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FLAMMABILITY PROPERTIES ANALYSIS OF METHYLPHENOL-CARBONATE IN DIPHENYLCARBONATE PRODUCTION PROCESS

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Diphenylcarbonate (DPC) has been regarded as a potential substitute material for highly toxic phosgene, reacting with bisphenol A (BPA) in a phosgene-free process to produce polycarbonate (PC). For synthesizing DPC, methylphenylcarbonate (MPC) was the critical intermediate with potential flammability in a transesterification reaction from dimethylcarbonate (DMC) and phenol. Under the National Fire Protection Association (NFPA) criterion, MPC is viewed as one sort of combustible liquid (Class IIIB). Once it fires or burns during storage, operation or transportation, it can cause a serious fire and explosion. However, researches are still scanty in mentioning the basic but crucial fire and explosion features of MPC to date. A sound background of material safety properties is essential for safe handling; in particular, flammability information is extremely crucial for a specific chemical during a unit operation to prevent any fire and explosion hazards. In this study, we investigated the explosion limits (LEL, UEL), maximum explosion pressure (P_{max}), maximum rate of explosion pressure rise ($(dP/dt)_{max}$), and gas or vapor explosion constant (K_g) of MPC, according to its practical operating conditions (1 atm, 250°C, 21 vol.% O_2) and by means of a 20 L vessel (20-L-Apparatus).

By surveying and defining the experimental data through flammability tests, these basic but crucial safety-related parameters on flammability characteristics of MPC were proposed, so as to advance understanding and to avoid fire and explosion accidents for such relevant processes.

Keywords: *20-L-Apparatus, diphenylcarbonate (DPC), explosion hazards, fire hazards, flammability characteristics, methylphenylcarbonate (MPC)*

Introduction

Chemicals are frequently and widely employed not only in modern petrochemical plants but in our daily lives as well [1]. However, engineering of general chemicals has not only brought convenience and comfort to the world for years, but chemical accidents as well.

The history of chemical use is replete with huge incidents and disasters via two types of inherent chemical hazards, i.e., energy (fire/explosion) and toxicity (poison/corrosion) damages for the safety and health, respectively [2, 3]. Table 1 shows the selected typical major chemical accidents that have occurred around the world in the past three decades [4]. Generally speaking, the three most common chemical plant accidents are fires, explosions and toxic releases, in that order [1, 2]. Among them, in contrast with toxic releases, the energy damage of fires and explosions as process accidents in Taiwan and other countries is rather frequent, comprising 75.6% of all industrial incidents [5]. Organic solvents are the most common source of fires and explosions in the chemical industries [3], especially under various abnormal scenarios that may create seriously contingent situations [1]. Fortunately, to date, many excellent researches focused on chemicals have been conducted and proposed by scientists all around the world [6–14]. At the present time, the most critical objective for industrial disaster prevention is to establish effective procedures for flammability hazard protection and control.

In the petrochemical industry nowadays, polycarbonate (PC) has been used widely and quite substantially, because of its desirable characteristics on thermal resistance, transparency, flexibility, and high intensity, etc. [15]. The global demand for PC has been growing more than 10% per year and about one million tons from 1999 [15, 16]. In general, PC can be prepared directly by the reaction of phosgene and bisphenol A (BPA) [17]. The presence of phosgene in operations is a very serious problem with health threat, and highly toxic risks are taken in this phosgene-needed process [18]. In consideration of environment, health, and safety (ESH), we wanted to replace the highly toxic phosgene route for generating this crucial chemical material. Therefore, another different economically feasible route was addressed

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Table 1 Selected typical major chemical process accidents around the world from past three decades [4]

Accidents type	Disaster	Consequence Deaths/injuries/damages in USD
Fire and explosion damage–UVCE (Unconfined vapor cloud explosion, UVCE)	Flixborough/Nypro Ltd., UK (June, 1974)	Deaths: 28 Injuries: 89 Damage: 161000000
Fire and explosion damage–LPG BLEVE (Boiling liquid expanding vapor explosion, BLEVE)	Mexico City/Mexico (November, 1984)	Deaths: 500 above Injuries: 2500 Damage: 20000000
Toxic release–MiC leakage (Methyl isocyanate, MIC)	Bhopal/UCC Ltd., India (December, 1984)	Deaths: 2500 immediately 4000 continually Injuries: 1700 Damage: 470000000 total

for the ESH promotions. With this concern, PC also can be prepared according to the transesterification route; in such another more environmentally benign phosgene-free PC production process, diphenylcarbonate (DPC) is an adequate and important intermediate [19]. It has been regarded as a potential substitute material for highly toxic phosgene, reacting with BPA to generate PC from the 1970's [18–20]; consequently, a possible health issue could be solved.

