Autoignition Studies of Unsaturated Methyl Ester: Methyl Crotonate

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1 Introduction

To meet the goals of the Paris Agreement [1], limiting the global warming to 2^{0} C above pre-industrial levels, CO₂ emissions from combustion-based power generation need to be reduced. Biofuels have attracted by the public and scientific communities as a partial or complete replacement of traditional fuels. Biofuels can also lead to reduction of carbon monoxide (CO), unburnt hydrocarbons (UHC) and particulate mass (PM) emissions compared to fossil fuels.

Biodiesel, the first-generation biofuels, can be synthesized from living organisms or from metabolic byproducts such as sugar, starch, vegetable oils, through an important process of transesterification to form fatty acid methyl esters (FAMEs) or fatty acid ethyl esters [2]. Some of the methyl esters are methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. Due to its large chain lengths and complicated components, it is quite challenging to study the biodiesel combustion experimentally and computationally. Hence, smaller surrogate fuels with similar chemical functional groups and properties are considered to meet the requirement of real fuels [3]. In this study, methyl crotonate (MC, $C_5H_8O_2$) was considered to understand the impact of unsaturation, due to (C=C) double bond on its combustion behavior.

Sarathy et al. [4] studied the detailed effect of FAME molecular structure on the combustion chemistry of saturated (i.e., methyl butonate) and an unsaturated (i.e., methyl crotonate) that were oxidized in opposed flow diffusion flame and a jet stirred reactor. Methyl crotonate combustion produces high levels of unsaturated hydrocarbons and aromatics that lead to soot production. Furthermore, Gaïl et al. [5] performed similar experiments in a jet-stirred reactor (JSR) at atmospheric pressure under dilute conditions over the temperature range 850-1400 K, and two equivalence ratios ($\phi = 0.375, 0.75$) with the residence time of 0.07 s to expand the experimental database. A new chemical kinetic reaction mechanism was developed with 301 species and 1516 reactions. This model of MC oxidation provides a better understanding on the effect of ester function and effect of unsaturation in combustion. Most recent Zhai et al. [6] performed pyrolysis experiments of these two methyl esters at 30, 150, and 780 Torr in a flow reactor over the temperature range of 773-1323 K, using gas chromatography-mass spectrometry. This study also observed the effect of C=C

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double bond in FAMEs might give rise to growing tendency of initial PAH and soot precursors in the whole thermal decomposition. In addition, an updated kinetic reaction mechanism was developed to validate the experimental data.

To date, most of the experimental data of the methyl crotonate oxidation were performed at atmospheric pressure or below conditions. However, modern combustion engines are working at high pressures, therefore understanding the kinetics of methyl crotonate oxidation at high pressures is essential. The current study is designed to investigate the auto-ignition property of methyl crotonate mixtures in rapid compression machine at varying fuel/oxidizer ratios ($\phi = 0.25$ -1.0) at pressures 20 and 40 bar over the temperature range 850-1100 K. Table 1. lists the experimental conditions of studied methyl crotonate mixtures based on the balanced chemical reaction (R1) for combustion of Methyl Crotonate (MC). Furthermore, chemical kinetic modeling was performed to obtain deeper insight of relevant ignition chemistry.

$$C_5H_8O_2 + 6(O_2 + 3.76N_2) = 5CO_2 + 4H_2O + 22.56N_2$$
 R1

Mix No	Mole Fraction				Equivalence Ratio(φ)	Pressure(bar) P _c
	MC	O ₂	N ₂	Ar		
1	0.008	0.192	0.36	0.44	0.25	20
2	0.0073	0.0877	0.4525	0.4525	0.5	20
3	0.0073	0.0877	0.5882	0.3167	0.5	40
4	0.008	0.064	0.6496	0.2784	0.75	40
5	0.008	0.064	0.4176	0.5104	0.75	20
6	0.008	0.048	0.3776	0.5664	1	40
7	0.008	0.048	0.4248	0.5192	1	20
8	0.0115	0.1385	0.4250	0.4250	0.5	20

Table 1. Experimental conditions of the RCM of methyl crotonate (MC)

