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DOI: 10.1007/s12209-013-1936-5

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## Chemical Kinetic Modeling for the Effects of Methyl Ester Moiety in Biodiesel on PAHs and NO<sub>x</sub> Formation<sup>\*</sup>

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**Abstract:** In order to investigate the effects of methyl ester moiety on polycyclic aromatic hydrocarbons (PAHs) and NO<sub>x</sub> formation in biodiesel combustion, the combined models were developed based on detailed methyl butanoate (MB) oxidation model and n-butane model. Also, PAHs detailed reaction mechanism and NO<sub>x</sub> formation mechanism were added to the detailed models to form the combined models. The combined models were used to compare the combustion of n-butane and MB in a shock tube simulation to understand the effects of methyl ester moiety. The results indicated that compared with n-butane, the methyl ester moiety in MB leads to different reaction pathways, more CO and CO<sub>2</sub> formation and less formation of PAHs precursors such as ethylene and acetylene. In addition, a better chemical insight into the effects of methyl ester moiety on NO<sub>x</sub> formation was given, which will help to understand the combustion process of biodiesel.

**Keywords:** biodiesel; methyl butanoate; PAHs; NO<sub>x</sub>; chemical kinetics

The environment deterioration and climate change caused by using petroleum push people to seek sustainable surrogate fuels. Biodiesel consisting of fatty acid methyl esters (FAMES) has been proved to be an attractive choice as it can produce less carbon monoxide and particulate matter compared with conventional diesel<sup>[1-3]</sup>. However, it is reported that there is a slight increase in NO<sub>x</sub> emission caused by the oxygen in the biodiesel<sup>[3, 4]</sup>. With the wide use of biodiesel, increasing researches were conducted to better understand the combustion behavior of biodiesel.

Kinetic modeling has been proved to be an effective way to investigate fuel combustion characteristics, in which surrogate molecules are usually used due to the complexity of biodiesel. Methyl butanoate (MB), called methyl ester moiety, is usually chosen as a surrogate of biodiesel since the alkyl chain of MB is long enough to reproduce the behavior of biodiesel combustion and possesses the primary features of biodiesel.

Fisher *et al.*<sup>[5]</sup> developed a detailed chemical kinetic model for methyl butanoate as a surrogate of biodiesel. The detailed model was combined with n-butane mechanism which is obtained from Lawrence Liver National

Laboratory (LLNL) n-heptane mechanism<sup>[6]</sup>. Metcalfe *et al.*<sup>[7]</sup> and Dooley *et al.*<sup>[8]</sup> developed this detailed model further and verified it with a series of experiments. Lin *et al.*<sup>[9]</sup> studied the role of methyl ester moiety in biodiesel with the comparison of combustion characteristics between methyl butanoate and n-butane. They found that the fuel-bound oxygen contained in the methyl ester moiety leads to the significant production of both carbon monoxide and carbon dioxide which cannot occur in the combustion of n-butane, and that the soot precursors have a reduction in methyl butanoate. Sarathy *et al.*<sup>[10]</sup> conducted an experiment with methyl trans-2-butenate (C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>, MC) to analyze the double-radical effects of methyl ester in biodiesel under jet stir reactor (JSR) and opposed-flow diffusion flame conditions. They observed the combustion process of MC and compared the experimental data with those of MB<sup>[11]</sup>. Westbrook *et al.*<sup>[12]</sup> applied several oxygenated fuels such as methanol, ethanol and methyl butanoate to study the effects of molecular structure of the oxygenated species on soot-suppression efficiency. They found that the C—O imbedded in oxygenated species effectively displaces carbon in the original diesel fuel, so less carbon will be available to form

Accepted date: 2012-08-17.

<sup>\*</sup>Supported by National Natural Science Foundation of China (No. 50776077).

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polycyclic aromatic hydrocarbons (PAHs). These studies suggested a strong relationship between the oxygen in biodiesel and the formation of PAH precursors. How methyl ester moiety affects the pathways to form PAHs and NO<sub>x</sub> still need be further researched.

To better understand the relationship between PAHs and NO<sub>x</sub> formation with chemical structure, a combined chemical kinetic model was developed based on methyl butanoate mechanism<sup>[8]</sup> which was combined with PAHs detailed reaction mechanism<sup>[13]</sup> and NO<sub>x</sub> formation mechanism<sup>[14]</sup>. As n-butane is the alkane corresponding to MB, and the chemical structure of n-butane is only a methyl ester moiety less than MB, a combined n-butane model was also developed to isolate the effects of ester moiety on PAHs and NO<sub>x</sub> formation.

