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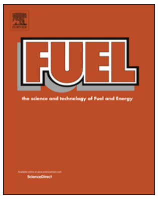

Full Length Article

Thermal stability and safety of dimethoxymethane oxidation at low temperature

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A R T I C L E I N F O

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A B S T R A C T

In this work, thermal oxidation reaction of dimethoxymethane (DMM) at low temperature was investigated with a custom-designed mini closed pressure vessel test (MCPVT) employed. The initial auto-oxidation, thermal decomposition and deep radical oxidation processes were revealed by analyzing the behavior of oxidation temperature (T) and pressure (P) in the process of MCPVT monitoring. Peroxides generated from DMM auto-oxidation were measured by iodimetry and thin-layer chromatography (TLC). The dominant peroxide was separated from oxidation products via column chromatography, with structure characterized by mass spectrometry (MS), ^{1}H and ^{13}C nuclear magnetic resonance (NMR). The thermal decomposition characteristics were determined by differential scanning calorimeter (DSC). Results show that the oxidation was mainly initiated by hydrogen abstraction on the methylenedioxy (O-CH_2-O) of DMM when temperature was above about 310 K. The primary product of hydroperoxide, hydroperoxy(methoxymethoxy)methane was found in DMM oxidation for the first time, with a high level. Its exothermic onset temperature (T_0) and decomposition heat (Q_{DSC}) are 372.87 K and 2431.37 J·g^{-1}, respectively. The thermal decomposition could lead to thermal runaway of oxidation, and further transform into an explosion. In most cases, the release of radical pool after peroxides decomposition would induce a rapidly radical oxidation of DMM through an endothermic reaction at about 410 K.

1. Introduction

Poly (oxymethylene) dimethyl ethers (OME$_n$: CH_3-O-(CH_2-O)$_n$-CH_3) have aroused great interest as potential diesel fuel sources in recent years [1]. These compounds contain no C–C bonds, have oxygen content of almost 50% by weight and are toxicologically safe. OME$_n$ with n = 3, 4, 5 have more diesel-like properties and exhibit remarkable cetane numbers [2]. The usage of OME$_n$ fuels can not only significantly reduce soot emissions [3] but also increase the efficiency of internal combustion engines [4], which make them more attractive in face of environmental pollution and health risks caused by diesel particle matters exposure [5]. Dimethoxymethane (DMM) is the simplest OME$_n$, with n = 1, and has been widely proposed and tested as a diesel fuel additive and a pure diesel fuel [6]. It is particularly notable that DMM with representative O-CH_2-O structure can be investigated as a model compound of OME$_n$. Moreover, DMM has been successfully employed as solvent in pharmaceutical and perfume industries [7] and is considered as an alternative fuel for hydrogen carrier in direct oxidation fuel cell [8,9], because of its high energy density, ease of completely electrooxidation and raising availability as derivatives of natural gas.

The combustion and emission characteristics of pure DMM fuel and DMM blended fuels under engine conditions have been extensively studied in past decades [10–13]. It has been demonstrated that DMM has important emission and resource benefits. The auto-ignition characteristics of DMM have been investigated in a shock-tube facility [14]. The effects of DMM addition on auto-ignition of n-heptane were also studied [15]. It was found that the addition of DMM can largely decrease the ignition delay times of DMM/n-heptane mixtures. Detailed chemical kinetic models of DMM have been developed and validated [16,17]. The radicals formed in DMM combustion and their reaction pathways have been investigated experimentally [18,19]. The combustion process of DMM was proposed that mainly proceeds by initial hydrogen abstraction and subsequent hot β-scission. Thermodynamic data including formation heats, heat capacities and entropies of DMM and its radicals ($CH_3O\dot{C}HOCH_3$, $CH_3OCH_2O\dot{C}H_2$) has been calculated in high-level model chemistry (G3B3) [17]. Kopp et al. have investigated the evolution of the DMM radicals by ab initio calculations and determined the rate constant of hydrogen abstraction [20]. It was found that the H-abstraction performing on the O-CH_2-O of DMM is favored

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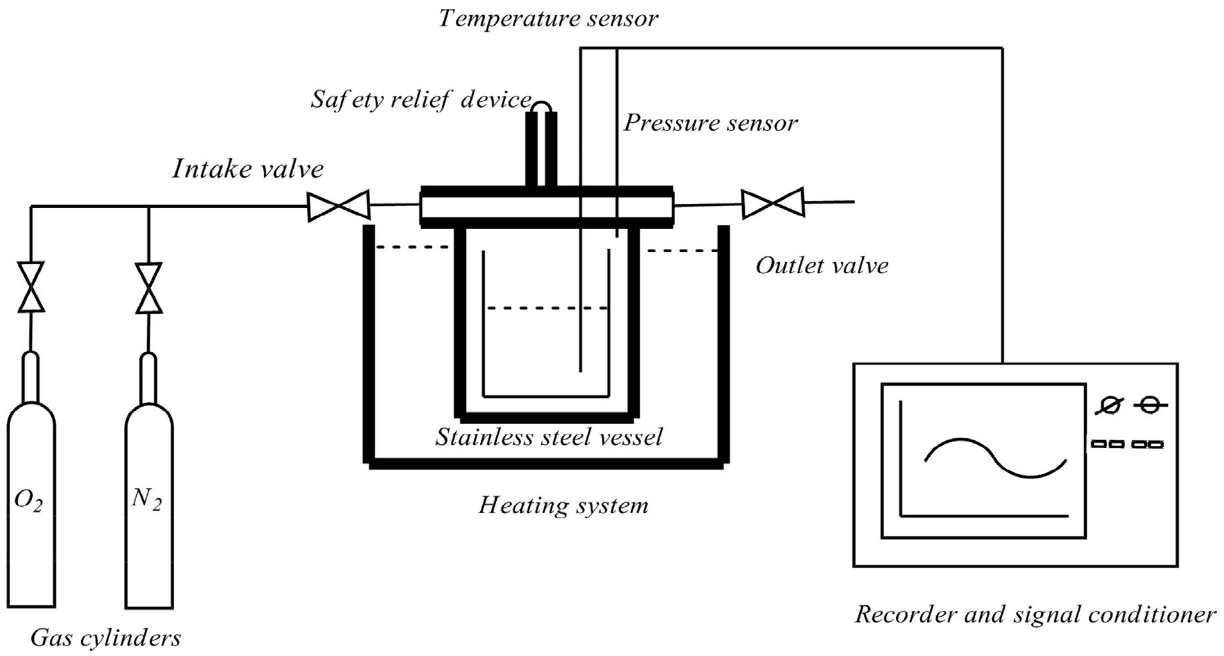

