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A chemical kinetic mechanism for the low- and intermediate-temperature combustion of Polyoxymethylene Dimethyl Ether 3 ($PODE_3$)

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ABSTRACT

Polyoxymethylene Dimethyl Ether ($PODE_n$, n = 3–5) is a potential alternative fuel or a green fuel additive for diesel engines, owing to the unique C–O alternating chain structure ($CH_3O[CH_2O]_nCH_3$) and high cetane number. In this paper, the rate constants for five reaction classes about the model molecule $PODE_1$, including hydrogen abstraction, beta-scission of corresponding R radicals, isomerization of RO_2 radicals, and decomposition of QOOH radicals, were calculated with canonical transition state theory (CTST) at the CCSD(T)-F12a/aug-cc-pVTZ//M06-2X/def2-TZVPP or CBS-QB3//B3LYP/CBSB7 level of theory. Based on the quantum chemistry and chemical kinetic study of the model molecule $PODE_1$, the first detailed reaction mechanism (225 species, 1082 reactions) which can describe the ignition characteristics of $PODE_3$ at low and intermediate temperature was developed. To validate this mechanism, rapid compression machine (RCM) was used to conduct the quasi-homogeneous experiments to measure the total ignition delay time at various effective temperatures (640–865 K) for three different $PODE_3/O_2/N_2$ mixtures (ϕ = 0.5, O_2:N_2 = 1:8; ϕ = 1.0, O_2:N_2 = 1:15; ϕ = 1.5, O_2:N_2 = 1:20) and two different effective pressures (10 bar, 15 bar). Homogeneous Charge Compression Ignition (HCCI) experiments fueled with $PODE_n$ (n = 1–4) mixture, in which the mass fraction of $PODE_3$ is 88.9% were also conducted in a naturally aspirated single-cylinder HCCI research engine at 1600 r/min, two exhaust gas recirculation (EGR) rates (0%, 42%), and three different charge-mass equivalence ratios for each EGR rate 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 $PODE_3$. This surrogate model will contribute to the design of fuels blended with $PODE_n$, and to the prediction of the combustion and emission characteristics of engines using $PODE_n$.

1. Introduction

Human are always searching for alternative and clean ways to better utilize energy and to protect the environment. Polyoxymethylene Dimethyl Ether ($PODE_n$) is a potential alternative fuel for diesel engines. The condensed structural formula of $PODE_n$ is $CH_3O(CH_2O)_nCH_3$; the alternating chain structure consisting of carbon and oxygen atoms guarantees a high oxygen content and generates less soot precursors such as C_2H_2, C_2H_4, and C_3H_3 in combustion because of the lack of bonds connecting two carbon atoms, thus providing a potential to reduce particulate matter (PM) emissions. Furthermore, with an ability to produce lower level of PM emissions, a higher rate of exhaust gas recirculation (EGR) might be applied, thus suppressing the production of NO_x. The increased EGR compatibility may even help break the soot-NO_x trade-off typically observed in diesel engines [1–4]. In addition, $PODE_n$ has a high ignition propensity, though its cetane number depends on the degree of polymerization. When the specific value of n is larger than 1, the cetane number excesses 60 [5], higher than the minimum cetane number required by the European Standard EN 590 [6], which is 51. The good ignitability together with the high oxygen content can also contribute to reduce CO and unburned hydrocarbon (HC) emissions.

The capability of $PODE_n$ to reduce multiple harmful emissions has been reported by a series of former studies. In 2003, Sanfilippo et al. received a patent in which they demonstrated that the $PODE_{2\text{-}6}$ mixture as the fuel for a four-cylinder 1910 jtd FIAT diesel engine would extremely reduce the NO_x, PM, and HC emissions to a level below the Euro V limits [7]. The reduction in PM, NO_x, and HC emissions was also found by Fleisch and Sills, who conducted the engine test experiments with the blends of $PODE_{3\text{-}8}$ and diesel in 2004 [8]. In 2011, Lump et al.