2 Experimental apparatus

The Rapid Compression Machine (RCM) experiments were performed at Physikalisch-Technische Bundesanstalt (PTB), Germany. The design is similar to the one designed by Mittal et al. [7]. It is a single piston rapid compression machine, which is pneumatically driven and hydraulically braked. The RCM consists of three chambers, namely reactor, hydraulic and pneumatic chamber. The reactor chamber has an internal diameter of 50 mm and consists of 6 ports for pressure sensors, gas inlets, and gas outlets. The reactor chamber was designed to sustain a maximum working pressure of 200 bar and can be operated in a temperature range of 600–1100 K. A creviced piston is used to compress the gas in the reactor chamber, which is driven by an arrangement of a pneumatic piston and high-pressure air tank. A solenoid valve connected to the hydraulic chamber and the oil reserve chamber can be triggered to release the hydraulic pressure to move the piston forward. Towards the end of the compression stroke, the piston is smoothly decelerated and finally stopped by the piston stopping groove. The machine is designed with a variable volumetric ratio, accessible through substitution of the end wall by different end wall inserts that results in the change of the distance between the piston front and the end wall at the top dead center position.

Heating tapes were used to vary the initial temperature of the gas mixtures from 296 K to 380 K. The temperatures of the mixtures in the combustion chamber were measured with a Pt-Rh thermocouple located in the wall of the combustion chamber and of the mixing cylinder. This setup ensures a homogeneous initial temperature and also allows to study various initial temperatures. The pressure time histories were recorded using a Kistler (601H) pressure transducer with a charge amplifier (Type 5018) and is digitized using a spectrum data acquisition card (M2i.3016-Exp). In this study, test mixtures were first prepared manometrically in a stainless-steel tank at room temperature using a MKS manometer to measure the partial pressures of the respective gases. The steel tank was cleaned in advance with bath gases to remove impurities before filling the final mixture. Argon and nitrogen were used as bath gases in the RCM experiments to obtain the appropriate value of the compressed gas temperature (Tc). These gaseous mixtures were allowed to homogenize for around 12 h before transferring them into the reaction chamber.

2.1 Kinetic Modeling

Simulations were performed using an in/house Cantera [8] code. In order to account heat losses in the rapid compression machine, volume profiles were given to the constant volume reactor model to simulate the heat loss during and after compression. The literature mechanism of Gaïl et al. [5] and Salamanca et al. [9] were selected for the simulation. Gaïl et al.'s model contains 301 species and 1516 reactions and was validated against MB and MC oxidation in the Jet stirred reactor (JSR) and under counterflow diffusion flames. The mechanism of Salamanca et al. contains 404 species 2561 reactions and was validated against laminar flames of blends of petroleum-based fuels with MB and MC. The selected mechanisms were first validated against the literature experimental data of ignition delay times of methyl crotonate measured in a shock tube at 8 bar and temperature between 1450-1600 K [10]. Figure 1 presents the comparison between simulation and the literature data [10], good agreement was found for both mechanisms however the predicted ignition delay time from the mechanism of Salamanca et al are longer than that from Gail et al. To further validate the performance of both mechanisms, they were applied for the simulation of the ignition delays measured in this work.



Figure 1. Measured (closed symbols) [10] and simulated (lines) ignition delay time of methyl crotonate/O₂ mixtures at pressure = 8 bar, phi = 1.0

3 Results & Discussion

Figure 2 despites the measured IDTs of mixture 8 and the measured IDTs from our previous study [11] on the methyl butanoate at 20 bar. Both mixtures have an equivalence ratio of 0.5 and the same dilution. In general, the IDTs of MC are higher than MB and this discrepancy decreases when the temperature decreases. This behavior demonstrates that the reactivity of the FAMEs decreases with increasing degree of unsaturation. Figure 3 presents the comparison between the measured ignition delay times (IDTs) of the studied mixtures (1-7) together with the simulated results based on the selected mechanisms [5], [9]. In general, the measured IDTs decrease with decreasing equivalence ratio at both 20 and 40 bar. However, at 40 bar the dependence of ignition delay on the equivalence ratio is smaller compared to that at 20 bar. Moreover, the measured IDTs at 40 bar are getting closer at lower temperatures, i.e., the activation energy varies slightly with the equivalence ratio which was not observed for the measurements at 20 bar.



