, and 150/200 °C, respectively.

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

By the opening references of Chang et al. [10] and Shu et al. [18] previously, a spherical explosion vessel, or the so-called 20-L-Apparatus, was treated as an ideal device to detect various flammability properties of flammable material (Fig. 2). Figure 3 shows the 20-L-Apparatus and its control system, built and operated accompanied with NFPA 68 (National Fire Protection Association 68) and ASTM 1226 (American Society for Testing and Materials, USA) and VDI 2263 (Verein Deutscher Ingenieure, Germany) [24, 25]. The explosion test vessel is a stainless steel of 20 L. The stainless steel reaction vessel is equipped with

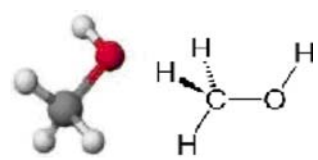

Fig. 1 Methanol chemical structure [21]

Table 2 Basic physical properties of methanol [22, 23]

Properties	Methanol
Formula	CH_3OH
Flash point (T_f, Open Cup)	12 °C
Boiling point (T_b, 101 kPa)	65 °C
Normal explosion limits	6.0–36.5 vol.%
Specific gravity (25 °C)	0.7866
Autoignition temperature	464 °C

T_f flash point, T_b boiling point

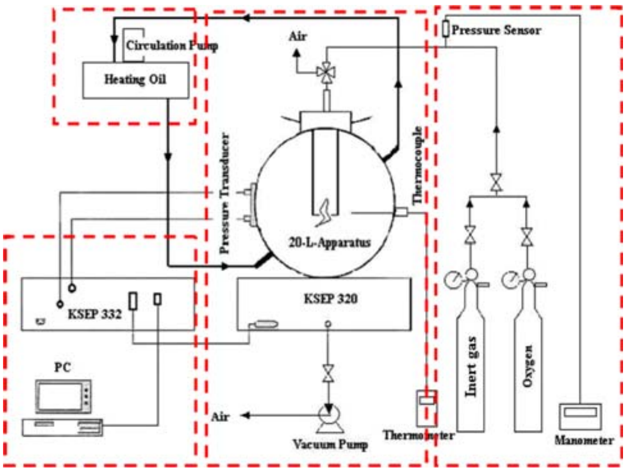

Fig. 2 Schematic diagram of the experimental set-up and its control system [10]

Fig. 3 The 20 L spherical explosion vessel (20-L-Apparatus) for this study

pressure transducers to measure the pressure during an explosion. Also, thermocouples measure the temperature at the core. The ignition source is located in the center of the sphere. On the measuring flange two "Kistler" piezoelectric pressure sensors are installed.

In this study, the main modification of the apparatus by us was the liquid injection port which was connected to the reaction vessel [10, 18]. By the lead wires to the ignition system and ignition source, an induction spark between two electrodes was used. The electrode range is 0.6 mm, and ignition energy released is approximately 10 J [17], which is sufficiently high to ignite a combustible mixture and customary to determine the explosion parameter. KSEP 6.0 is control and analysis software for the vessel [26]. The calculated flammability parameter method is also useful for KSEP 6.0 of the vapor mixture that the test is generally accomplished in a quiescent state (ignition delay time, tv = 0 s) [26–28].

The experimental data were stored in a text format that could be opened by using a variety of spreadsheets or other programs. Those data files include the UEL, LEL, P_{max}, and $[(dP\ dt^{-1})_{max}]$ and the concentration (vol.%) of testing sample, operation date, etc., during an explosion series.

Effects of inert/oxygen concentrations and gas or vapor deflagration index (K_g)

Accordingly, experimental results were based upon an initial normal pressure of 101 kPa under 150, 200 °C and various oxygen concentrations (21, 17, 13, 11, 9 vol.% and so on) to MOC for methanol. Herein, the data pointed 20 vol.% methanol, meaning the rest of 80 vol.% of a air comprised N_2 for 79 vol.% and O_2 for 21 vol.%. The addition of inert substance component to the methanol/inert gas mixtures determined the decrease of UEL.

