



Experimental and modeling studies of small typical methyl esters pyrolysis: Methyl butanoate and methyl crotonate

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ABSTRACT

In order to examine in detail the effect of C = C bond on the combustion chemistry of biodiesel fuels, two C4 fatty acid methyl esters (FAMES) were investigated, namely methyl butanoate (MB) and methyl crotonate (MC). Pyrolysis experiments of these two FAMES at 30, 150 and 780 Torr were conducted in a flow reactor over the temperature range of 773–1323 K, using gas chromatography-mass spectrometry. A number of pyrolysis species including C1 to C4 hydrocarbons, oxygenated products, esters and aromatics were observed and identified. A comprehensive kinetic model for MB and MC combustion was developed, and applied to validate against the new experimental data. In this work, peak mole fraction of benzene, as well as other unsaturated hydrocarbons in MC pyrolysis, was found to be in slightly higher amounts in comparison with that of MB. Kinetic modeling analysis revealed that the dominant formation pathway of benzene was the self-combination reaction of propargyl radical. Furthermore, the model was also validated against the previous experimental data on MB and MC combustion, including oxidation in jet stirred reactor, pyrolysis in shock tube and laminar premixed flame. This study suggests that the effect of C = C double bond in FAMES might give rise to a growing tendency of initial PAH and soot precursors in the whole thermal decomposition process.

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1. Introduction

Over the past decades, fossil fuels have contributed a large proportion (about 88%) to energy consumption [1]. However, due to the massive pollutant emissions and diminishing fossil fuel resources, environmental pollution and energy crisis have been triggered concerns evenly around the world [2]. Herein, the clean, eco-friendly and regenerative biofuels, especially biodiesel fuels [3] have attracted a great deal of the public and scientific attentions. With the carbon-neutral natures, biodiesel fuels have the potential to reduce toxic pollutant emissions, particulate matters and unburned hydrocarbons [4–10], which hence are considered as the best succedaneum for fossil fuels.

Biodiesel, the first-generation biofuel, can be synthesized from a variety of renewable feedstocks such as animal fats, waste cooking grease, or vegetable oils [11–14], through an important process of transesterification with a simple monohydric alcohol [15]. Virtually, typical biodiesel is a mixture of alkyl esters with large molecules, or rather, saturated and unsaturated fatty acid methyl esters (FAMES) [16,17], e.g., methyl palmitate, methyl oleate and

methyl linoleate. Due to its complicated components, it is pretty hard to study the biodiesel combustion experimentally and computationally, the kinetics measurements and model simulations in particular. Herein, smaller surrogate fuels with similar chemical functional groups and properties are considered to be preferable to represent the real fuel [18]. With a long enough C4 hydrocarbon chain and a methyl ester group, methyl butanoate (MB, saturated FAME) and methyl crotonate (MC, unsaturated FAME) are chosen in this work to limit the number of pyrolysis products and the kinetic mechanism to a manageable level.

Various experimental and modeling studies for methyl esters focused on the effect of C = C double bond on the fuel combustion have been investigated, consisting of ignition delay times, oxidations and flames [19–24]. Nevertheless, experimental and modeling efforts which concentrate on the impact of C = C double bond upon soot formation were very limited. Sarathy and co-workers [25] investigated the opposed-flow diffusion flames and oxidations of MB and MC in a jet-stirred reactor (JSR) to reveal the effect of C = C bond; similar reactivities were observed for these two fuels. However, greater amounts of unsaturated hydrocarbons and aromatics were observed in MC combustion. Furthermore, same experiments in JSR and opposed-flow diffusion flame were carried out by Gail et al. [26] to obtain the new MB and MC experimental data.

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Table 1
Experimental conditions of the flow reactor pyrolysis of MB and MC.

P (Torr)	T (K)	D_M^a (g/s/cm ²)		Flow rate(SLM ^b)		Total flow Rate (SCCM)
		MB	MC	MB/MC:	Ar	
30	873–1323	0.102	0.098	0.020	0.980	1000
150	773–1223	0.102	0.098	0.020	0.980	1000
780	773–1173	0.102	0.098	0.020	0.980	1000

^a Inlet mass flow rate.

^b Standard liter per minute.

They also demonstrated that the unsaturated ester would produce higher levels of soot precursors. Based on their MB mechanism, they expanded their previous model by adding and modifying a variety of reactions, e.g. H-atom abstraction and unimolecular dissociation reactions of MC, to simulate MC oxidation. More recently, Wang and co-workers [27] studied the effect of the biodiesel's saturation degree on soot formation in diesel engines. On the basis of their experimental results, they revealed that biodiesel with less C=C bond could result in lower soot emissions. Moreover, the investigations of esters in non-premixed flames performed by Das et al. [28] and Feng et al. [29] also uncovered that the presence of C=C double bond in alkyl chain plays a significant role in the increase of soot propensities in biodiesel combustion.

To date, hardly any accurate and integrated information on speciation has been reported to illustrate the soot tendency under the ester pyrolytic conditions, which necessitates new pyrolysis experimental endeavors. Additionally, many experimental studies of MB including ignition delay times [30–32], oxidations [33,34], premixed laminar flames [35,36] and pyrolysis [34, 37] have been carried out; while a few experiments on MC combustion were only confined to the ignition delay times, oxidations and premixed laminar flames [20,25,26,38]. Thus, in order to gain a deep insight into the combustion performance of biodiesel and provide experimental data for further validation of the future models, the pyrolysis experiments of MB and MC in a flow reactor over the temperature range of 773–1323 K at 30, 150 and 780 Torr were performed. Furthermore, the experimental data and reliable kinetic model are presented in this work to address the effect of C=C double bond on the chemical structure of MC in the pyrolysis process, which can enhance the formation of unsaturated species.

