

Development of Surrogate Model for Oxygenated Wide-Distillation Fuel with Polyoxymethylene Dimethyl Ether

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ABSTRACT

Polyoxymethylene Dimethyl Ether (PODE_n) is a promising green additive to diesel fuel, owing to the unique chemical structure (CH₃O[CH₂O]_nCH₃, n≥2) and high cetane number. Together with the general wide-distillation fuel (WDF), which has an attractive potential to reduce the cost of production of vehicle fuel, the oxygenated WDF with PODE_n can help achieve a high efficiency and low emissions of soot, NO_x, HC, and CO simultaneously. In this paper, the first detailed reaction mechanism (225 species, 1082 reactions) which can describe the ignition characteristics of PODE₁ and PODE₃ at low temperature was developed. To validate this mechanism, rapid compression machine (RCM) was used to conduct the quasi-homogeneous experiments to measure the ignition delay time at various effective temperatures (600 K - 1000 K) for four different PODE₁/O₂/N₂/Ar mixture (φ=0.25, O₂:Ar=1:5; φ=0.5, O₂:Ar:N₂=1:2.5:2.5; φ=1.0, O₂:Ar:N₂=1:2.5:2.5; φ=1.0, O₂:Ar:N₂=1:5:5) and two different effective pressures (10 bar, 19 bar). Homogeneous Charge Compression Ignition (HCCI) experiments fueled with PODE_n (n=1-4) mixture, in which the mass fraction of PODE₃ is about 88.9% were also conducted in a naturally aspirated single-cylinder HCCI research engine at 1600 r/min, 0.4 charge-mass equivalence ratio, and 42% exhaust gas recirculation (EGR) to take the real engine working condition into consideration. Good agreement was achieved in the comparison of the experimental data and the simulation results utilizing our newly developed mechanism for PODE₁ and PODE₃. Considering the fact that PODE_n is more frequently used as a blending component in diesel engine, a reduced multi-component mechanism (354 species, 943 reactions) for oxygenated WDF with PODE_n (covering surrogates like PODE₃, *n*-heptane, *iso*-octane, etc.) was developed and then validated with Direct-Injection Compression Ignition (DICI) engine experiments fueled with oxygenated WDF (gasoline/diesel/PODE_n mixture) at 1600 r/min, 0.8 MPa indicated mean effective pressure (IMEP), and 25% EGR. This surrogate model will contribute to the design of oxygenated WDF by blending PODE_n, and to the prediction of the combustion and emission characteristics of engines using oxygenated WDF.

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INTRODUCTION

The impending depletion of petroleum resources, climate change effects, and energy security have been the driving force of human's searching for alternative and clean fuels. Polyoxymethylene dimethyl ether (PODE_n) is an oxygenated fuel that can become alternative for diesel engines. The condensed structural formula of PODE_n is CH₃O[CH₂O]_nCH₃, which indicates that PODE_n has a high oxygen content and the potential to reduce particulate matter (PM) emissions. Lump et al. conducted the engine experiment with diesel blends with 10-20% PODE₃₋₄, and found a reduction of over 40% in emissions with PM, soot, and particulate number [1]. Moreover, the lower soot emission through the addition of PODE_n brings an increasing exhaust gas recirculation (EGR) compatibility, thus helping break the soot-NO_x trade-off relationship [1, 2, 3, 4]. The ignition propensity of PODE_n is usually high, though depending on the specific value of *n*. The cetane number will be over 60 if the value of *n* is no less than 2 [5], while the minimum cetane number required by the European Standard EN 590 is 51 [6]. The good ignitability and high oxygen content result in lower CO and unburned hydrocarbons (HC). In 2003, Sanfilippo et al. reported two set of engine test results using a

mixture of PODE₂₋₆ as the fuel in a patent, in which the NO_x, PM, and HC emissions were extremely reduced and remain below the Euro V limit [7]. In 2004, Fleisch and Sills tested blends of PODE₃₋₈ with diesel and also found a reduction in PM, NO_x, and HC emissions [8]. From 2012 to 2014, Pellegrini et al. published a series of study about the combustion behavior and emission performance of a mixture of PODE₃₋₅ and PODE₃₋₅ blended with diesel in a light-duty diesel engine [9, 10, 11]. Their experiments demonstrate that PODE_n enables the simultaneous optimization of NO_x, PM and noise. Recent research by Liu et al. in 2015-2016 shows the blends of gasoline/diesel/PODE₃₋₄ can significantly reduce CO, HC, PM, and NO_x emissions, and slightly increase thermal efficiency [3, 4, 12]. All these results prove the advantage of PODE_n on reducing emitted pollutions.