## 1 Chemical kinetic model

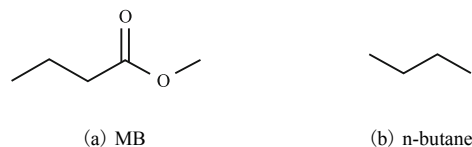
### 1.1 Combined models

Some researchers found the ignition delay time of MB does not match well with the experimental results of long chain FAMES. In addition, auto-ignition and low temperature experimental data<sup>[15,16]</sup> indicated that MB does not exhibit the behavior of cool flame and negative temperature coefficient (NTC), which are significant characteristics of long chain FAMES found in biodiesel. As a surrogate of methyl ester in biodiesel, MB does not seem as good as some long chain FAMES such as methyl decanoate (MD) whose detailed mechanism was developed by Herbinet *et al*<sup>[17]</sup>.

However, MB still has an important role in investigating biodiesel combustion because the chemical mechanism of large molecular methyl esters such as MD requires a robust numerical solver and enormous computing power. Therefore, the chemical mechanism of MB can be used to understand the effects of methyl ester moiety on PAHs and NO<sub>x</sub> formation. n-butane is the corresponding alkane of MB and can be used to isolate the effects of methyl ester moiety compared with MB.

The structures of MB and n-butane (C<sub>4</sub>H<sub>10</sub>) are shown in Fig.1. MB contains the essential chemical structure of long chain FAMES, methyl ester termination and alkyl chain. Fast RO<sub>2</sub> (R is a carbon chain of alkyl or alkenyl) isomerization reactions are important for low-temperature chemical reactions that control fuel auto-ignition in CI engines. The alkyl chain of MB is long

enough to show the effects of fast RO<sub>2</sub> isomerization reactions.



**Fig.1 Structures of methyl butanoate and n-butane**

The combined kinetic model of MB, containing PAHs and NO<sub>x</sub> formation mechanisms, was developed based on detailed MB mechanism<sup>[8]</sup>. The PAHs formation mechanism in this paper comes from the detailed PAHs formation mechanism<sup>[13]</sup>, which was validated by several premixed laminar flame experiments. The NO<sub>x</sub> formation mechanism in this paper is the extended Zeldovich NO<sub>x</sub> mechanism which contains 4 species and 9 reactions<sup>[14]</sup>. In addition, a combined n-butane model was also developed in the same way to serve as a reference.

### 1.2 Kinetic model validation

Since ignition delay time or reaction time<sup>[18-20]</sup> is one of the most important parameters characterizing the combustion process of different fuels, in this paper, the ignition delay time of each fuel was used to validate the combined chemical models with original detailed models and experimental results. Ignition delay time was defined as the time from the beginning of simulation to the mo-

ment when  $\frac{d[\text{OH}]}{dt}$  increased to the maximum. The ignition delay time of MB was calculated in the shock tube module of CHEMKIN 4.1<sup>[21]</sup> under a condition given by Ref.[8], and its experimental data were taken from Ref.[8]. The ignition delay time of n-butane was calculated under a condition given by Ref.[22], and its experimental data were taken from Ref.[22].

As shown in Figs. 2(a) and (b), the ignition delay time of both MB and n-butane calculated with the combined models matches well with that calculated with the original detailed models and the experimental data. It means that the combined models can accurately reproduce the combustion of MB and n-butane, and that the PAHs and NO<sub>x</sub> formation mechanisms barely affect the accuracy of the models. However, there are slight differences, since the reactions of those PAHs precursors such as acetylene (C<sub>2</sub>H<sub>2</sub>) and propyne (C<sub>3</sub>H<sub>4</sub>) forming benzene (A<sub>1</sub>) are heat-absorbing reactions and lead to temperature decrease.

