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Chemical kinetic modeling of diethoxymethane oxidation: A carbon neutral fuel

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8 Abstract

| 9 | Diethoxymethane (DEM) is a carbon-neutral fuel with high cetane number (57.3). A detailed chemical |
|----|--|
| 10 | kinetic mechanism for DEM oxidation covering low and high temperature reactions is first developed in |
| 11 | this work. The reaction scheme and rate rules of DEM sub-mechanism are determined by the analogy |
| 12 | method to n-heptane. Aramco 3.0 mechanism is used as a base mechanism to consider C0-C4 fuels while |
| 13 | dimethoxymethane mechanism is included to ensure the mechanism compatibility and rate rule |
| 14 | consistency. Thermodynamic and transport properties of new species in DEM sub-mechanism are |
| 15 | computed by the methods of group additivity and properties correlation. The mechanism is validated |
| 16 | against ignition delay times and premixed laminar flame speed measured by shock tube, rapid |
| 17 | compression machine and spherical flame in combustion vessel. The verification covers a pressure range |
| 18 | of 2~30bar, an equivalence ratio range of 0.5~2.0, a temperature range of 540~1371K. A satisfactory |
| 19 | agreement between the experimental and computed results is observed, supporting the proposed reaction |

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| 20 | scheme and rate rules. Comparison of the ignition delay times between DEM and n-heptane indicates: (i) |
|----|---|
| 21 | DEM is more reactive at low temperature (500~670K) than n-heptane which favors low temperature |
| 22 | combustion mode. (ii) DEM ignition delay times demonstrate monotonous temperature dependence at |
| 23 | the full temperature regime but it is relatively independent of temperature at intermediate temperature |
| 24 | (620~960K). Therefore, a negative temperature coefficient (NTC) behavior is not observed in most |
| 25 | conditions. (iii) DEM may not be an efficient chemical ignition source compared to n-heptane due to |
| 26 | insufficient temperature increases and active radical accumulation. |

| 28 | |
|----|---|
| 29 | Highlights: |
| 30 | • A detailed chemical kinetic mechanism for DEM oxidation is developed. |
| 31 | • Current mechanism includes the low and high temperature reactions to extend application domain. |
| 32 | • Current mechanism is validated against ignition delay times and laminar flame speeds. |
| 33 | • DEM is more reactive at low temperature than n-heptane favoring advanced combustion modes. |
| 34 | • DEM ignition delay time decreases with increasing temperature and NTC behavior is weak. |
| 35 | |
| 36 | Keywords: |
| 37 | Carbon neutral fuels; Diethoxymethane oxidation; Mechanism development; Chemical kinetics; Fuel |

38 reactivity.

| Nomenclature | |
|-------------------|--|
| | |
| Symbols | |
| P _{init} | mixture initial pressure (used to describe boundary conditions) |
| T _{init} | mixture initial temperature (used to describe boundary conditions) |
| | |
| Greek letters | |
| φ | equivalence ratio |
| | |
| Abbreviations | |
| BECCS | bioenergy with carbon capture and storage |
| CaL | calcium carbonate looping |
| CCS | carbon capture and storage |
| CLC | chemical looping combustion |
| CFD | computational fluid dynamics |
| CN | cetane number |
| DAC | direct air capture |
| DEM | diethoxymethane |
| DMM | dimethoxymethane |
| EOR | CO2-enhanced oil recovery |
| FSC | Fuel Science Center |

| GHG | green house gas |
|------|----------------------------------|
| HTHR | high temperature heat release |
| LTC | low-temperature combustion |
| LTHR | low-temperature heat release |
| NTC | negative temperature coefficient |
| P2X | Power-to-X |
| PODE | Polyoxymethylene Dimethyl Ether |
| RCM | rapid compression machine |
| SCU | Sichuan University |
| SFN | Solar Fuels Network |
| ST | shock tube |
| UCL | Université catholique de Louvain |
| UOB | University of Birmingham |

1. INTRODUCTION

| 41 | European Union commits to cut greenhouse gas (GHG) emissions by 80~95% after 2050 to prevent a |
|----|---|
| 42 | global average temperature increase above 2°C within the 2015 Paris Agreement. Replacing fossil fuels |
| 43 | with carbon-neutral fuels could close the carbon cycle and reach zero net CO ₂ emission. The carbon- |
| 44 | neutral fuels produced in the sustainable carbon cycle are shown in Fig. 1 and the synthetic gas $(CO+H_2)$ |
| 45 | is the key platform chemicals. The CO or carbon atom is supplied by carbon capture and storage (CCS) |
| 46 | technology. The CO ₂ is collected and condensed from non-edible biomass, ambient and thermal power |
| 47 | plant emission. The commercial-scale or demonstration-scale CO2 capture technologies include chemical |
| 48 | absorption using aqueous amine solutions, polymeric membranes, bioenergy with carbon capture and |
| 49 | storage (BECCS), post-combustion adsorption, oxy-combustion coal power plant, direct air capture |
| 50 | (DAC). Chemical looping combustion (CLC) and calcium carbonate looping (CaL) technologies are still |
| 51 | conducted in pilot-scale operation [1]. The CO ₂ transportation technologies are well established through |
| 52 | worldwide on-shore & off-shore pipelines and transport ships [1]. The commercial scale or |
| 53 | demonstration-scale CO ₂ storage technologies include saline formation, CO ₂ -enhanced oil recovery |
| 54 | (EOR), depleted oil & gas fields while ocean storage and mineral storage are still in formulation and lab |
| 55 | test phases [1]. Afterward, the CO ₂ is processed and transformed through thermo-catalytic routes and |
| 56 | electrochemical routes to produce CO, O ₂ , CH ₄ as shown in Fig. 1. H ₂ is generated by water splitting |
| 57 | through electrochemical routes and the power source is supplied by renewable energy such as wind and |
| 58 | solar electricity. Ethers, alcohols and hydrocarbons can be produced from synthetic gas through Fischer- |
| 59 | Trosch synthesis under different types of catalysts [2]. These sustainable ethers, alcohols and |
| 60 | hydrocarbons used in the combustion process of transportation and industrial power generation sectors |
| 61 | can achieve zero net emission of CO2. As a result, the concept of carbon-neutral fuel receives increasing |

62 attention evidenced by the mainstream research projects including but not limited to:

- ENERGY-X project (European Commission): This Horizon 2020 project aims to address the
 efficient conversion from solar/wind energy to chemicals [2].
- 65 2. SUNENERGY project (European Commission): It builds on two Horizon 2020 projects of
- SUNRISE and ENERGY-X. It aims at using renewable energy from sunlight/wind and abundant
 molecules of CO₂/H₂O/N₂ to produce fossil-free fuels and chemicals [3].
- Solar Fuels Network (UK, SFN): It aims at using sunlight to electrolyze water into H₂ coupling
 CO₂ to make fuels [4]. The carbon-neutral fuels are manufactured by solar-driven fuel synthesis.