Each approach has advantages and disadvantages. Although PC manufacture evolved without the existence of phosgene, and then prior to preventing a toxic tragedy [21], for synthesizing DPC this route, methylphenylcarbonate (MPC, or also called PMC, phenylmethylcarbonate industrially) is an intermediate with potential flammability, as shown in Fig. 1 [21]. It might cause a serious fire or explosion when the process of transesterification reaction from dimethylcarbonate (DMC) and phenol mixing in the liquid phase using catalysts [10]. Even to date, there is still a lack of awareness of the basic flammability characteristics of MPC in the opening references [15–20].

Ensuring the fire and explosion safety of combustible or flammable substances used in processes is unlikely without a detailed understanding for their flammability characteristics and pertinent hazards [1]. The evaluation and analysis of fire and explosion properties is essential for safe storage, transportation, and operation. In this regard, we investigated the basic but crucial safety-related properties, such as explosion limits (from lower explosion limit (LEL) to upper explosion limit (UEL)), maximum explosion pressure (P_{max}), maximum rate of explosion pressure rise ($(dP/dt)_{max}$), and gas or vapor explosion constant (K_g) for MPC in this study. Experiments were carried out according to practical operating conditions (1 atm, 250°C) [20], by a 20 L spherical explosion vessel (20-L-Apparatus) for measuring those desired fire and explosion properties. Our ultimate goal is that the efforts on surveying and defining experimentally derived safety-related parameters through our flammability determinations will help. The results could then promote 'planning-ahead for' or 'anticipating' fire and explosion casualties for such relevant processes, and thereby avoid them.

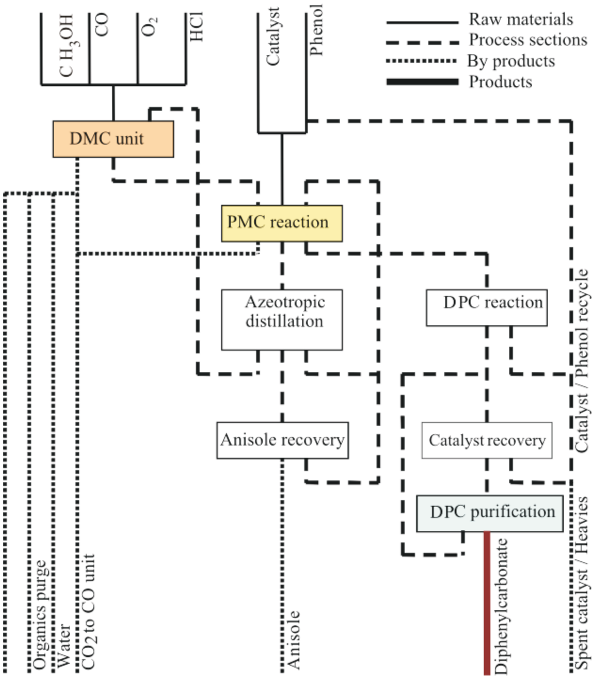


Fig. 1 The flowchart of DPC production process [21]

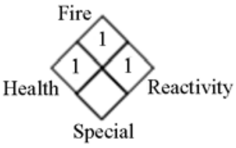
Experimental

Materials

Reagent (MPC)

MPC, i.e., methylphenylcarbonate, presents a liquid state with colorless appearance at room temperature. Figure 2 [22] depicts its chemical structure, which has the chemical formula of $C_8H_8O_3$, and shows the experimental sample image of our flammability mea-

Table 2 Basic properties and related hazardous material information of MPC [22]

Product name	Methyl phenyl carbonate (MPC)
Formula	$C_8H_8O_3$
CAS no.	13509-27-8 (100%)
Molecular mass	152.15 g mol^{-1}
Hazard information	Irritating to eyes, respiratory system and skin
HMIS rating (HMIS rating scales from 0 to 4 represent a specific material has its identified minimal, slight, moderate, serious or severe degrees on health, flammability, reactivity or other special hazards else, respectively)	 Health=1, flammability=1, reactivity=1
Flammability	1 Class IIIB (NFPA 30) [14]