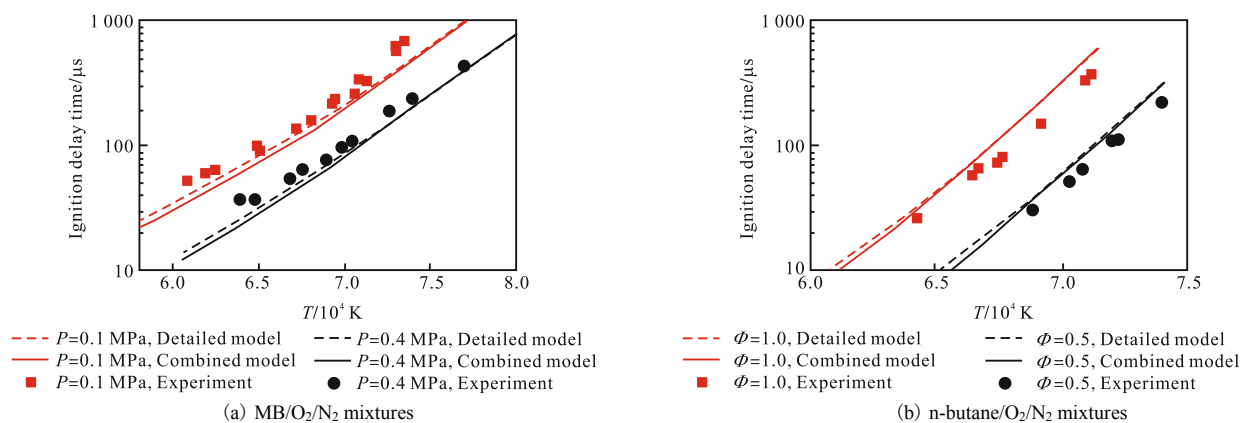


Fig.2 Calculated and measured ignition delay time of MB/O<sub>2</sub>/N<sub>2</sub> and n-butane/O<sub>2</sub>/N<sub>2</sub> mixtures

## 2 Modeling results and discussion

### 2.1 PAHs precursors

Since the unsaturated hydrocarbon species such as acetylene (C<sub>2</sub>H<sub>2</sub>) have been identified as major contributors to PAHs production in both diesel engines and laboratory flames<sup>[12, 13]</sup>, the PAHs formation pathways of rich MB fuel and n-butane fuel were traced with the proposed combined kinetic models.

The simulation was performed in the shock tube module of CHEMKIN 4.1 software package. Since PAHs were usually produced in the fuel-rich region, the ignitions of MB/n-butane fuels were calculated at an equivalence ratio of 3.0. The pressure and initial temperature were set as 1.0 MPa and 1 000 K, respectively. The major PAHs precursors, including acetylene (C<sub>2</sub>H<sub>2</sub>), propyne (C<sub>3</sub>H<sub>4</sub>) and propene (C<sub>3</sub>H<sub>6</sub>), are shown in Fig. 3. Com-

pared with MB, the carbon in n-butane is more likely to form unsaturated products after combustion. These unsaturated products will then form small aromatic species, including benzene (A<sub>1</sub>), naphthalene (A<sub>2</sub>), styrene, and eventually soot<sup>[13]</sup>. More CO and CO<sub>2</sub> are found in MB products than in n-butane products, and there are much fewer major PAHs precursors, such as acetylene (C<sub>2</sub>H<sub>2</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and alkene (C<sub>3</sub>H<sub>6</sub>), in MB products than in n-butane. The mole fractions of propargyl (C<sub>3</sub>H<sub>3</sub>) and propyne (C<sub>3</sub>H<sub>4</sub>p) are below  $2.5 \times 10^{-4}$  in both MB and n-butane products, however, they will be proved important in PAHs formation in later discussion. C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> show the largest mole fractions and seem to be the predominant PAHs precursors. The mole fraction of methyl aldehyde (CH<sub>2</sub>O) is higher in MB products than in n-butane, because the O atom bonded to C atom in methyl ester will be more likely to form oxygenated products.