4. Power-to-X (European Commission): Based on the prerequisite of full decarbonization of the

- power sector by 2050, appropriate energy carriers are required to store the sustainable electricity.
 It evaluates the potential and competitiveness of 3 major power-to-X technologies (including
 power-to-H₂, power-to-CH₄ and power-to-liquid fuels) as the energy carrier of sustainable
- 74 electricity by 2050. [5]

- Kopernikus project-P2X (Germany): The goal is to store renewable energy in a physical substance
 that converts renewable electricity (produced by solar, wind, and hydropower) into chemical
 energy. This chemical energy can be used in the transportation sector, industry sector or even highemission sector but still environmentally friendly. It tries to partially or replace fossil
 diesel/gasoline/aviation fuels with synthetic fuels derived from syngas [6, 7].
- 6. The Fuel Science Center (Germany): It integrates renewable electricity and bio-based carbon
 feedstock/CO₂ to supply high-density liquid energy carriers termed as "bio-hybrid fuels" [8, 9]. It
 aims at reducing the carbon footprint significantly by these tailor-made bio-hybrid fuels.
- 83 7. Co-Optimization of Fuels & Engines: It intends to improve the fuel economy and emission

performance by co-optimization of fuels and engines. One of the fuel screening criteria for both
SI and CI engines is that the candidates can be produced from renewable domestic biomass as
replacements for fossil fuels [10-12].

87 Table 1 summarizes the typical n-alkanes and ethers which can be synthesized through the Fischer-Trosch process. The fuel molecules located in the same column have the same total number of C-atoms 88 89 and O-atoms while those in a single row have an identical number of O-atoms. Those fuel compounds 90 with reference indicate that the comprehensive mechanisms covering low and high temperatures 91 reactions are available. Diethoxymethane (DEM) has a cetane number (CN) of 57.3 [13] which can be 92 synthesized by ethanol, H_2 and CO_2 using Ruthenium catalyst [14]. There are only two DEM high 93 temperature oxidation mechanisms available in the literature: one is proposed by Dias et al. [15, 16] 94 which is also known as UCL (Université catholique de Louvain) mechanism. It describes the flat flame 95 stabilized at low pressure of 50mbar and it may encounter convergence problem when running at engine 96 relevant pressure. The other is proposed by Zhang et al. [17] and it is referred to SCU (Sichuan University) 97 mechanism in this work. It testes the ignition delay times at $\varphi = 0.5, 1.0, 2.0, T_{init} = 1065 \sim 1370 \text{ K}, P_{init} = 2$, 98 4, 10 atm using shock tube. However, there are fundamental knowledge gaps in both mechanisms: First, 99 both mechanisms contain only high temperature reactions but lack low temperature reactions, thus they 100 cannot reproduce the ignition phenomenon occurred at low and intermediate temperature (500~1000K) 101 regimes. Second, the UCL mechanism applies only to low pressure since the impact of pressure is not 102 considered in the pressure dependent reactions. Third, the rate constants of elementary reactions used in those mechanisms are not up to date which has been developed 5~10 years ago. Recently, rate constants 103 104 for the reactions of H-atom abstraction from DEM by H, CH₃, C₂H₅ and the followed β-scission reactions 105 are computed by Kröger et al. [18] using high-level CCSD(T)/aug-ccpV(T+D)Z//B2PLYPD3BJ/6311++(d,p) theory and transition state theory. The experimental DEM ignition delay times covering the
full temperature range (590~1090K) measured in shock tube (ST) and rapid compression machine (RCM)
have been reported by Lehrheuer et al. [19]. The premixed laminar flame speeds at 1.01, 2.50 bar are
measured in a spherical flame by Kopp et al. [20]. These data provide the foundation to develop the fullscale DEM oxidation mechanism.

111 Detailed chemical kinetic mechanisms are required to mimic the conventional and alternative fuels 112 combustion process in devices (industrial burners, gas turbines, boilers, incinerators, gasifiers, internal 113 combustion engines, etc.) and formulate the fuel compositions. Detail mechanism contains reaction rate 114 constant of elementary reactions, species thermodynamic/transport parameters and reaction pathway. It 115 tries to incorporate all the necessary species and reactions to reproduce the experimental results [21]. 116 Rate constants need to be assigned to a large number of elementary reactions in the detailed mechanism, thus, elementary reactions are assigned to various reaction classes with associated reaction rate rules [22, 117 118 23]. The detailed mechanism assembles the species, reactions with specified rate constants and validates 119 against experimental data from fundamental combustion devices (e.g. shock tube, rapid compression 120 machine, flame burner, jet stirred reactor, flow reactor). Coupling detailed mechanism with 121 computational fluid dynamics (CFD) to study the combustion phenomena demands substantial 122 computing sources, therefore, several mechanism reduction technologies (skeletal reduction, chemical species lumping, time-scale analysis, stiffness reduction and on-the-fly reduction) can be applied to 123 124 obtain reduced mechanism [24].

A detailed chemical kinetic mechanism for DEM oxidation over the low, intermediate and high temperature regimes is first reported in this work. The latest Aramco 3.0 mechanism is employed as a base mechanism while the dimethoxymethane (DMM) mechanism is adopted to improve the mechanism

- 128 compatibility and connect the base mechanism and DEM sub-mechanism. The proposed mechanism is
- 129 validated against the observed ignition delay times and laminar flame speed. The ignition delay times
- 130 between DEM and n-heptane are compared under a wide range of conditions to reveal the fuel oxidation
- 131 characteristics.



Fig. 1. Carbon neutral fuels produced in a sustainable carbon cycle.