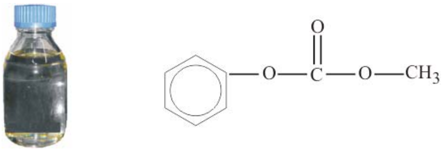
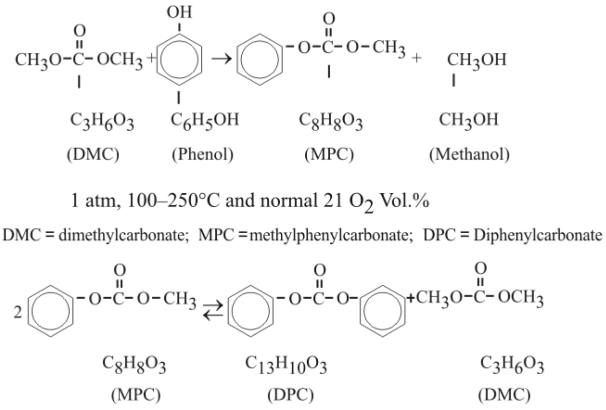


Fig. 2 The sample appearance of 100 vol.% MPC for this study and its chemical structure [22]

surements. In this study, the supply of 100 vol.% MPC sample was provided by CHIMEI-ASAHI Co., Ltd. in Taiwan.

The primary hazard information on safety and health of MPC is summarized in Table 2 [22] according to the hazardous materials information system (HMIS) and material safety data sheet (MSDS). Table 2 indicates that MPC irritates eyes, respiratory system, and skin [22]. The HMIS flammability rating scale 1 means this material must be preheated before ignition. Flammability liquids in this category have flash points (the lowest temperature at which ignition will occur), which is exactly what is considered as a combustible liquid (Class IIIB) by National Fire Protection Association (NFPA) criterion 30 [23] with achievable fire and explosion hazards. However, until now, no explosion limits, for example, have been recommended for practical storage, transportation, and operation in processes. Therefore, our research is an initial contribution for MPC.

Process description



1 atm, 100–250°C and normal 21 O_2 Vol.%

DMC = dimethylcarbonate; MPC = methylphenylcarbonate; DPC = Diphenylcarbonate

Fig. 3 Transesterification reaction routes of DPC production in industry [15–20]

Industrially, MPC is an intermediate obtained from transesterification of DMC and phenol for synthesizing DPC, which is a potential substitute material for highly toxic phosgene in the production of PC. Figure 1 discloses a feasible commercial process for DPC [21]. In general, the process conditions are the following: high reaction temperature (100–250°C), low or normal pressure (1 atm) [20]. Its continuous reaction routes are given in Fig. 3 [15–20].

Based on real industrial operating conditions, we deliberately set the initial pressure and temperature at 1 atm and 250°C, which refers to the highest operating temperatures between 100–250°C, and normal pressure at 1 atm in process [20].

Methods

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

Investigations were carried out on the experimental set-up presented in Fig. 4 [24]. A 20 L spherical explosion vessel (20-L-Apparatus) was purchased

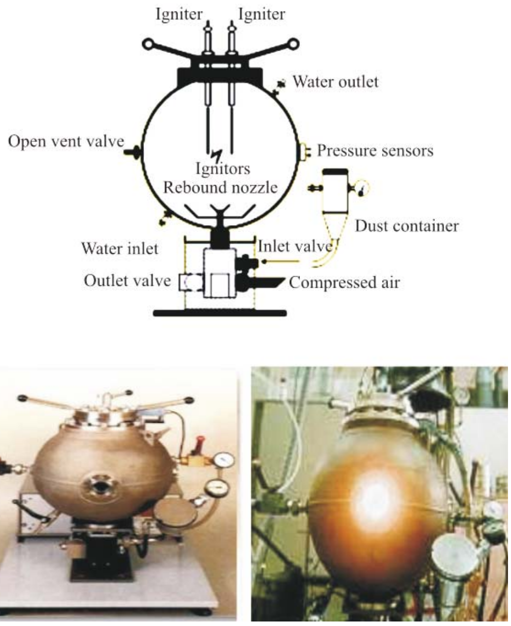


Fig. 4 The experimental 20-L-Apparatus for this study [24]