Effects on vapor deflagration index (K_g) by different initial temperatures

The inerting capacity of an inert gas is expressed by the dimensionless K_g value, the so-called "vapor deflagration index". The experimental determination of K_g values is demonstrated by means of the cubic law [29].

$$V^{1/3}\left(dP\ dt^{-1}\right)_{max} = K_g \qquad (1)$$

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.

Results and discussion

Effects of inert gases on methanol

Experimental results were detected and compared from the initial normal pressure of 101 kPa and under the two initial temperatures of 150/200 °C, and various oxygen concentrations (21, 17, 13, 11, 9 vol.% and so on) to MOC for methanol. In Fig. 4, the P_{max} and UEL were 5.3 bar and 39 vol.% measured of N_2 as tested gas; with changing inert gas, P_{max} and UEL were decreased to 0.8 bar and 21 vol.%

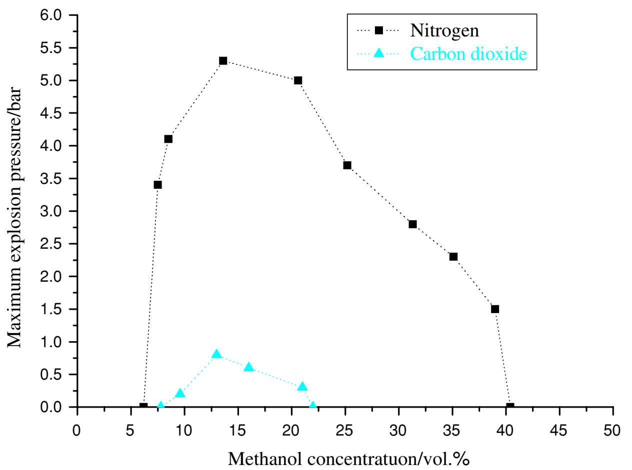

Fig. 4 P_{max} versus methanol with two inert gases at 150 °C, 101 kPa and 21 vol.% oxygen

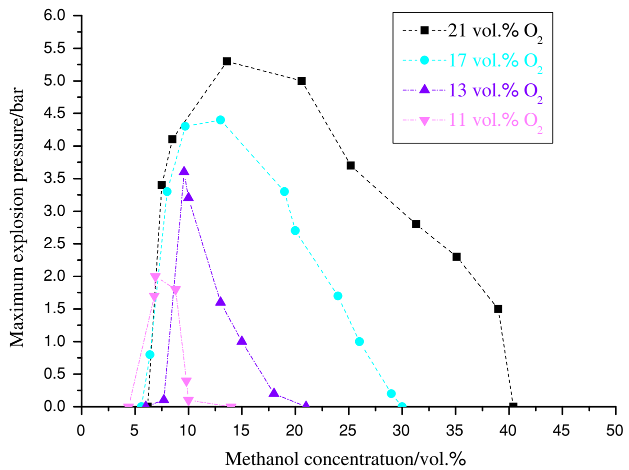

Fig. 6 P_{max} versus methanol with N_2 at 150 °C and various oxygen concentrations

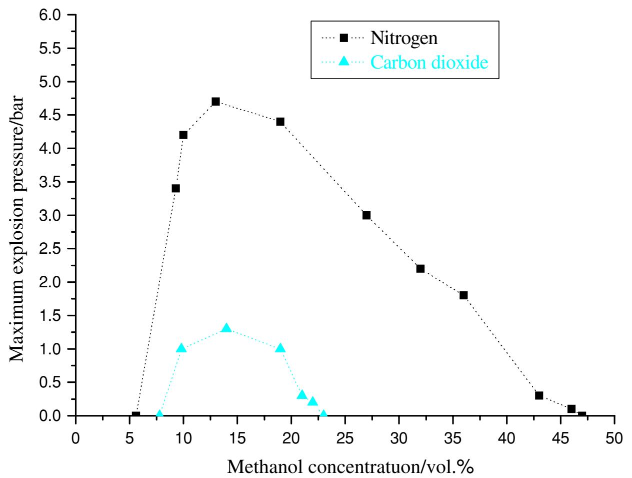

Fig. 5 P_{max} versus methanol with two inert gases at 200 °C, 101 kPa and 21 vol.% oxygen