Fig. 1. Experimental installation of DMM oxidation.

over the abstraction performing on the terminal methyl (–CH_3), which accounts quite well with previous experimental results of the gas-phase oxidation of DMM labeled with C^{14} conducted by Molera et al. [21]. A cool flame phenomenon and explosion were detected in DMM oxidation at temperature of 543 K, there is a close connection between them [22]. The reaction activation energy is about 177 kJ·mol^{-1} for fuel-rich mixtures of DMM and oxygen at temperatures from 600 K to 685 K [23]. The oxidation of DMM at high pressure and atmospheric pressure were investigated by Marrodán et al. They found that the oxidation regime of different oxygen concentrations is very similar in reducing and stoichiometric conditions [24,25]. The thermal decomposition of DMM on solid acid [26], tropospheric degradation mechanisms [27] and the radicals initiated oxidation [28] have also been reported in past literatures.

However, quite limited fundamental research focused on DMM auto-oxidation and DMM peroxide. The influence of methylenedioxy (O-CH_2-O) on its oxidative stability and safety has never been investigated. It has been well established that the auto-oxidation of various substrates, especially ethers take places via free radical chain reactions and the principal products are peroxides [29]. These compounds are unstable and prone to decompose when exposed to physical shock or heat. Their thermal decomposition has been assumed responsible for the auto-ignition and occurrence of cool flames phenomenon [30,31]. Recently, this assumption has been demonstrated by Battin-Leclerc et al. The formation of hydroperoxides under conditions close to those actually before auto-ignition has been observed by coupling a jet-stirred reactor to a molecular-beam mass spectrometer combined with tunable synchrotron vacuum ultraviolet photo-ionization [32]. Besides, there have many severe thermal explosion accidents been associated with peroxide thermal decomposition [33,34]. DMM has been large-scale used in chemical industry and also has broad prospect in fuel application, especially for portable and household fuel application due to its extremely low toxicity. The potential hazard of DMM oxidation must be carefully examined.

Therefore, the purpose of this study was to investigate the stability and safety of DMM oxidation at low temperature and mainly focused on the formation and thermal decomposition processes of DMM peroxide. The oxidation experiments were performed in a well-controlled mini closed pressure vessel testing system at both accelerated and fixed conditions. The dominant primary product of hydroperoxide was isolated from oxidation products by using a series of modified conventional experimental method with consideration of its instability. The thermal runaway and explosion caused by peroxide thermal decomposition were also detected in the monitored DMM oxidation. The thermal runaway onset temperature (T_c), maximum temperature rise rate $(dT/dt)_{max}$ and maximum pressure rise rate $(dP/dt)_{max}$ were determined from the MCPVT studies. In addition, an endothermic reaction was detected at after DMM peroxides decomposition, and then the induced deep oxidation of DMM and oxygen happened. This research can not only provide an insight into gas-phase ignition of DMM, but also obtain a better understanding of thermal stability and safety of OME_n. Results of these studies may be quite instructive for avoiding accidents in production, transportation and application of oxygenated methylethers.

2. Materials and methods

2.1. Materials

DMM (purity 99.0 wt%) was obtained from Aladdin Industrial Corporation, China. It was pre-treated through reduced pressure distillation to remove oxidation products and stabilizers before use. The O_2 and N_2 (purity 99.99%) gases were obtained from Guangxi Guoxin Gas Research Co., Ltd., China. Cyclohexane and ethyl acetate (purity 99.0 wt%) were obtained from XiLong Scientific Co., Ltd., China. Silica gel and silica gel plate of type GF were obtained from Yantai Xin Nuo Chemical Co., Ltd., China. KI (purity 99.50 wt%) and $Na_2S_2O_3$ (purity 99.95 wt%$_)$ were obtained from Aladdin Industrial Corporation, China.

2.2. Thermal oxidation of DMM by MCPVT

A custom-designed mini closed pressure vessel test (MCPVT) was used to trace thermal oxidation reaction of DMM. It consists basically of a mini closed pressure vessel (10 mL), heating system and temperature/pressure measuring system, as shown in Fig. 1. According to the US Recommendations on the Transport of Dangerous Goods and using MCPVT, this installation has been well used for evaluating the thermo oxidative stability of ethers under a closed condition [35–38].

A small glass beaker (5mL) was used as a sample container for avoiding possible contamination. About 1.0 g DMM sample was loaded