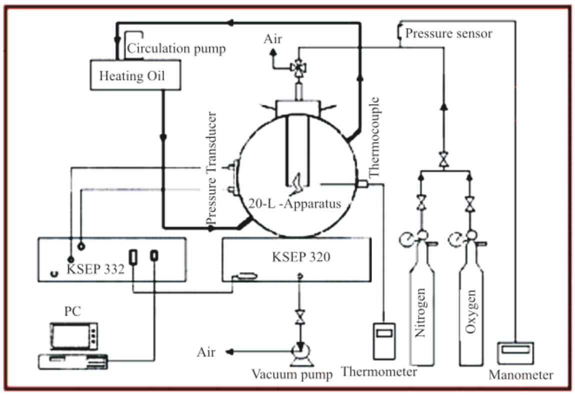


Fig. 5 Schematic diagram of the 20-L-Apparatus and its control system sections [24]

from Adolf Kühner. AG was available for this study. The flammability of MPC was examined in this device and its control system. In general, the main structure of the 20-L-Apparatus can be roughly separated into four parts: spherical explosion vessel, heating, and circulation device, pressure setting system, and transmission computer interface, as illustrated in Fig. 5 [24]. The test chamber is a stainless steel hollow sphere 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 [25]. The KSEP 332 unit uses two ‘Kistler’ piezoelectric pressure sensors on the flange to measure the pressure as function of time [25, 26]. 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 [27].

In the past, many types of measurement apparatus for fire and explosion characteristics have been proposed. Among these devices, the 20-L-Apparatus has the highest reliability, because of its standard spherical shape [28]. 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) [29]. Essentially, it is suitable for measuring explosion behaviors of combustible materials, such as solvent vapors, flammable gases, or combustible dusts [30, 31], and deriving the flammability properties of LEL, UEL, $P_{\max}$, $(\mathrm{d}P/\mathrm{d}t)_{\max}$, K_g, and minimum oxygen concentration (MOC) in a series of test procedures [25]. Taking account of normal operation [24], we could utilize it to set various simulating conditions for preventive measures *vs.* fire and explosion hazards by investigating the flammability safety-related properties with this equipment.

LEL and UEL for gas and solvent vapors

Explosion limits include the LEL and UEL. The explosion range is from LEL to UEL of a specific substance. Vapor-air mixtures will ignite and burn only over a well-specified range of compositions [3]. The LEL/UEL of gas or vapor is the lowest/highest concentration at which gas or vapor explosion is not detected in three consecutive tests [26]. Generally, for a material, the lower the LEL or wider explosion range, the greater its flammability hazard degree would be [32].

Maximum explosion pressure ($P_{\max}$), maximum rate of explosion pressure rise $(\mathrm{d}P/\mathrm{d}t)_{\max}$, and gas or vapor deflagration index (K_g)

The explosion indices, $P_{\max}$ and $(\mathrm{d}P/\mathrm{d}t)_{\max}$, are defined as the mean values of the maximum values of all three series. Subsequently, the vapor deflagration index (K_g) is calculated from $(\mathrm{d}P/\mathrm{d}t)_{\max}$ by the cubic law [28]:

$$V^{1/3}(\mathrm{d}P/\mathrm{d}t)_{\max} = K_g \tag{1}$$

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.

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

Table 3 K_g and explosion classes (St) [28, 29, 31]

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

given in Table 3, and to use these as a basis for sizing explosive relief [28, 29, 31].

Results and discussion

Through our flammability characteristics investigations for MPC in normal air conditions of O_2 21 vol.%, 1 atm, and 250°C, these experimentally derived data have been proposed and also presented in Table 4, indicating its properties in such required scenarios. Each explosion limit was 1.33 (LEL) and 8.02 vol.% (UEL), so that the explosion range was 6.69 vol.%. The explosion range of MPC was inside the two well-specified boundaries from LEL to UEL (1.33–8.02 vol.%). As we know, vapor–air mixtures will explode upon encountering an effective ignition source. Hence, getting MPC's explosion range outcome would be very useful and quite significant for industrial process safety to keep chemical plant from accidents. Based on the 'inherent safety design' concern, we should carefully avoid setting the concentration of the loading fuels into this dangerous fire/explosion region.

Correspondingly, MPC had a P_{max} and $(dP/dt)_{max}$ for 4.8 bar and 426 bar s^{-1}, respectively. As for the flammability hazard degree, its potential ability of gas or vapor deflagration was 115.63 m bar s^{-1} as the K_g value, which quite amounted to the St-1 explosion class (K_g value from 1–200) by the cubic law. Due to the operating limit of the 20-L-Apparatus at experimental conditions, we will attempt to enhance or reduce the initial pressure/temperature to establish completed experimental scenarios for creating a comprehensive model for MPC in the future.