134 Table 1. Overview of C3, C5, C7, C9, C11 alkanes and corresponding ethers with 1~5 O-atom substituents.

135 ^α Number in the first row is the total number of C-atoms and O-atoms;

136 $^{\beta}$ Number in the first column is the total number of O-atoms.

 γ The newly-published comprehensive mechanisms covering low and high temperature reactions are provided in the reference and those without reference denote comprehensive mechanisms

138 are unavailable so far.

139 2. CHEMICAL KINETIC MECHANISM FORMULATION

140 **2.1 Mechanism development and naming of species**

141 The physicochemical properties of DEM are listed in Table 2. Two sets of detailed DEM oxidation mechanisms 142 have been developed, one covering low and high temperature reactions (735 species, 3488 reactions) and the other 143 containing high temperature reactions only (333 species, 1661 reactions). Both low-high temperature and high temperature version UOB (University of Birmingham) mechanisms (chemical kinetic mechanisms, 144 145 thermodynamic parameters and transport parameters) are available in the Supplementary Material and the Data in 146 Brief. The DEM low-high temperature mechanism is specially developed to model gas-phase combustion process 147 (e.g. ignition-delay times, steady-state gas-phase combustion, temperature and species evolution in autoignition 148 process) which composes of Aramco 3.0 sub-mechanism [44], dimethoxymethane (DMM) sub-mechanism [38] 149 and DEM sub-mechanism. Aramco 3.0 sub-mechanism describes the oxidation process of C_0 - C_4 fuels (H₂, CO, 150 methane, ethane, ethylene, acetylene, formaldehyde, acetaldehyde, propane, butane, etc.), C5-C7 normal paraffin 151 and their isomers (n-pentane, iso-pentane, neo-pentane, n-hexane), monoaromatics (benzene, phenol, 152 cyclopentadiene, fulvene, etc.), PAHs (indene, naphthalene, fluprene etc.), C1-C3 alcohols (methanol, ethanol, n-153 propanol, iso-propanol etc.) as shown in Fig. 2. DMM mechanism proposed by Javob et al. [38] is adopted to 154 connect the Aramco 3.0 [44] and DEM sub-mechanism developed in this work. This DMM mechanism uses Aramco 2.0 [45] as a base mechanism which ensures the overall compatibility of Aramco 3.0 [44], DMM and 155 156 DEM sub-mechanism.

The DEM high temperature oxidation mechanism is specifically developed for flame modeling (e.g. laminar flame speed, burner-stabilized flame, opposed-flow flame, flame extinction analysis, stagnation flame analysis, etc.) which comprises of $PODE_{2-4}$ base mechanism [38] and diethoxymethane sub-mechanism. $PODE_{2-4}$ mechanism [38] is employed to describe the reactions of C_0 - C_4 small molecules which commonly appearing in the oxidation of the large hydrocarbon. Meanwhile, this mechanism also incorporates DMM sub-mechanism. The role of the PODE₂₋₄ base mechanism [38] in DEM high temperature oxidation mechanism plays the same role as Aramco 3.0 [44] and DMM [38] mechanisms in DEM low-high temperature oxidation mechanism. But the PODE₂₋₄ base mechanism [38] mainly focuses on the high temperature oxidation process and thus the mechanism size is much smaller than Aramco 3.0 [44] and DMM [38] mechanisms.

166 DEM and n-heptane have similar molecular structures such as straight-chain and symmetric structures as shown 167 in Fig. 3. Replacing two C-atoms at position 3 in n-heptane molecule with O-atoms becomes DEM molecule. The 168 analogy method can be implemented to design the reaction scheme and estimate the rate constants of elementary 169 reactions for DEM sub-mechanism due to their similar molecular structure. C7H15_1, C7H15_2, C7H15_3, C7H15_4 170 are the four products of H-atom abstraction from n-heptane [23, 30]. O-atoms occupy position 3 for DEM, thus there are 3 H-atom abstraction pathways at positions 1, 2, 4. They are C2H4OCH2OC2H5 (DEM1), 171 172 CH3CHOCH2OCH2CH3 (DEM2) and CH3CH2OCHOCH2CH (DEM3) respectively [15, 16] [17]. The 173 represented species in DEM mechanism and the analogical species in the n-heptane mechanism are presented in Table 3. The full species glossary for DEM sub-mechanism is provided in supporting information. 174

175 The similar molecular structures between DEM and n-heptane result in a similar oxidation pathway as shown 176 in Fig. 4. Low temperature (T_{init}=500~625K) oxidation initiates with H-atom abstraction from DEM to form 177 DEMx (DEM1, DEM2 DEM3). The first O₂ addition to DEMx to form DEMxO₂ (including DEM1O₂, DEM2O₂, 178 DEM3O₂) and then DEMxO₂ isomerizes to produce QOOH. The second O₂ addition takes place on QOOH to 179 produce O2QOOH. 1st O2 addition, QOOH isomerization and 2nd O2 addition are the typical reactions for DEM 180 low temperature oxidation. QOOH takes place low temperature degenerated branched chain reaction to produce 181 carbonylhydroperoxide and OH radical. The carbonylhydroperoxide further decomposes to form oxygenated and 182 OH radicals by chain branching reactions. EROOH is the isomerized product of O2QOOH and low temperature

- chain branching reaction takes place to produce ERO and OH radical. QOOH decomposition occurs at the mediate temperature ($T_{init}=625\sim900K$) through three pathways: (1) QOOH<=>cyclic ether+OH; (2) QOOH<=>ether with carbon double bond+HO2; (3) QOOH<=> β -scission products. At high temperature regime ($T_{init}>900K$), DEM comes across carbon-oxygen bond cleavage to form active radicals while the n-heptane takes place carbon-carbon
- 187 bond cleavage.





Fig. 2. The hierarchical/modular structure and overall interrelationships between component libraries in the detailed DEM mechanism.





Fig. 3. Molecular structure of (a) DEM, (b) n-heptane and major products by H-atom abstraction from fuel.





Fig. 4. Comparison of major oxidation pathways between DEM and n-heptane [30].

Table 2. Physicochemical properties of DEM.

| Name | Diethoxymethane or Ethylal |
|-----------------------------------|----------------------------|
| CAS | 462-95-3 |
| Formula | C5H12O2 |
| Molecular structure | |
| Molecular weight | 104.15 |
| Boiling point (°C) | 88.05 [46] |
| Melting Point (°C) | -66.5 [47] |
| Flash point (°C) | -5 [48] |
| Enthalpy of vaporization (kJ/mol) | 35.74 [46] |
| Cetane number | 57.3 [13] |
| Lower heating value (MJ/kg) | 29.7 [19] |

Table 3. Represented species in DEM mechanism and analogy species in n-heptane mechanism [30].