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carried out experiments in diesel engines fueled with diesel blends containing 10–20% $PODE_{3-4}$, and found a reduction of over 40% in PM, soot, and particulate number emissions [1]. From 2012 to 2014, Pellegrini et al. studied the combustion and emission characteristics of the mixture of $PODE_{3-5}$ and the blends of $PODE_{3-5}$ and diesel in a light-duty diesel engine and in a light-duty diesel car [9–11]. Pellegrini et al. pointed out that the neat $PODE_n$ and the 50% blend of $PODE_n$ in diesel minimize the NO_x, PM, and noise simultaneously. Blending $PODE_n$ by 50% can bring a reduction of NO_x by ~80% and a reduction of PM by ~30% in their multi-cylinder engine test at 2500 rpm and 8 bar brake mean effective pressure (BMEP) with high EGR rate. The research by Liu et al. and Wang et al. in recent two years showed that by fueling gasoline/diesel/$PODE_{3-4}$ (35%: 35%: 30%) blends the emissions including CO, HC, and PM were reduced by 63%, 25%, and 90%, respectively, and the thermal efficiency was slightly increased by 1–2% in a diesel engine at 1600 rpm, 8 bar indicated mean effective pressure (IMEP) with EGR rate 30% [3,4,12]. In addition, the physical properties of $PODE_n$ are similar to diesel [1]. $PODE_n$ is non-toxic and miscible with diesel fuel in any desired ratio [1], which is beneficial to the practical utilization of $PODE_n$ as a fuel or a fuel additive. Burger et al. stated that $PODE_{2-5}$ can be blended to diesel fuel and used without changing the engine design [13]. Pellegrini et al. also reported that $PODE_{3-5}$/diesel blends with the volume fraction of $PODE_{3-5}$ up to 10–12% can be used in non-dedicated engines [9].

The $PODE_n$ can be synthesized using feedstocks with end-group (CH_3O–, CH_3–) providers, such as methanol, dimethyl ether (DME), or $PODE_1$, and chain-group (–CH_2O–) providers, such as formaldehyde, trioxane, or paraformaldehyde. The detailed synthesis procedure has been depicted in Ref. [4,5,15]. The production costs are relatively low compared to hydrocarbons [1], especially in China, where the coal-based C_1 chemicals like methanol and formaldehyde are facing serious oversupply [5,15]. Low-cost commercial production of $PODE_n$ has been realized in China recently [5,14]. Tsinghua University developed the technique for producing $PODE_n$ in large scale in 2012, and established the industrial reactor with the capacity of 10 kton/year in 2014. The cost of production is close to that of diesel [4], making $PODE_n$ an attractive diesel additive.

The critical properties of $PODE_{1-6}$ [3], which are usually concerned in the design of fuels, are listed in Table 1. For $PODE_n$ with difference value of n, the optimal chain length is n = 3–5 [5,9] or n = 3–4 [13]. Due to the excessive saturated vapor pressure and low boiling point, $PODE_1$, which is also known as methylal, may vaporize gradually while in storage and is prone to cause “gas lock effect” [16]. As an exception, the cetane number (29) of $PODE_1$ is extremely low compared with other ethers in the family of $PODE_n$, preventing $PODE_1$ from being a proper fuel for diesel engine. $PODE_2$ has a proper cetane number of 63, but the flash point is too low to fulfill the security criterion [5]. $PODE_{n>5}$ is not suitable for low-temperature usage, because the melting point is higher than room temperature, and $PODE_{n>5}$ is tend to precipitate at low temperatures and may clog filters and other parts of the fuel system [5,13]. Hence, $PODE_3$ is the smallest-sized $PODE_n$ compound that is qualified for utilization in practical conditions. Comparing with $PODE_4$ and $PODE_5$, the melting point and boiling point of $PODE_3$ is also lower, indicating a better low-temperature fluidity and volatility. $PODE_3$ has a boiling point of 156 °C, lower than the general boiling range of hydrocarbons in diesel, 180–360 °C. It is also expected that such a volatile component increases the proportion of a premixed combustion in diesel engine.