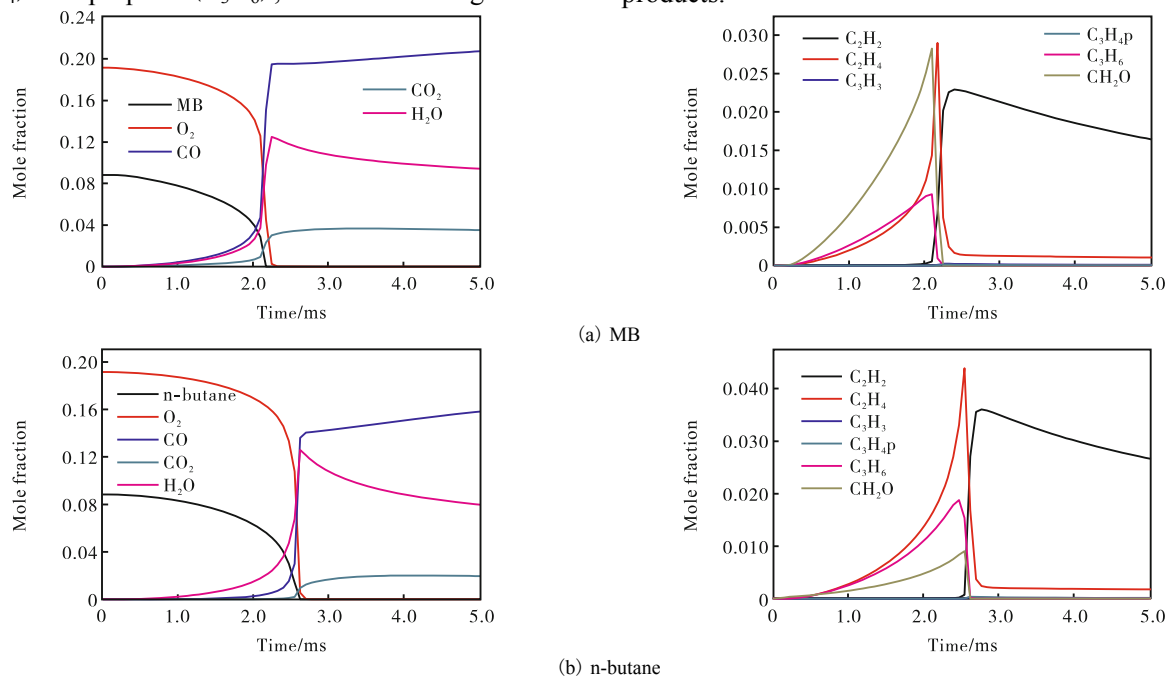
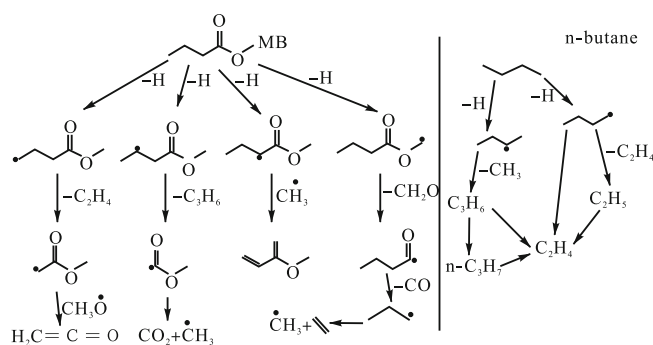


Fig.3 Mole fractions of major species in the fuel-rich ignition of MB and n-butane

As shown in Fig.4, MB mainly formed 4 alkylester radicals through H-abstraction reactions: MB2J ( $\text{CH}_3\text{CH}_2\text{CHC}(=\text{O})\text{OCH}_3$ ), MB3J ( $\text{CH}_3\text{CHCH}_2\text{C}(=\text{O})\text{OCH}_3$ ), MB4J ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$ ) and MBMJ ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2$ ). MB2J forms  $\text{HO}_2$  and  $\text{OH}$  through an isomerization reaction. MB4J is transformed into ME2J ( $\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$ ) through a  $\beta$ -scission reaction, and then into  $\text{CH}_3\text{O}$  and  $\text{CH}_2\text{CO}$ , and  $\text{CH}_3\text{O}$  primarily forms  $\text{CH}_2\text{O}$ , then  $\text{CHO}$ , and finally  $\text{CO}$ . The analysis of production rate showed that about 20% of MB turns into methoxycarbonyl ( $\text{CH}_3\text{OCO}$ ) which is an important intermediate product in MB combustion<sup>[23]</sup>, and finally produces  $\text{CO}_2$ . Therefore, with the methyl ester moiety of MB, the fuel forms more oxygenated products such as  $\text{CO}$ ,  $\text{CO}_2$  and methyl aldehyde ( $\text{CH}_2\text{O}$ ), and less C atom is left to form unsaturated hydrocarbons such as ethane and acetylene which are thought of as PAHs precursors.