198 2.2 Classes of reactions

199 Reaction classes generalize the kinetic information of reaction pathways and rate constants that 200 systematically embody the analogies and physical principles. They essentially describe: (1) when the 201 reaction classes should be applied within particular chemical reactants; (2) how the specific reactants 202 transform to products through a series of elementary reactions; (3) the rate constants associated with the 203 conversion from reactants to products [21]. There are 13 high temperature reaction classes and 24 low 204 temperature reaction classes considered in the current DEM oxidation mechanism as shown in Table 4 205 and Table 5 respectively. The rate constants of elementary reactions from the Aramco 3.0 base 206 mechanism [44] and DMM sub-mechanism [38] remain unchanged. For the DEM sub-mechanism, the 207 elementary reactions from high temperature reaction classes derive from the UCL mechanism [15, 16] 208 and SCU mechanism [17] respectively. Those reactions belong to low temperature reaction classes 209 mainly refer to the n-heptane oxidation mechanism [30] according to the analogy method. 210 The DEM low temperature oxidation reaction pathways have been discussed in the last paragraph of 211 section 2.1 and the major reaction routes are presented in Fig. 5. The full reaction pathway is provided 212 in Fig. S1 of supporting information in Supplementary Material. The major difference between DEM and 213 n-heptane is the low temperature oxidation reactivity, thus the ignition delay time of DEM is lower by 214 an order of magnitude than n-heptane at T_{init}=500~650K [49]. Therefore, both pre-exponential factor A, 215 temperature exponents n of reaction class 3 (H-atom abstraction from fuel, initiation reactions) in DEM 216 mechanism increase compared to n-heptane to elevate low temperature reactivity. Their rate constants 217 are compared in Fig. 6 and the pre-exponential factor A, temperature exponents n and the activation 218 energy E_a are listed in Table 6. The H-atom abstraction from DEM by C_2H_5 radical is first introduced in

the DEM oxidation mechanism which is not included in the SCU mechanism [17] and UCL mechanism

| 220 | [15, 16]. C ₂ H ₅ radical is DEM β -scission products through Eq. (1) ~ Eq. (2) (belong to reaction | n class 1), |
|-----|--|----------------------|
| 221 | thence this radical play a non-negligible role in DEM low temperature ignition. DEM1, DEM1 | 2, DEM3 |
| 222 | occur the 1^{st} O ₂ addition to produce DEM1O ₂ , DEM2O ₂ , DEM3O ₂ through Eq. (3) ~ Eq. (5). If | DEM1O ₂ , |
| 223 | DEM2O ₂ , DEM3O ₂ undergo isomerization by internal H-atom transfer to form QOOH. 5 to 10 |) member |
| 224 | ring is the intermediate transition state structure during the isomerization reaction as shown | in Fig. 7. |
| 225 | QOOH radicals take place 2^{nd} O ₂ addition to produce O ₂ QOOH which decompose | oses into |
| 226 | carbonylhydroperoxide and OH radicals as shown in Fig. 5. Carbonylhydroperoxide further dec | composes |
| 227 | to produce oxygenated radicals and OH radicals. These two steps constitute the degeneration | ate chain |
| 228 | branching reactions for DEM low temperature oxidation. Reaction class 1 and 4, for example Ed | q. (6) and |
| 229 | Eq. (7), also play a key role to reduce the fuel reactivity at low and intermediate temperatur | e regime |
| 230 | (ranges from 500K to 960K) in addition to reaction class 3. | |
| 231 | DEM<=>C2H5OH+C2H5+HCO | (1) |
| 232 | DEM<=>C2H5OCH2O+C2H5 | (2) |
| 233 | C2H4OCH2OC2H5+O2<=>C2H5OCH2OC2H4OO | (3) |
| 234 | CH3CHOCH2OCH2CH3+O2<=>CH3COOHOCH2OC2H5 | (4) |
| 235 | CH3CH2OCHOCH2CH3+O2<=>C2H5OCOOHOC2H5 | (5) |
| 236 | DEM<=>CH2OCH2OC2H5+CH3 | (6) |
| 237 | CH2OCH2OC2H5<=>C2H5OCH2+CH2O | (7) |





Fig. 5. Proposed key DEM low temperature oxidation reaction pathways and the full pathway is provided in supporting information.







Fig. 7. Internal H-atom abstraction of \dot{RO}_2 radicals via transition state ring structure, reaction class 24: $\dot{RO}_2 \ll QOOH$.

| 245 | Table 4. High | temperature | reaction | classes | considered | in the | e DEM 1 | mechanism. |
|-----|---------------|-------------|----------|---------|------------|--------|---------|------------|
|-----|---------------|-------------|----------|---------|------------|--------|---------|------------|

| Class ID | High temperature reaction classes | Rate constant source | | | | | |
|----------|---|----------------------|--------------|----------------|--------------|--------------|--------------|
| | | Aramco 3.0 [44] | DMM [38] | n-Heptane [30] | DEM [15, 16] | DEM [17] | This work |
| 1 | Unimolecular fuel decomposition: Fuel $\leq \dot{R} + \ddot{R}$ | \checkmark | \checkmark | × | \checkmark | \checkmark | \checkmark |
| 2 | Fuel decomposition: $RH \le \dot{R} + \dot{H}$ | × | \checkmark | \checkmark | × | \times | \checkmark |
| 3 | H-atom abstraction from the fuel by | \checkmark | \checkmark | \checkmark | \checkmark | \checkmark | \checkmark |
| | $O_2/\dot{H}/\dot{O}/\dot{O}H/H\dot{O}_2/\dot{C}H_3/CH_3\dot{O}/CH_3\dot{O}_2/\dot{O}_2CHO/\dot{C}_2H_3/\dot{C}_2H_5$ | | | | | | |
| | (primary/secondary carbon sites): RH+ $\dot{X} \ll \dot{R} + XH$ | | | | | | |
| 4 | R radical decomposition | \checkmark | × | × | \checkmark | \checkmark | \checkmark |
| 5 | R radical isomerization | \checkmark | \checkmark | × | × | \checkmark | \checkmark |
| 6 | C–O: β -scission of \dot{R} radicals | × | \checkmark | × | × | \times | \checkmark |
| 7 | O–C–O: β -scission of \dot{R} radicals | × | \checkmark | × | × | \times | \checkmark |
| 8 | H-atom abstraction reactions from alkenes | \checkmark | × | × | × | × | \checkmark |
| 9 | Addition of radical species O and OH to alkenes | \checkmark | × | × | × | \times | \checkmark |
| 10 | Reactions of alkenyl radicals with $H\dot{O}_2$, CH3O2, and C2H5O2 | \checkmark | Х | × | × | × | \checkmark |
| 11 | Alkenyl radical decomposition | \checkmark | × | × | × | × | \checkmark |
| 12 | Alkene decomposition | \checkmark | × | × | × | × | \checkmark |
| 13 | Retroene decomposition reactions | \checkmark | × | × | × | \times | \checkmark |