It should be noted that the combination of general Wide-distillation fuel (WDF) and PODE_n can bring an effect of win-win cooperation. Originally proposed by Wang et al. [13], WDF refers to fuels with a wide distillation range from the initial boiling point (IBP) of gasoline to the final boiling point (FBP) of diesel. In the distillation process covering the entire range of gasoline, kerosene, and

diesel can be used to produce a novel fuel called full-distillation fuel (FDF) [14] from petroleum directly. Thereby, WDF has the potential to simplify the process and reduce the cost during the production of vehicle fuel. Currently, the most convenient way to obtain WDF is to blend commercial gasoline and diesel directly [15, 16, 17]. Gasoline/Diesel (GD) blends reduce the soot emissions of diesel engines with the penalty of combustion efficiency. The addition of PODE_n into GD blends can achieve a higher combustion efficiency and thermal efficiency than GD blends, even slightly higher than diesel fuel, and can further lower the level of soot emissions and bring the best NO_x -soot trade-off [3]. These characteristics revealed by former researchers makes PODE_n an attractive diesel additive or substitute.

In the process of evaluating the performance of blends of conventional fuels and PODE_n , as well as other possible additives, and of optimizing the percentages of different constituents, computation modeling of the combustion of PODE_n in laboratory-scale and engine experiments is valuable because it is relatively inexpensive and allows great flexibility. In order to simulate the combustion characteristics of engines fueled with PODE_n , a chemical kinetic mechanism describing the combustion of PODE_n is needed. Considering the fact that PODE_n might be used as an additive to diesel or other fuels, the mechanism should be capable of simulating the combustion processes of blended fuels. Therefore, this work is aimed at developing the oxidation mechanism for pure PODE_3 as a surrogate fuel for PODE_n and the multi-component mechanism for the mixture of PODE_3 and 11 other important surrogates, including *n*-heptane, *iso*-octane, toluene, ethanol, methanol, *n*-decane, *n*-dodecane, *n*-hexadecane, diisobutylene, cyclohexane, and methyl-cyclohexane, to represent the blends of oxygenated WDF containing PODE_n .

Although there are quite a few studies about the combustion and emission performance of PODE_3 or PODE_3 blends in real engines, the research about the chemical mechanism for PODE_3 is rather limited. To our best knowledge, only high-temperature kinetic mechanism for PODE_3 has been presented by Sun et al. [18]. The high-temperature mechanism plays a significant role in PODE_3 flames. However, it is not sufficient to describe the combustion of PODE_3 in real engines due to the absence of reaction mechanism in low-temperature range. For lack of low-temperature mechanism, the ignition phenomenon cannot be correctly predicted, and impractical pressure and temperature variation and even misfire will happen in the simulation. In order to close the gap and develop a comprehensive mechanism for PODE_3 , the low-temperature region (lower than ~ 900 K) should be studied. The low-temperature mechanism is especially important in many advanced combustion engines in which ignition time scale has large effects on the organization of spray and combustion progress. Thereby, this work places more emphasis on the low-temperature combustion of PODE_3 and PODE_3 blends.

It is useful to review and learn from the chemical kinetic mechanisms about analogous molecules such as dimethyl ether (DME), PODE_1 , etc. Their sub-structure around the reactive site and reaction rate constants may be similar to those about PODE_3 , though the reactants are not completely the same.

There have been numerous experimental and theoretical studies about DME. In 1997, Edgar et al. proposed a kinetic mechanism to describe the pyrolysis, oxidation, and auto-ignition of DME at high pressures,

and compared with the experiments in a constant volume apparatus [19]. In 1998, Curran et al. proposed a detailed chemical kinetic model for DME oxidation over a wide range of temperature and pressure conditions, and validated their mechanism with the experiments in a jet-stirred reactor (JSR) and shock tube (ST) [20]. Afterward, Fischer et al. and Curran et al. improved their mechanism according to the high- and low-temperature oxidation experiments in flow reactors in 2000 [21,22]. In 2008, Zhao et al. studied the unimolecular decomposition reaction of DME theoretically using RRKM/master equation (ME) calculations [23]. They developed a new mechanism for DME combining their theoretical computation, the mechanism from Curran et al., and some updated small molecule/radical kinetic and thermochemical data. A large set of experimental data, including flow reactor, JSR, ST, and laminar flame, were used to validate their revised mechanism. In 2013, Liu et al. updated the DME model based on Zhao's mechanism in 2008 [23], and compared with the experimental results in premixed flat flames and the computational prediction from previous mechanisms [24]. In 2015, Burke et al. incorporated high-level rate constant measurements and calculations where available for the reactions of DME, and validated the improved mechanism with a wide range of available literature data including flow reactors, JSR, ST ignition delay times, ST speciation, rapid compression machine (RCM) ignition delay times, flame speeds, and flame speciation data [25]. In the same year, but later than Burke et al., Rodriguez et al. studied the low-temperature chemistry of DME using quantum calculations [26]. They also developed a new detailed kinetic model for DME, and achieved satisfactory agreement with experiments in JSR, flow reactors, ST, RCM, and flames.