As discussed above, the O atom in methyl ester moiety bonded to C atom likely leads to oxygenated products, accordingly, more methyl aldehyde ( $\text{CH}_2\text{O}$ ) will occur in MB products, which is consistent with Westbrook's research<sup>[12]</sup>. However, the O atom in methyl ester moiety is not fully used in every reaction pathway. In the pathway of MB3J, two O atoms finally lead to  $\text{CO}_2$ , which means that two O atoms capture only one C atom from a pool of carbon atoms that may form PAHs precursors.



**Fig.4** Main reaction pathways of MB/n-butane at  $T = 1\,000\text{ K}$

## 2.2 Pathway to form PAHs

The production rate can reflect the influence of elementary reactions on the corresponding products. The production rate of each reaction was calculated to find out the most important reactions and the main pathways for the formation of PAHs, as listed in Tab.1. In this paper, for both MB and n-butane, the production rates of the reactions (1)–(4) are very close to the total production rates of benzene ( $\text{A}_1$ ) and phenyl( $\text{A}_1$ —), which

means that these reactions are the main pathways to form benzene ( $\text{A}_1$ ). The formation of  $\text{A}_1$  is highly related to the production rates of unsaturated hydrocarbons. Accordingly, the role of methyl ester moiety is to reduce the production rate of  $\text{C}_2\text{H}_5$  and cause more MB4J to form ME2J and then oxygenated products. The reduction of unsaturated hydrocarbons such as acetylene ( $\text{C}_2\text{H}_2$ ) and propargyl ( $-\text{C}_3\text{H}_3$ ) consequently leads to the less formation of  $\text{A}_1$ .

$\text{A}_2$  is mainly formed through H-abstraction- $\text{C}_2\text{H}_2$ -addition (HACA) reactions<sup>[13]</sup>. The production rate of  $\text{A}_2$  in reaction (5) is close to its total production rate, which illustrates that this reaction is the major pathway to form  $\text{A}_2$ , although some  $\text{A}_2$ -1 is formed through reaction (6) that leads to the formation of  $\text{A}_2$  through reaction (7). Once the first ring is formed, consecutive reactions will only lead to the formation of substituted benzenes and larger PAHs with the HACA mechanism, and then  $\text{A}_2$  forms  $\text{A}_3$  and  $\text{A}_4$ . The formation of large PAHs is highly related to the formation of  $\text{A}_1$  and  $\text{C}_2\text{H}_2$ , while the methyl ester moiety of MB causes the less formation of unsaturated hydrocarbons and finally large PAHs.

**Tab.1** Important reactions of  $\text{A}_1$  and  $\text{A}_2$  formation

No.	Reactions
1	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \Rightarrow \text{A}_1$
2	$\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_2 = \text{A}_1$ —
3	$\text{n-C}_4\text{H}_5 + \text{C}_2\text{H}_2 = \text{A}_1$ — + H
4	$\text{A}_1$ — + H = $\text{A}_1$
5	$\text{A}_1$ — + $\text{C}_4\text{H}_4 = \text{A}_2$ + H
6	$\text{A}_1\text{C}_2\text{H}^* + \text{C}_2\text{H}_2 = \text{A}_2$ -1
7	$\text{A}_2$ -1 + H (+ M) = $\text{A}_2$ (+ M)

## 2.3 NO<sub>x</sub> formation

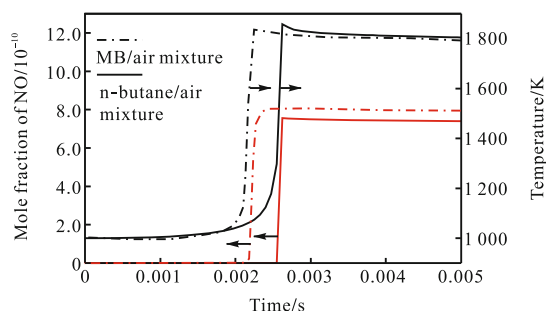
Some researchers found that the use of biodiesel in diesel leads to a slight increase in  $\text{NO}_x$  emission<sup>[23-25]</sup>. It is necessary to figure out the role of methyl ester moiety in the increase of  $\text{NO}_x$  formation. Since NO is the major content in  $\text{NO}_x$  emission, only NO is discussed here. Currently there are three NO formation mechanisms: Zeldovich (thermal) NO mechanism, Fenimore (prompt) NO formation mechanism<sup>[26]</sup> and NO formation via  $\text{N}_2\text{O}$ . Prompt NO is mainly produced at low temperature (below 1 000 K), and one of the important reactions,  $\text{CH} + \text{N}_2 \Rightarrow \text{HCN} + \text{N}$ , has lower activation energy than thermal NO formation reactions<sup>[27]</sup>. Therefore, prompt NO formation accounts for a small amount of total  $\text{NO}_x$  formation.  $\text{N}_2\text{O}$  mechanism is significant only when lean air-fuel mixtures repress the formation of CH, thus it can be ignored in internal combustion engines. In this paper, an