| 247 | Table 5. | Low | temperat | ure reaction | n classes | considered | in the | DEM | mechanisn |
|-----|----------|-----|----------|--------------|-----------|------------|--------|-----|-----------|
| | | | | | | | | | |

| Class ID | Low-temperature reaction classes | Rate constant source | | | | | | |
|----------|--|----------------------|--------------|----------------|--------------|----------|--------------|--|
| | | Aramco 3.0 [44] | DMM [38] | n-Heptane [30] | DEM [15, 16] | DEM [17] | This work | |
| 14 | Addition of O_2 to \dot{R} radicals: $\dot{R} + O_2 \le \dot{R}O_2$ | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 15 | $\dot{\mathbf{R}}$ +O ₂ <=>E+HO ₂ (E: radicals contain carbon-carbon double bond) | × | × | \checkmark | × | × | \checkmark | |
| 16 | $\dot{\mathbf{R}} + \mathbf{R}\dot{\mathbf{O}}_2 \ll \dot{\mathbf{R}}\dot{\mathbf{O}} + \dot{\mathbf{R}}\dot{\mathbf{O}}$ (including $\dot{\mathbf{R}} + \dot{\mathbf{H}}\dot{\mathbf{O}}_2 \ll \dot{\mathbf{R}}\dot{\mathbf{O}} + \mathbf{O}\mathbf{H}$) | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 17 | \dot{RO}_2 +Fuel<=>ROOH+R | × | × | \checkmark | × | × | \checkmark | |
| 18 | $\dot{RO}_2 + \dot{RO}_2 = \dot{RO} + \dot{RO} + \dot{O}_2 \text{ (including } \dot{RO}_2 + CH_3\dot{O}_2 = \dot{RO} + CH_3\dot{O} + O_2)$ | \checkmark | × | \checkmark | × | × | \checkmark | |
| 19 | $\dot{RO}_2 + \dot{HO}_2 \leq ROOH + O_2$ | \checkmark | × | \checkmark | × | × | \checkmark | |
| 20 | $\dot{RO}_2 + H_2O_2 \le ROOH + HO_2$ | \checkmark | × | \checkmark | × | × | \checkmark | |
| 21 | $ROOH \le R\dot{O} + \dot{O}H$ | × | × | \checkmark | × | × | \checkmark | |
| 22 | RO decomposition | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 23 | $\dot{RO}_2 \leq E + H\dot{O}_2$ | × | × | \checkmark | × | Х | \checkmark | |
| 24 | \dot{RO}_2 radical isomerization: $\dot{RO}_2 \ll QOOH$ | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 25 | \dot{RO}_2 concerted eliminations: $\dot{RO}_2 \ll H\dot{O}_2$ | \checkmark | × | × | \checkmark | × | \checkmark | |
| 26 | QOOH = cyclic ether + OH (cyclic ether formation) | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 27 | QOOH decomposition (β -scission products) | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 28 | QOOH = alkene + HO2 (radical site beta to OOH group) | \checkmark | \times | \checkmark | × | × | \checkmark | |
| 29 | QOOH = ether with carbon-carbon double bond + HO2 | × | \times | × | × | \times | \checkmark | |
| 30 | QOOH = alkene + carbonyl + OH (radical site gamma to OOH group) | \checkmark | × | \checkmark | × | \times | \checkmark | |
| 31 | Addition of O_2 to $\dot{Q}OOH$: $\dot{Q}OOH + O_2 \le \dot{O}_2 QOOH$ | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 32 | \dot{O}_2 QOOH isomerization to form carbonylhydroperoxide and $\dot{O}H$ | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 33 | Carbonylhydroperoxide decomposition to form oxygenated radicals and OH | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 34 | Cyclic ether reactions with $\dot{O}H$ and $H\dot{O}_2$ | \checkmark | \checkmark | \checkmark | × | × | \checkmark | |
| 35 | Decomposition of large carbonyl species and carbonyl radicals | \checkmark | Х | \checkmark | × | × | \checkmark | |
| 36 | \dot{O}_2 QOOH <=>EROOH+ $H\dot{O}_2$ (EROOH: olefinic hydroperoxy) | × | × | \checkmark | × | × | \checkmark | |
| 37 | EROOH decomposition | × | × | \checkmark | × | X | \checkmark | |

| DEM reactions | $A\left(cm^{3}mol^{-1}s^{-1}K^{-n}\right)$ | n | E _a (cal/mole) | n-Heptane reactions | A (cm ³ mol ⁻¹ s ⁻¹ K ⁻ⁿ) | n | E _a (cal/mole) |
|--------------------|--|-------|---------------------------|--------------------------|--|-------|---------------------------|
| DEM+O2=DEM1+HO2 | 4.20E+13 | 1.7 | 52800 | NC7H16+O2=C7H15-1+HO2 | 4.20E+13 | 0 | 52800 |
| DEM+O2=DEM2+HO2 | 2.80E+13 | 1.7 | 50160 | NC7H16+O2=C7H15-2+HO2 | 2.80E+13 | 0 | 50160 |
| DEM+O2=DEM3+HO2 | 1.40E+13 | 1.7 | 50160 | NC7H16+O2=C7H15-4+HO2 | 1.40E+13 | 0 | 50160 |
| DEM+OH=DEM1+H2O | 5.46E+07 | 3.513 | 868.4 | NC7H16+OH=C7H15-1+H2O | 2.73E+07 | 1.813 | 868.4 |
| DEM+OH=DEM2+H2O | 2.82E+10 | 2.635 | 504.7 | NC7H16+OH=C7H15-2+H2O | 1.41E+10 | 0.935 | 504.7 |
| DEM+OH=DEM3+H2O | 1.12E+12 | 2.02 | 846.5 | NC7H16+OH=C7H15-4+H2O | 5.62E+11 | 0.32 | 846.5 |
| DEM+C2H5=DEM1+C2H6 | 1.00E+11 | 2 | 13400 | NC7H16+C2H5=C7H15-1+C2H6 | 1.00E+11 | 0 | 13400 |
| DEM+C2H5=DEM2+C2H6 | 1.00E+11 | 2 | 10400 | NC7H16+C2H5=C7H15-2+C2H6 | 1.00E+11 | 0 | 10400 |
| DEM+C2H5=DEM3+C2H6 | 5.00E+10 | 2 | 10400 | NC7H16+C2H5=C7H15-4+C2H6 | 5.00E+10 | 0 | 10400 |