As to PODE_1 , it was also studied by Edgar et al. in a similar way to their study on DME in 1997 [19]. In 2001, Daly et al. developed a detailed mechanism for PODE_1 through estimation of the rate constants, and investigated the oxidation of PODE_1 in a JSR [27]. The low-temperature chemistry was lumped as several contracted reactions and the second oxidation stage which leads to the chain branching effect at low temperatures was neglected. They found the agreement obtained for the conversion of PODE_1 and for the formation of products was satisfactory, except for temperatures below ~ 900 K. In 2010-2011, Dias et al. elaborated a new mechanism for PODE_1 , and successfully simulate lean and rich premixed PODE_1 flames in good agreement with experiments [28,29]. In 2014, Zhang et al. performed the ignition delay time measurements with ST and modified previously published PODE_1 mechanism [27,30]. In 2016, Sun et al. updated the Daly's model for PODE_1 [27] by incorporating the relevant kinetic parameters for DME and DEE in recent studies [18]. However, low-temperature chemistry was not included in all these mechanisms for PODE_1 .

In this work, we combined former researchers' work on these model fuel molecules like DME, PODE_1 , DEE, etc. with quantum chemistry computation on PODE_1 to construct the mechanism for PODE_3 in a systematic way based on well-defined reaction classes and hierarchical structure (section Modeling and Computation). That means, the mechanism for PODE_3 also includes PODE_1 and PODE_2 , and the same rate rules were employed for analogous reaction pathways in the sub-mechanisms for PODE_1 , PODE_2 , and PODE_3 . The mechanism was validated with RCM experiments for PODE_3 .

and Homogeneous Charge Compression Ignition (HCCI) engine experiments for PODE_n mixture of which the mass fraction of PODE₃ is about 90% (section Results and Discussion). Then the mechanism was merged with the multi-component mechanism for WDF surrogates [31] to characterize the performance of oxynated WDF (gasoline/diesel/PODE_n mixture) in a Direct-Injection Compression Ignition (DICI) engine (section Results and Discussion). The mechanism can be downloaded from

https://github.com/zhugeyicixin/PODEn_release.

MODELING AND COMPUTATION

Kinetic Mechanism Development

This detailed mechanism was developed in a systematic way based on well-defined reaction classes and hierarchical structure. The mechanism for PODE₃ is based on our assembled reaction network, the reaction rate constants we developed with *ab initio*/density functional theory (DFT) calculations, the reaction rate constants we assigned based on established rate rules, and the donor base mechanism from NUI Galway (DME part in AramcoMech 2.0) [25] and Sun's work [18]. The major classes of reactions listed in Table 1 were considered in the sub-mechanisms for PODE₁, PODE₂, and PODE₃. Considering the insufficient understanding about PODE₁, which is one of the most important model molecules for PODE₃, the rate constants for the key reactions about PODE₁ highlighted in bold in Table 1 were studied with electronic structure methods and reaction rate theory.

Table 1. Reaction classes considered in the mechanism for PODE₁₋₃. The classes highlighted in bold were studied with electronic structure methods and reaction rate theory.

Class ID	Reaction class
1	$RH = R' + R''$
2	$RH = R'H + CH_2O$
3	$RH + M = R + HM$
4	$R = R' + \text{Carbonyl molecule}$
5	$R + O_2 = RO_2$ (First addition of O ₂)
6	$RO_2 = QOOH$
7	$RO_2 + RO_2 = RO + RO + O_2$
8	$ROOH = RO + OH$
9	RO decomposition
10	$QOOH = \text{Cyclic ether} + OH$
11	$QOOH = \text{Carbonyl molecules} + OH$
12	$QOOH + O_2 = OOQOOH$ (Second addition of O ₂)
13	$OOQOOH = KET$ (carbonylhydroperoxide) + OH
14	$KET = \text{Oxygenated species} + OH$
15	Cyclic ether reactions with OH and HO ₂
16	Decomposition of carbonyl species