Figure 2. Comparison of ignition delay times of MB and MC mixtures of same dilution



Figure 3. Measured (symbols) and simulated (lines) ignition delay times of MC mixtures in RCM at 20 (left) and 40 (right) bar. Applied mechanisms: Solid lines Gaïl et al. [5]; Dashed lines Salamanca et al. [9]

The obtained experimental data were then applied to validate the performance of the mechanism from Gail et al. [5] and Salamanca et al. [9] at intermediate temperatures and elevated pressures. The simulated IDTs using the mechanism of Gaïl et al. and Salamanca et al are plotted in Figure 3 with full and dashed line, respectively. In general, the simulated IDTs using the mechanism of Salamanca et al. are longer than using the mechanism of Gaïl et al. At 20 bar, for the equivalence ratios 0.5 and 1.0 both mechanisms underpredict the ignition delay at temperature higher than 1040 K and overpredict the ignition delay at temperatures below 1040 K. For the equivalence ratio 0.25, both mechanisms overpredict the IDTs over the studied temperature range and the discrepancy between simulation and measurement becomes larger at lower temperatures. Moreover, no ignition was observed in the simulation applying both mechanisms at temperatures below 970 K. At 40 bar, both mechanisms overpredict the ignition delay of the MC mixtures at the RCM conditions and the discrepancy becomes larger at lower temperatures as well. The slight variation of activation energy at 40 bar is captured by both mechanisms, although the interception points of the simulated IDTs from the simulation are at higher temperature compared to the measurement. The temperature of ignition onset at 40 bar is lower than that at 20 bar, however, no ignition was observed in the simulation at temperatures below 950 K with both mechanisms. By analyzing the reaction path in both mechanisms, neither mechanism contains the low temperature chemistry pathway describing the oxidation of MC.

None of the literature mechanism is able to predict the measured ignition delay in RCM, however, to investigate the chemistry behind the ignition, a sensitivity analysis (SA) was conducted on the formation of OH radical which can represent the ignition delay. Figure 4 presents the normalized sensitivity on OH radical at the time of ignition for stoichiometric mixture at 1000 K and 20 bar. The key reactions that are most sensitive to the formation of OH radical are very different between mechanism of Gaïl et al. [5] and mechanism of Salamanca et al. [9]. In the mechanism of Gaïl et al. reactions between methyl crotonate (named as MB2D in mechanism) and OH radical namely MB2D + OH = MB2DMJ + H₂O and MB2D + OH = MB2D4J + H₂O dominate the formation and consumption of OH radical, reaction of C3 molecules/radicals such as C₃H₅O plays also important role for the ignition. In the mechanism of Salamanca et al. reaction of H₂O₂ (+M) = 2OH (+M) is the most sensitive reaction of OH formation while reaction of OH formation. However, no C3 reaction was identified to be important by the mechanism of Salamanca et al. Moreover, the chemistry of HO₂ radical is found to be more important in the mechanism of Salamanca et al. than in the mechanism of Gaïl et al.



Figure 4. Normalized sensitivity analysis of MC at $\phi = 1$, P = 20 bar, T = 1000 K Left: Gaïl et al.[5], Right: Salmanca et al. [9]

In the modeling study of the literature shock tube data, the selected mechanisms [5] [9] are able to predict the ignition delay at elevated temperatures (cf. Figure 1). Therefore, a sensitive analysis is performed to investigate the chemistry differences at high and intermediate temperatures. Figure 5 presents the SA on OH radicals for stoichiometric MC/O₂ mixture at 1400 K and 8 bar. Reaction of $H + O_2 = O + OH$ shows domination of OH formation at elevated temperature in both mechanism, however, the decomposition of methyl crotonate (MB2D in mechanism) into crotonyl oxyl (BAOJ2D) and methyl (CH₃) radicals also shows great importance for the OH formation in the mechanism of Gail et al. [5] and this may lead the performance of the mechanism of Gail et al. better than Salamanca et al. at elevated temperatures. Moreover, unlike at the intermediate temperatures, the C1-C3 chemistries in both mechanisms show minor importance for the OH formation at elevated temperature although the key reactions from both mechanisms are more in common.



Figure 5. Normalized sensitivity analysis on OH radical for MC ignition at $\phi = 1$, P = 8 bar, T = 1400 K Left: Gaïl et al. [5], Right: Salmanca et al. [9]

4 Conclusions

In this study, the ignition delay time of different methyl crotonate/oxygen mixtures are measured in a Rapid Compression Machine over temperature range of 900 - 1100 K at 20 and 40 bar. The methyl crotonate shows lower reactivity compared to methyl butanoate due to its higher degree of unsaturation. The experimental data were further applied as validation target for the literature mechanism of Gail et al. [5] and Salamanca et al. [9]. Both mechanisms were applied first to simulate the literature experimental data of ignition delay time at elevated temperatures measured in a shock tube [10] and good agreement was found between simulation and measurement. However, none of the mechanisms can predict the ignition delay times measured in this work satisfactorily. The sensitivity analysis showed that both mechanisms do not contain low temperature chemistry pathways for methyl crotonate oxidation, while the chemistry for elevated temperatures are more in common.

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