2. Experimental apparatus

A flow reactor combined with a gas chromatography (GC) system was utilized to investigate the fuel pyrolysis. The pyrolysis apparatus has been described elsewhere [39–41]. Briefly, the pyrolysis apparatus consists of three parts: a high temperature furnace fitted in the pyrolysis chamber, a sample injection system, and a GC detecting system, as shown in Fig. 1(a). Besides, an α -alumina flow tube of 6.4 mm inner diameter (ID) and 229 mm length, with its inconsequential catalytic properties for the pyrolysis of the oxygenated fuels [42,43], was fixed in the pyrolysis chamber.

Table 1 lists the experimental conditions of MB and MC, respectively. In this work, high purity reactants were used. MB (99%) and MC (98%) were purchased from Aladdin Chemical Reagent Co. Ltd. in Shanghai, China. Argon (99.999%) was purchased from Nanjing Special Gases Ltd. in China. The liquid esters were introduced into an electrically heated vaporizer through a liquid chromatography pump and then be mixed with the diluting gas argon. The temperature of vaporizer was maintained at 423 K to ensure the efficient vaporization of fuel. The flow rate of argon was 980 standard cubic centimeter per minute (SCCM), controlled by a mass flow controller. The flow rate of liquid fuels was 0.102 mL/min for MB and 0.098 mL/min for MC, which is equivalent to 20 SCCM in gas phase at room temperature. Thus, the total inlet flow rate of fuel/Ar

mixture (2% in mole) was fixed at 1.0 standard liter per minute (SLM). Furthermore, the residence time in terms of pressure (P) and temperature (T) was computed with the following empirical equation $\tau = V_1/Q_V$, wherein Q_V refers to the volumetric flow of the gas and V_1 is the volume of the flow reactor. In this work, V_1 was estimated to be 7.36E-6 m³ and Q_V was estimated from another equation $Q_V = \frac{R}{PT} F_{Ar}$. In Q_V equation, R represents the gas constant and F_{Ar} represents the molar flow rate of gas which was computed as 7.44E-4 mol s⁻¹. Consequently, the nominal residence times in this experiment are estimated to be 3–6 ms, 19–31 ms, and 104–157 ms with its corresponding temperature range at 30, 150 and 780 Torr, respectively.

A quartz tube with 3-mm-ID was placed at 10 mm downstream of the outlet to sample the gaseous pyrolysates. After sampling, the products passed through a stainless steel transfer line (maintaining at 473 K to avoid condensation) and entered the six-way valve of GC analyzer (Bruker 450-GC). The pyrolysis species were detected and discriminated by a GC combined with mass spectrometer (MS, namely, Bruker 320-MS). A flame ionization detector (FID) with capillary columns and diagnostics was used to quantify the gaseous pyrolysis products. Detection of CO and CO₂ was carried out by a separate thermal conductivity detector (TCD) with another GC analyzer (Agilent Technologies 7820A). Additionally, the quantitative loop was used to keep a constant sample size. A loop volume of 100 μ L was applied at 780 Torr, and a volume of 2.5 mL was applied at 30 and 150 Torr. For the mole fraction measurement of pyrolysis products, direct calibration was performed with a gas mixture of known standard composition, such as methane, acetylene, ethylene, ethane and propane, to evaluate the response factor, which was considered as the proportionality coefficient between the mole fraction of a peculiar species and the signal intensity. As for indirect calibration, it was named effective carbon number which also ensured the reliability of mole fraction profiles for other pyrolysis products [44]. The uncertainties of measured mole fractions are estimated to be within $\pm 10\%$ for pyrolysis products using the direct calibration method, while for the effective carbon number method, the uncertainties increase to $\pm 20\%$.

The temperature distribution in the flow reactor along the centerline was measured by an S-type thermocouple with a 1.0 SLM flow rate of argon, which can reflect the physical changes in pyrolysis chamber and provide the exact proximal temperature profiles as the experimental conditions for the kinetic modeling. Four temperature profiles were performed, as shown in Fig. 1(b). Each temperature profile was denoted by its maximum temperature (T_{max}), which was considered as the experimental temperature. The uncertainties of the temperature measurement were estimated to be within ± 30 K [39].

3. Kinetic modeling

The simulations were performed using the Plug Flow Reactor (PFR) module in the CHEMKIN-PRO software [45]. Calibrated temperature profiles along the centerline of the flow tube were used as the input parameters to keep consistence with the experiments. An updated kinetic model based on the Gail model [26], containing 304 species and 1790 reactions, was developed. Table S1 in the *Supplementary Materials* presents some reactions in the sub-mechanism of esters, such as the unimolecular dissociation, H-atom abstraction and H-atom addition reactions, along with their corresponding rate coefficients and source. The unabridged model, associated with kinetic, transport and thermochemical files, is provided in the *Supplementary Materials*. The species mentioned in this paper, along with their formulas, names and chemical structures are listed in Table S2 of the *Supplementary Materials*.

Unimolecular dissociation reactions are essential reactions of the fuel consumption under pyrolytic condition. MB and MC

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