Similar to the definitions in mechanisms for regular alkanes [32], R, R', and R'' in Table 1 refers to the C_nH_{2n+1}O_x radicals or structures, and Q denotes C_nH_{2n}O_x radicals or structures. However, the reaction classes in the sub-mechanism for PODE₁₋₃ are quite different from those for regular alkane molecules. Because of the absence of C-C bonds in the C-O chain structure of PODE_n, there is no pathway leading to the formation of alkene. Instead of C=C, C=O is formed in the reaction classes (4) and (11). Besides, the concerted HO₂ elimination reaction ($RO_2 = \text{Alkene} + HO_2$) and reaction $QOOH = \text{Alkene} + HO_2$ [33], which contribute to the formation of alkene at low temperatures in the mechanism for regular alkane fuels, does not appear in the oxidation process of PODE_n. As a result, the subsequent reactions about alkene, including H-atom abstraction reactions from alkenes, addition of radical species O and OH to alkenes, reactions of alkenyl radicals with HO₂, CH₃O₂, and C₂H₅O₂, alkenyl radical decomposition, alkene decomposition, and retroene decomposition reactions [33], are also cancelled.

The core reactions can be mainly classified into two parts, high-temperature reaction classes (i.e. reaction classes (1) and (3-4)) and low-temperature classes (i.e. reaction classes (5-6) and (10-14)). The high-temperature reaction classes has been identified by Sun et al. [18], while the low-temperature chemistry about PODE₁₋₃ is introduced in this work for the first time. The low-temperature reaction classes can be further divided into two stages, the first oxidation stage (i.e. reaction classes (5-6) and (10-11)) and the second oxidation stage (i.e. reaction classes (12-14)). The first oxidation stage is critical because it includes the entrance channel (reaction class (5)) in the low-temperature chemistry, and the central species RO₂ and QOOH are produced during this stage. The second oxidation stage is also important because it accounts for the chain branching effect, thus having a significant impact on the overall reactivity. It is ideal to study all elementary reactions utilizing high-level theoretical calculation or experiments, but the large number of reactions make this idea less possible. In consideration of the computational power and the significance of different reaction classes, the reaction classes (3-4), (6), (10-11) for PODE₁ were investigated with quantum chemistry methods. For reaction class (3), the radical species M can be OH, HO₂, CH₃, H, O, O₂, CH₃O, CH₃O₂, O₂CHO, or OCHO, and only the reaction $RH + OH = R + H_2O$ was calculated because it is the most important one in these hydrogen abstraction reactions.

Other than $RH + OH = R + H_2O$, and reaction classes (4), (6), (10-11), the rate constants for those not studied theoretically were estimated based on analogous reactions. The reaction classes (1-2) were kept the same as the kinetic parameters in Sun's work [18], except that the pressure dependence of reaction class (1) was cancelled for a slightly better fitting to the experimental data from RCM. In the reaction class (3), the rate constant for the abstraction of the secondary hydrogen atom by CH₃ was taken to be the value in Dias' mechanism for PODE₁, namely $A = 5.0 \times 10^{12} \text{ cm}^3/\text{mol/s}$, $\beta = 0$, and $E_a = 9.7 \text{ kcal/mol}$ in the modified Arrhenius expression as shown in equation 1.