Figure 6 shows the relationship between MPC and its fitted P_{max}, all at 21 O_2 vol.%, 250°C, and 1 atm scenarios, which clearly indicate that the LEL was even less than 2 vol.%. As we know, the lesser the LEL or broader the explosion range, the greater the flammability hazard degree for a material [32].

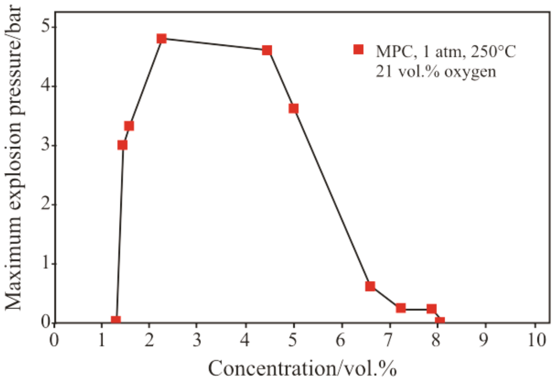


Fig. 6 P_{max} *vs.* 100 vol.% MPC at 21 vol.% O_2, 250°C and 1 atm

Table 4 Flammability characteristics of MPC at 250°C, 21 O_2 vol.%, and 1 atm

MPC/ vol.%	LEL/ vol.%	UEL/ vol.%	Explosion range/vol.%	P_{max}/ bar	$(dP/dt)_{max}$/ bar s^{-1}	K_g/ m bar s^{-1}	Explosion class (St)
100/pure	1.33	8.02	6.69	4.80	426.00	115.63	St-1

Table 5 Comparisons of the flammability danger, H_f value with other selected flammable chemicals [33–38]

Material concentration/ CAS no.	Molecular mass/ g mol^{-1}	Formula	H_f	LEL/ vol.%	UEL/ vol.%	Explosion range/vol.%
Methanol 100%/ 00067-56-1	32.04	CH_3OH	5.08	6.00	36.50	30.50
Acetone 100%/ 00067-64-1	58.08	C_3H_6O	4.12	2.50	12.80	10.30
Benzene 100%/ 71-43-2	78.11	C_6H_6	4.46	1.30	7.10	5.80
Toluene 100%/ 108-88-3	92.14	C_7H_8	4.92	1.20	7.10	5.90
3-Picolin 100%/ 00108-99-6	93.10	C_6H_7N	5.69	1.30	8.70	7.40
o-Xylene 99%/ 95-47-6	106.18	$C_6H_4(CH_3)_2$	3.47	1.70	7.60	5.90
MPC 100%/ 13509-27-8	152.15	$C_8H_8O_3$	5.03	1.33	8.02	6.70

In accordance with this principle, the flammability danger degree by its UEL and LEL was:

$$H_f = (\mathrm{UEL} - \mathrm{LEL})/\mathrm{LEL} \quad (2)$$

where H_f represents the danger of flammability for a material [32]. We found that the H_f value of MPC was 5.03, exactly derived from (8.02–1.33)/1.33. Furthermore, we compared it with other flammable chemicals generally used in the petrochemical industry or as household solvents. The comparisons of the flammability danger H_f value with other selected materials are displayed in Table 5 [33–38], in that order by their molecular masses (i.e., from methanol to MPC). Actually, the MPC H_f had the third rating among for these seven well-known flammable chemicals.

Conclusions

Under the experimental initial conditions for simulating operation situations (1 atm, 250°C and normal 21 O_2 vol.%), we have drawn the following conclusions:

- For pure MPC's each explosion limit was 1.33 (LEL) and 8.02 vol.% (UEL). Its explosion range was 6.69 vol.%. About the flammability danger degree by its UEL and LEL, the H_f value of MPC is 5.03. We recommend that attention be paid to its fire and explosion hazards for every necessary storage, transportation, and operation in processes.
- Correspondingly, the $P_{\max}$ and $(\mathrm{d}P/\mathrm{d}t)_{\max}$ of pure MPC was 4.8 bar and 426 bar s^{-1}, respectively. Its K_g value was 115.63 m bar s^{-1}, in other words, tantamount to the St-1 explosion class.
- By these experimental flammability tests, several basic but critical flammability characteristics of MPC were investigated and proposed, in order to inaugurate an initial contribution for MPC, prior to comprehending, recommending, and avoiding any fire and explosion accidents for such relevant processes.

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