extended Zeldovich NO mechanism was used based on Ref.[14], and the reactions are shown in Tab.2.

**Tab.2 Reactions of NO<sub>x</sub> formation**

Reactions	$A_i$	$n_i$	$E_i$
$N + CO_2 = NO + CO$	$1.90 \times 10^{11}$	0.0	3 400.0
$N_2 + O = NO + N$	$1.80 \times 10^{14}$	0.0	76 100.0
$N + O_2 = NO + O$	$9.00 \times 10^9$	1.0	6 500.0
$NO + M = N + O + M$	$9.64 \times 10^{14}$	0.0	148 300.0
$N_2O + M = N_2 + O + M$	$1.26 \times 10^{12}$	0.0	62 620.0
$N_2O + N = N_2 + NO$	$1.00 \times 10^{13}$	0.0	20 000.0
$N_2O + O = N_2 + O_2$	$1.00 \times 10^{14}$	0.0	28 200.0
$NO + NO = N_2 + O_2$	$3.00 \times 10^{11}$	0.0	65 000.0
$N_2O + O = NO + NO$	$6.92 \times 10^{13}$	0.0	26 630.0

The simulation was performed with the shock tube module of CHEMKIN 4.1 soft package at the pressure of 1 MPa and the temperature of 1 000 K. Since NO<sub>x</sub> formation is related to high oxygen concentration, the equivalence ratio was set as 1.0. As shown in Fig. 5, the NO mole fraction in MB products is higher than that in n-butane. As discussed before, the methyl ester moiety in MB leads to the advancement of combustion phase and the timing of maximum temperature, and thus to the increase of NO formation, which is consistent with Ref.[28]. Otherwise, each O atom in methyl ester moiety bonded to one C atom will lead to the increase of CO/CO<sub>2</sub> formation. The higher the mole fraction of CO<sub>2</sub> is, the more N will form NO with reaction (1). In addition, the double bond in methyl ester leads to a high combustion temperature, and consequently the increase of thermal (Zeldovich) NO<sub>x</sub> formation. It is indicated that the methyl ester moiety can change not only the physical properties of fuel but also the ignition time and combustion temperature which have a great influence on NO<sub>x</sub> formation.



**Fig.5 Simulation of temperature and NO mole fraction for n-butane/air and MB/air mixtures ( $\Phi = 1$ , 1 MPa, initial temperature 1 000 K)**

It is reported that there is a coupling existing between NO and PAHs, which is caused not only by radiation-induced thermal effects, but also by reaction-induced

chemical effects<sup>[29]</sup>. The chemical effects are caused by the competition for C<sub>2</sub>H<sub>2</sub> between CH and PAHs, where CH is one of the species that appear in the pathways for the formation of prompt NO. With a sensitive analysis of the formation of NO, it is found that NO formation is sensitive to some reactions of PAHs precursors such as C<sub>2</sub>H<sub>4</sub>.

### 3 Conclusions

(1) Combined MB and n-butane kinetic models were developed, and then validated by the original detailed models and experimental data. Simulation results showed that the methyl ester moiety in MB can change the combustion pathways of MB, and that there are more PAHs precursors, such as C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, in MB combustion than in n-butane.

(2) With O atoms in methyl ester moiety, there are more oxygenated compounds such as CO, CO<sub>2</sub> and CH<sub>2</sub>O in the combustion products of MB, and then more C atoms are drawn from the carbon atoms pool of forming PAHs precursors.

(3) The oxygen imbedded in methyl ester moiety will advance combustion phase and lead to high combustion temperature, which facilitates the NO<sub>x</sub> formation. In addition, high concentration of CO<sub>2</sub> caused by methyl ester moiety in MB contributes to the NO<sub>x</sub> formation.

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(Editor: Zhao Yang)