This work is focused on the development of chemical kinetic mechanism for $PODE_3$, which would be valuable in the simulation of the combustion process of $PODE_n$ and would help reduce the time and cost when designing fuels blended in $PODE_n$ and optimizing engines fueled with $PODE_n$. To date, there is not too much research about the combustion mechanism for $PODE_3$, though quite a few studies about the engine performance of $PODE_3$ or blends containing $PODE_3$ exist. To our best knowledge, only the high-temperature mechanism for $PODE_3$ has been investigated with estimation methods by Sun et al. [17]. In order to close the gap and develop a comprehensive combustion mechanism for $PODE_3$, this work is focused on the low- and intermediate-temperature region (typically < 800 K and 800–1200 K). The low- and medium-temperature mechanism plays an important role when simulating diesel engine combustion. Especially in many advanced combustion engines, ignition time scale has large effects on the organization of spray and combustion progress, and the mechanism capable of describing the ignition phenomenon is necessary.

In this work, we constructed the mechanism for $PODE_3$ in a hierarchical way, which means, the mechanism for $PODE_3$ also includes $PODE_1$ and $PODE_2$. The same rate rules were employed for analogous reactions in the sub-mechanisms for $PODE_1$, $PODE_2$, and $PODE_3$. The rate constants came from estimation based on former researchers’ work on model molecules including $PODE_1$ [17–21], dimethyl ether (DME) [18,22–28], and diethyl ether (DEE) [29,30], and from the theoretical study on $PODE_1$ utilizing quantum chemistry in this work. To validate the proposed model, experiments were carried out to measure the total ignition delay time and pressure profile using a Rapid Compression Machine (RCM) and a Homogeneous Charge Compression Ignition (HCCI) engine.

2. Computation and modeling methods

2.1. Kinetic mechanism development

The detailed mechanism for $PODE_3$ was developed based on the assumption that the reaction classes for $PODE_n$ and regular alkanes are similar, because the active reaction sites are still the carbon atoms in the structure of $PODE_n$, where the important reactions such inter- or intramolecular hydrogen transfer and oxygen addition happen. The major classes of reactions listed in Table 2 were considered in the sub-mechanisms for $PODE_1$, $PODE_2$, and $PODE_3$. Similar to the definitions in mechanisms for regular alkanes [31], R, R′, and R″ in Table 2 refers to the $C_nH_{2n+1}O_x$ radicals or structures, and Q denotes $C_nH_{2n}O_x$ radicals or structures. The formation and consumption of R, RO_2, and QOOH are the core process in the mechanism for both $PODE_n$ and regular alkanes. Different from regular alkanes, because of the absence of C—C bonds in the molecular structure of $PODE_n$, the pathways leading to the formation of alkenes do not exist. When a double bond is formed, carbonyl species containing C═O bonds are produced instead of alkene products.

The reactions in Table 2 can be mainly classified into two parts, high-temperature reaction classes (i.e. reaction classes (1–4)), which

Table 1
Properties of $PODE_n$ with n = 1–5.

Molecule	Molecular formula	Density at 25 °C (g/cm^3)	Melting point (°C)	Boiling point (°C)	Cetane number	Oxygen content (%)	Lower heating value (MJ/kg)
$PODE_1$	$C_3H_8O_2$	0.86	−105	42	29	42.1	22.4
$PODE_2$	$C_4H_{10}O_3$	0.96	−65	105	63	45.3	20.3
$PODE_3$	$C_5H_{12}O_4$	1.02	−41	156	78	47.1	19.1
$PODE_4$	$C_6H_{14}O_5$	1.06	−7	202	90	48.2	18.4
$PODE_5$	$C_7H_{16}O_6$	1.10	18.5	242	100	49.0	17.9
$PODE_6$	$C_8H_{18}O_7$	1.13	58	280	104	49.6	17.5