Table 6. Elementary reactions of H-atom abstract from fuel and rate constant for DEM and n-heptane [30].

251 **2.3 Thermochemical and transport data**

The thermodynamic and transport parameters of the species are used to determine reverse rate 252 253 constants. They are mainly taken from Aramco 3.0 mechanism [44], dimethoxymethane mechanism [38], 254 n-heptane mechanism [30], DEM high temperature mechanism [15-17], 2-methylalkanes (C_7 to C_{20}) 255 mechanism [31], dibutyl ether mechanism [36] and $PODE_{2-4}$ mechanism [40]. The thermochemical properties of species not present in the above mechanisms are calculated using group additivity theory 256 257 proposed by Benson [50], Bozzelli et al. [51] and Glaude et al. [52]. The transport properties of 258 unreported stable species are computed by the correlation proposed by Tee et al. [53]. The critical 259 pressure, critical temperature, and acentric factor are needed to determine the Lennard-Jones potential 260 well depth and collision diameter which are derived from Yaws' handbook [54], AP1700 Material 261 property calculation and inquiry platform [55] and NIST Chemistry WebBook [46]. The transport 262 properties of unreported radical species are adopted from radicals with identical chemical formulas and 263 similar molecular structures or parent species.

3. RESULTS AND DISCUSSION

265 **3.1 Ignition delay time validation**

266 The full temperature regime (500~1400K) ignition delay times of DEM-air mixture at φ =1.0, Pinit=30bar have been measured in shock tube (ST) and rapid compression machine (RCM) by Lehrheuer 267 268 et al. [19]. The initial mixture compositions and boundary conditions are listed in Table 7. The 269 comparison of the experimental data measured by Lehrheuer et al. [19] and prediction using the current 270 UOB mechanism are plotted in Fig. 8. This kinetic model can reproduce the oxidation reactivity with 271 varying initial gas temperature (500 \sim 1400K) and dilution ratio (N₂/O₂=3.76, 12). The NTC (negative 272 temperature coefficient) behavior does not appear in the DEM ignition delay time profiles, but it emerges 273 a shallow plateau at 620~920K when N₂/O₂=3.76. Similarly, the ignition delay time plateau presents at 274 $580 \sim 840$ K when N₂/O₂ increases to 12. The DEM ignition delay times increases as dilution ratio N₂/O₂ 275 increases from 3.76 to 12 while the intermediate temperature plateau moves toward lower temperature 276 regime and narrows. 277 A sensitivity analysis on OH species respective to reaction A-factors is conducted at 500K, 800K, 278 1200K to identify the dominant reactions at low, intermediate, high temperature oxidation as shown in 279 Fig. 9 (a) \sim Fig. 9 (c). The OH radical is the ignition indicator, accordingly those reactions with positive 280 sensitivity coefficients promote OH radical production and enhance oxidation reactivity, vice versa. At 281 T_{init} =500K, reaction sequence Eq. (8) ~ Eq. (10) is a main low temperature chain branching pathway.

282 C_2H_5 is the β -scission product of DEM decomposition while CH₂O is the major β -scission product of 283 oxygenated radicals (here refer to those formed by reaction class 33). H-atom abstraction by O₂, OH, 284 HO₂, CH₃, CH₃O₂ and C₂H₅ from DEM to produce DEM2 (CH3CHOCH2OCH2CH3) all contribute to 285 reactivity enhancement because after the 1st O₂ addition DEM2O2 (CH3COOHOCH2OC2H5) exists

| 286 | four isomerized pathway. On the contrary, H-atom abstraction by OH, HO ₂ , CH ₃ , CH ₃ O ₂ from | n DEM to | | |
|-----|---|------------------------|--|--|
| 287 | form DEM3 (CH3CH2OCHOCH2CH3) inhibits oxidation reactivity because of t after the 1st O | ² addition. | | |
| 288 | DEM3O2 (C2H5OCOOHOC2H5) has only two isomerization pathways. At T _{init} =800K, | , reaction | | |
| 289 | sequence Eq. (11) ~ Eq. (15) is the main OH radical source to sustain the system reactivity | 7. H-atom | | |
| 290 | abstractions from DEM by CH_3 and C_2H_5 to form DEM2 and DEM3 are detrimental to O | H radical | | |
| 291 | accumulation as shown in Fig. 9 (b). DEMx takes place the 1^{st} O ₂ addition to produce DEM | IxO2 and | | |
| 292 | sequentially isomerizes to form QOOH as shown in Fig. 4. But as the initial gas temperature | e exceeds | | |
| 293 | 620K, QOOH reaction pathway would transfer from the 2^{nd} O ₂ addition toward QOOH decord | mposition | | |
| 294 | to produce cyclic ether, ether with carbon double bond and β -scission products. At interval | ermediate | | |
| 295 | temperature, the low temperature chain branching reactions (reaction class 31, 32, 33) sus | pend and | | |
| 296 | transfer to chain propagation reactions (reaction class 26, 27, 29). At 1200K, DEM decomposes by C-O | | | |
| 297 | bond fission (reaction class 1), it replaces H-atom abstraction from fuel (reaction class 3) becoming the | | | |
| 298 | major initiated reaction. The dominant OH radical formation pathway at a high temperature | re regime | | |
| 299 | (above 920K) following the reaction sequence of Eq. (16) ~ Eq. (18), Eq. (15). While Eq. (19) | consumes | | |
| 300 | C2H5 radical which competes with the major OH radical production pathway, thus inhibits O | H radical | | |
| 301 | accumulation. | | | |
| 302 | C2H5+O2<=>C2H5O2 | (8) | | |
| 303 | C2H5O2+CH2O<=>C2H5O2H+HCO | (9) | | |
| 304 | C2H5O2H<=>C2H5O+OH | (10) | | |
| 305 | C2H5+O2<=>C2H5O2 | (11) | | |
| 306 | C2H5O2<=>CH3CHO+OH | (12) | | |