$$k(T) = A * T^\beta * \exp(-E_a / RT)$$



Where,

A = pre-exponential factor

T = temperature

β = temperature exponent

E_a = activation energy

R = universal gas constant

The reaction $RH + HO_2$ was taken to be the value for DME and HO_2 reacting [24,26], namely $A = 2.0 \times 10^{13} \text{ cm}^3/\text{mol/s}$, $\beta = 0$, and $E_a = 16.5 \text{ kcal/mol}$. On the basis of Sun's work, three reactions $RH + CH_3O_2/O_2CHO/OCHO$, which also appear in the Burke's mechanism for DME [25], were added in the reaction class (3), and the rate constants were also based on the corresponding reactions $DME + CH_3O_2/O_2CHO/OCHO$ in Ref. [25]. The rate constants for addition of first and second O_2 , the reaction classes (5) and (12), were estimated as $A = 1.3 \times 10^{15} \text{ s}^{-1}$ for primary carbon radical site, and $A = 2.8 \times 10^{15} \text{ s}^{-1}$ for secondary carbon radical site, respectively, and $\beta = -1.0$, $E_a = 0.0 \text{ kcal/mol}$ [34]. For the reaction class (7), the rate parameters: $A = 1.3 \times 10^{14} \text{ cm}^3/\text{mol/s}$, $\beta = -1.07$, and $E_a = -0.4 \text{ kcal/mol}$ for the corresponding reaction in the system of DME [25] were adopted. The reaction class (8), the dissociation of ROOH was assumed to have the same rate constant as the dissociation of CH_3OCH_2OOH , giving $A = 4.0 \times 10^{15} \text{ s}^{-1}$, $\beta = 0.0$, and $E_a = 42.9 \text{ kcal/mol}$ [26]. The rate constant for reaction class (9) was taken to be the values for the decomposition of CH_3OCH_2O radical, i.e. $A = 9.7 \times 10^{15} \text{ s}^{-1}$, $\beta = -1.1$, and $E_a = 20.6 \text{ kcal/mol}$ [26]. The rate constants for reaction class (13) were assumed as the same as those for reaction class (6). The rate constant for reaction class (14) was taken as that for the decomposition of carbonylhydroperoxide in Yasunaga's DEE mechanism [35], but the A-factor was multiplied by 5 and activation energy was lowered by 3 kcal/mol, i.e. $A = 5.0 \times 10^{15} \text{ s}^{-1}$, $\beta = 0$, and $E_a = 40.0 \text{ kcal/mol}$, when considering more C-O bonds, which are weaker than regular C-C bonds [18], are contained in the $PODE_n$ system. The reaction class (15) was estimated by analogy with the reaction between cyclic ether and OH/HO_2 in Rodriguez's mechanism for DME [26]. As for the reaction class (16), there are dozens of carbonyl species produced in the foregoing reactions. The rate constants for the decomposition of these carbonyl species were taken as the values for analogous reaction in Refs. [25,26,36,37].

The rate rules applied to $PODE_2$ and $PODE_3$ are the same with those applied to $PODE_1$ for the same reaction classes. However, in the reaction class (6), the secondary hydrogen atom transfer through a 8-membered ring transition state (TS) does not exist in the low-temperature chemistry for $PODE_1$ due to the limited chain length. The rate constant was estimated as that for the primary hydrogen atom transfer through a 8-membered ring TS in the system of $PODE_1$, while the activation energy was decreased by 3 kcal/mol due to the more labile nature of the secondary hydrogen atoms [27,34]. Similarly, in the reaction class (10), the formation of 6-membered ring cyclic ether from the QOOH with a secondary radical site was estimated by analogy with the formation of 6-membered ring cyclic ether from QOOH with a primary radical site while cutting down the

activation energy by 2 kcal/mol, because for a given ring size, the barrier for ring closure follows the order tertiary < secondary < primary [38].

The thermodynamic properties, including enthalpy, entropy, and heat capacity, are essential because they are used to determine the equilibrium constants, the reverse reaction rate constants, the enthalpy of reaction and so on. Electronic structure methods were used to calculate the thermodynamic properties for the new species in the sub-mechanisms for $PODE_{1-3}$, including RH, R, RO_2 , QOOH, OOQOOH, carbonylhydroperoxide, etc. The details can be found in section *Rate Constants Computation* because all thermodynamic properties can be easily obtained from the partition function, which is also the key in rate constants computation.

Rate Constants Computation

Ab initio and DFT methods were used to explore the potential energy surface (PES) related to the reactions in Figure 1. All electronic structure calculations were carried out with the Gaussian 09 software suit [39].

For reaction classes (4), (6), (10-11), a systematic conformational analysis [40] by simultaneously rotating every bond in the initial structure by -120° , 0° , 120° for optimization at the B3LYP/6-31G(d) level of theory was conducted to find all the low-energy stationary points on the PES. Then all reactants and products were located with the lowest single point energy on the PES. For a balance of accuracy and efficiency, a hybrid nonlocal density functional theory, Becke's three-parameter nonlocal exchange functional, and the Lee-Yang-Parr nonlocal correlation functional (B3LYP) [41,42] with CBSB7 basis set [43] were utilized to implement the optimization and analyze the vibrational frequencies. All the TSs were identified by the existence of singular imaginary frequencies and normal-mode vibration analysis. The cases with ambiguity were confirmed with intrinsic reaction coordinate (IRC) calculations, in which the TSs were rested on the maximum energy point in the reaction coordinate. To obtain a higher level of accuracy, the single point energies of all reactants, TSs, and products were calculated using a complete basis set method, CBS-QB3 [43], which is a compound method for accurate energy computation. For the purpose of hindered rotation correction in further rate constants calculation, the internal rotor potentials were calculated at the B3LYP/6-31G(d) level of theory. Relaxed scan was performed for the torsion around every rotatable bond between 0° and 360° with an incremental step of 10° . The high-pressure limit rate constants were calculated with canonical transition state theory (CTST), i.e.

$$k(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R} \exp\left(-\frac{V^\ddagger}{k_B T}\right) \quad (2)$$

Where,

k_B = Boltzmann's constant

h = Planck's constant