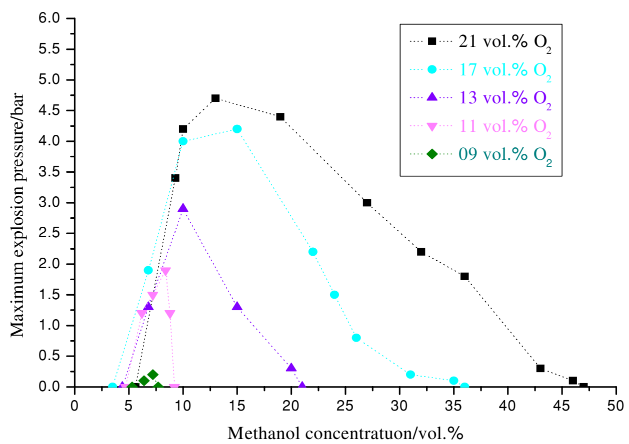

Fig. 7 P_{max} versus methanol with N_2 at 200 °C and various oxygen concentrations

measured of CO_2 as tested gas. In Fig. 5, at elevated temperature of 200 °C, with two inert gases (N_2/CO_2), P_{max} and UEL were 4.7 and 46 vol.% as decreased to 1.3 and 22 vol.%. We compared of the N_2/O_2 and CO_2/O_2 mixtures at temperature to 150 or 200 °C with 101 kPa and 21 vol.% oxygen concentration, the rank of the inerting ability was $CO_2 > N_2$.

As far as the inerting ability is concerned, CO_2 is greater than N_2. In other previous references, Molnarne et al. [20] used methane, and N_2, CO_2 and other materials of testing inert gases for testing according to the DIN 51649-1 standard at 20 °C and 101 kPa, together with different testing systems and conditions. The experimentally-derived results were close to the foregoing reference, which indicates that the CO_2 inert efficiency exceeds the one of N_2, as well as the same outcome in this present work. Figures 6 and 7 display the relationships of P_{max} and methanol/N_2, under 150, 200 °C, and various oxygen concentrations. When initial temperature rose to 200 °C, the MOC of the N_2 was reduced to 9 vol.%, but the CO_2 was 21 vol.%. Accordingly, we learned that CO_2 was a better choice as inert gas than N_2 in this study.

From these tests, we recognized that the results affected the consequences of elevated initial temperatures on "explosion limit" specifically, and realized their implied meaning. This provided the crucial safety-related parameters to protect the relevant process plants.

Conclusions

In practice, the 20-L-Apparatus simulation is a unique way to understand the explosion parameter of chemicals. In this study, the flammability investigations for methanol under the experiment initial conditions at the pressure of 101 kPa and the temperatures of 150 and 200 °C were derived, respectively. By augmenting the inert gas, the explosion range became thinner, and the flammability parameters (P_{max}) and degree of hazard were reduced accordingly. The explosion limits of methanol with CO_2 were not notably between 150 and 200 °C by comparing with N_2. We deduced that CO_2 is insensitive to temperature variation and increasing the inert gas concentration was tantamount to diminishing the oxygen concentration for the prevention of fire and explosion.

In general, these data were necessary for safe conditions of application, storage, and transportation of a chemical product. Future studies will focus on reaction mechanism analysis in a batch reactor. When initial temperature rose to 200 °C, the MOC of the N_2 was reduced to 9 vol.%, but the CO_2 was 21 vol.%. Accordingly, we learned that CO_2 was the better choice as an inert gas. In summary, we could draw the inhibited ranking as follows: $CO_2 > N_2$. This would be very useful and quite significant for industrial process safety to keep chemical plants from fire/explosion calamities, by avoiding the concentration of the loading fuels into this dangerous explosion zone.

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