307 CH3CHO+HO2<=>CH3CO+H2O2 (13)

| 308 | CH3CHO+CH3O2<=>CH3CO+CH3O2H | (14) |
|-----|----------------------------------|------|
| 309 | H2O2(+M)<=>2OH(+M) | (15) |
| 310 | DEM<=>C2H5OCH2O+C2H5 | (16) |
| 311 | C2H5OCH2O<=>C2H5O+CH2O | (17) |
| 312 | CH2O+HO2<=>HCO+H2O2 | (18) |
| 313 | DEM+C2H5<=>CH3CH2OCHOCH2CH3+C2H6 | (19) |

The high temperature regime (1100~1400K) ignition delay times of DEM/O₂/Ar mixture at 314 315 φ =0.5/1.0/2.0, P_{init}=2/4/10bar have been measured in shock tube (ST) by Zhang et al. [17]. UCL 316 mechanism proposed by Dias et al. [15, 16] is developed and validated against 50mbar and does not 317 apply to the pressure range of $2 \sim 10$ bar. So the simulation results of the current UOB mechanism and 318 SCU mechanism proposed by Zhang et al. [17] are validated against shock tube ignition delay times as 319 shown in Fig. 10. Both mechanisms have their advantages and disadvantages: (1) current UOB 320 mechanism is more specific to engine relevant pressure and the discrepancy reduces as increasing initial 321 pressure; (2) current UOB mechanism obtains high predictive accuracy at stoichiometric and fuel-rich 322 conditions and under-estimates the oxidation reactivity at fuel-lean condition; (3) the experimental 323 ignition delay times below 1160K are better reproduced by current UOB mechanism than SCU 324 mechanism [17]. This work incorporates both low temperature and high temperature reaction classes 325 while the SCU mechanism [17] contains only high temperature reaction classes. UCL mechanism 326 proposed by Dias et al. [15, 16] confronts the same issue as the SCU mechanism [17], hence both 327 mechanisms do not apply to ignition delay time validation over the full temperature regime in Fig. 8.





329 Fig. 8. Experimental (symbols [19]) and modeling results (lines) for DEM ignition delay times at $\varphi = 1.0$,









-0.4 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 Normalized sensitivity coefficient



Fig. 9. Sensitivity analysis on OH species respective to reaction A-factors for DEM oxidation at $\varphi = 1.0$, T_{init}=500/800/1200K, P_{init}=30bar, N₂/O₂=3.76.



Fig. 10. Experimental (symbols [17]) and modeling results (lines) of DEM/O₂/Ar mixture ignition delay times at φ =0.5/1.0/2.0, T_{init}=1000~1400K, P_{init}=2/4/10bar.

| | Compositions | φ | T _{init} (K) | P _{init} (bar) |
|-----------------------|----------------------|-----|-----------------------|-------------------------|
| Lehrheuer er al. [19] | DEM:02:N2=1:7:26.32 | 1.0 | 500~1400 | 30 |
| | DEM:O2:N2=1:7:84 | 1.0 | 500~1400 | 30 |
| Zhang et al. [17] | DEM:O2:Ar=1:14:85 | 0.5 | 1000~1400 | 2/4 |
| | DEM:O2:Ar=1:7:92 | 1.0 | 1000~1400 | 2/4/10 |
| | DEM:O2:Ar=1:3.5:95.5 | 2.0 | 1000~1400 | 2/4 |

340 Table 7. Boundary conditions of DEM oxidation for ignition delay time experiments/simulations

342 **3.2 Laminar flame speed validation**

343 The current UOB mechanism has been validated against the premixed laminar flame speed of DEM-344 air mixture at φ =0.5~2.0, T_{init}= 1atm, P_{init}=1.01/2.50bar reported by Kopp. et al. [20]. The comparisons 345 are plotted in Fig. 11. The high temperature version UOB mechanism is adopted to simulate the flame 346 phenomenon which removes the low-temperature species and reactions to accelerate the computational 347 speed. The dependence of flame speed on equivalence ratio is well captured by the current UOB 348 mechanism except for the impact of initial gas pressure. Current UOB mechanism overestimates the 349 flame speed by 2.8 cm/s at φ =1.1, P_{init}=1.01bar while under-estimates the flame speed by 1.5 cm/s at ϕ =1.1, P_{init}=2.50bar. This deviation becomes more distinct at ϕ =1.5, P_{init}=2.50bar and it causes difficulty 350 351 in reaction rate constant calibration. More experimental flame speed data are required to refine the kinetic 352 model and reduce experimental uncertainty. 353 The peak flame speed appears at $\varphi=1.1$ under 1.01bar and 2.50bar as shown in Fig. 11. Sensitivity 354 analysis on laminar flame speed respective to reaction A-factors is conducted to distinguish the dominant 355 reactions at $\varphi = 0.8/1.1/1.5$ as shown in Fig. 12 (a) ~ Fig. 12 (c). High temperature chain branching

356 reaction H+O2<=>O+OH are the dominant reaction of flame speed at varying equivalence ratio. And 357 CO+OH<=>CO2+H is the secondary dominant reaction to enhance the flame speed at $\varphi=0.8$ and $\varphi=1.1$ which are also the major heat release reaction. Especially, H-atom abstraction from DEM by C_2H_5 to 358 359 produce DEM3 benefit the flame speed acceleration at the fuel-lean condition. This further supports that 360 C₂H₅ radicals play a key role in DEM decomposition by reaction class 1 and reaction class 3. At fuelrich conditions (φ =1.5), HCO+M<=>CO+H+M replace CO+OH<=>CO2+H becoming the major heat 361 362 release reaction to promote flame speed due to oxygen deficiency. Endothermic reaction H2O+M<=>H+OH+M and chain termination reaction CH3+H(+M)<=>CH4(+M) decrease reaction 363

364 temperature and retard the active radical accumulation, thus contributes to flame speed reduction.





366 Fig. 11. Experimental (symbols [20]) and modeling results (lines) for the laminar flame speed of DEM

367 in air at ϕ =0.5~2.0, T_{init}= 1atm, P_{init}=1.01/2.50bar.







Fig. 12. Sensitivity analysis on laminar flame speed respective to reaction A-factors for DEM oxidation at $T_{init}=398K$, $P_{init}=1.01$ bar, (a) $\varphi=0.8$, (b) $\varphi=1.1$, (c) $\varphi=1.5$.

3.3 Comparison of ignition delay times between DEM and n-heptane

| 373 | The oxidation reactivity between DEM and n-heptane is examined at φ =0.25 ~ 2.0, T _{init} = 500~1400K, |
|-----|---|
| 374 | P_{init} = 13.5 ~ 55bar as shown in Fig. 13 and the boundary conditions are chosen from ref. [56, 57]. The |
| 375 | DEM ignition delay times have three characteristics: (1) It decreases with increasing initial pressure and |
| 376 | equivalence ratio under 500~1400K being similar to n-heptane. (2) The ignition delay time profiles exist |
| 377 | a wide shallow plateau at a temperature range of 620~960K and the plateau narrows as the equivalence |
| 378 | ratio decreases from 2.0 to 0.5. A weak NTC region appears until the equivalence ratio further decreases |
| 379 | to 0.25 and it moves towards higher temperature as increasing pressure. On the contrary, n-heptane |
| 380 | demonstrates NTC behavior for all studied conditions. (3) DEM has greater low temperature oxidation |
| 381 | reactivity than n-heptane thus its ignition delay times are lower than n-heptane at 500~670K. The species |
| 382 | evolution of the DEM and n-heptane ignition process at low (560K)/intermediate (800K)/high |
| 383 | temperature (1200K) are illustrated in Fig. 14. The DEM ignition process has two key characteristics: |
| 384 | (i) The low temperature heat release (LTHR) intensity of DEM is weaker than n-heptane being |
| 385 | similar to PODE ₃ reported by Li et al. [41]. The initiated temperature and amplitude of DEM |
| 386 | LTHR are 575K and 205K while those of n-heptane are 832K and 316K respectively. From |
| 387 | the perspective of active radical pool production, DEM completes 45.13% $\mathrm{H_2O_2}$ |
| 388 | accumulation at LTHR while n-heptane reaches 87.86%. DEM has greater low temperature |
| 389 | oxidation reactivity (namely low ignition delay times) but the LTHR intensity (temperature |
| 390 | increase) and active radical accumulation are not sufficient. Therefore, DEM is not |
| 391 | appropriate to undertake the role of chemical ignition source compared to n-heptane which is |
| 392 | similar to $PODE_3$ (polyoxymethylene dimethyl ether 3). |
| | |

393 (ii) The DEM heat release process transits from two-stage heat release (LTHR+HTHR) to single-

- stage heat release (HTHR) as the initial gas temperature increases from 500 to 1400K. There
 is no distinct LTHR stage at intermediate temperature (640~940) which is different from n-
- 396 heptane as shown in Fig. 14 (b) and Fig. 14 (e).



Fig. 13. Ignition delay times of DEM-air mixture and n-heptane-air mixture at T_{init} = 500~1400K, P_{init} = 13.5, 20, 38, 55bar, (a) φ =0.25, (b) φ =0.5, (c) φ =1.0, (d) φ =2.0.





4. CONCLUSIONS

| 402 | A detailed reaction mechanism for diethoxymethane (DEM) oxidation covering low and high |
|-----|---|
| 403 | temperature reactions is first reported in this study. The DEM low temperature reaction scheme is |
| 404 | designed by analogy method based on the updated n-heptane mechanism while the high temperature |
| 405 | reaction scheme follows the published DEM mechanisms. The reaction rate rules are consistent with |
| 406 | Aramco 3.0 mechanism which is taken as a base mechanism to consider the C0-C4 fuels, C1-C3 alcohols, |
| 407 | n-pentane and their isomers, n-hexane, mano-aromatics and PAHs. Dimethoxymethane mechanism is |
| 408 | also introduced to ensure the compatibility between DEM sub-mechanism and Aramco 3.0 base |
| 409 | mechanism and adopted the same reaction rate rule. The thermodynamic and transport parameters for |
| 410 | new species in DEM sub-mechanism are determined by the group additivity method and properties |
| 411 | correlation method. This mechanism has been successfully validated against the macroscopic combustion |
| 412 | parameters of ignition delay times and laminar flame speed which are measured by shock tube/rapid |
| 413 | compression machine and spherical flame in constant volume vessel. A reasonable agreement between |
| 414 | experimental observation and numerical results is obtained, thus the reaction scheme should be |
| 415 | reasonably correct. But the rate constants of the DEM low temperature reactions computed by the |
| 416 | quantum chemistry and transition state theory are highly recommended in future research to reduce the |
| 417 | mechanism uncertainty. Besides, the experimental data of species profiles measured in the jet-stirred |
| 418 | reactor is needed for mechanism development and validation in the future. |
| 419 | A thorough comparison on the ignition delay times between DEM and n-heptane is conducted and it |
| 420 | reveals that: (i) DEM is more reactive at low temperature (500~670K) oxidation compared to n-heptane |
| 421 | which makes DEM an ideal carbon-neutral fuel for low temperature combustion (LTC) mode. (ii) The |

422 DEM ignition delay times exhibit a monotonous temperature dependence at the full temperature regime

| 423 | (500~1400K) |) which also favor | s LTC mode | . NTC behavior | only occurs at | $\varphi = 0.25$ and the | ne negative slope |
|-----|-------------|--------------------|------------|----------------|----------------|--------------------------|-------------------|
|-----|-------------|--------------------|------------|----------------|----------------|--------------------------|-------------------|

424 is weak. (3) DEM may not be a good chemical ignition source compared to n-heptane due to the

- 425 insufficient temperature increase and active radical accumulation at the low temperature heat release
- 426 stage. A similar conclusion is also reported for PODE₃ (polyoxymethylene dimethyl ether 3) which is an
- 427 ether with multiple oxygen atoms.

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