Kinetic Modelling and Experimental Study of Small Esters: Methyl Acetate and Ethyl Acetate

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Abstract

A detailed chemical kinetic mechanism comprising methyl acetate and ethyl acetate has been developed based on the previous work by Westbrook *et al.* [1]. The newly developed kinetic mechanism has been updated with new reaction rates from recent theoretical studies. To validate this model, shock tube experiments measuring ignition delay time have been conducted at 15 & 30 bar and equivalence ratio 0.5, 1.0 and 2.0. Another set of experiments measuring laminar burning velocity was also performed on a heat flux burner at atmospheric pressure over wide range of equivalence ratios [~0.7-1.4]. The new mechanism shows significant improvement in prediction of experimental data over earlier model across the range of experiments.

1 Introduction

Global energy trends show continuous increase in consumption of bio-based fuels for transportation sector [2]. This trend supports growing efforts to mitigate climate change by offsetting the consumption of fossil fuels. At present, a wide variety of bio-based fuels are proposed as alternatives to fossil fuels. Esters represent one such an important class of bio-derived fuels with potential to supplement gasoline as well as diesel fuel supply. While longer chain esters such as methyl oleate, methyl linoleate etc. are found suitable for diesel engine applications [3], smaller esters with higher RON values are found suited to gasoline range applications [4]. In principle, esters can be synthesized using various feasible pathways including vegetable oils, animal fats [5], algae [6] etc. Esters as a bio-based fuel makes an attractive alternative to fossil fuels due to its suited combustion properties and with proven synthesis pathways. However in the literature, there has been more focus on larger esters [3] and studies on combustion characteristics of smaller esters are limited. In past a couple of flame studies have been conducted with these fuels by Gasnot *et al.* [7], Dayma *et al.*[8] and Badawy *et al.*[9] in which various parameters like flame speeds, low pressure oxidation were investigated, Gasnot *et al.* [7] also proposed a kinetic model. There have been a few studies investigating ignition behavior of these fuels, Zhang *et al.* [10] studied high temperature ignition of methyl acetate in a shock tube and developed a kinetic mechanism. Kumegh *et al.* [11] also studied the high temperature ignition of methyl acetate and ethyl acetate in a shock tube, and proposed a kinetic model entailing these fuels. There is another work by Yang *et al.* [12] studying pyrolysis and oxidation of methyl acetate in low pressure flames, a mechanism was also proposed. There have been some other attempts to study these fuels blends in engines [13, 14] as well. Additionally, there have been some theoretical studies discussing the rates of H atom abstraction from fuel [15], decomposition of fuel [16] and fuel radicals [17].

In this study, a detailed chemical kinetic model for methyl and ethyl acetate (Fig. 1) has been developed. This model is advanced from the mechanism proposed for laminar premixed flames by Westbrook and coworkers in 2009 [1]. Acetates studied in this work are both high RON fuels with suitable physical and chemical properties [Table 1] to be considered as potential fuels in advanced gasoline engines [4]. Shock tube experiments measuring ignition delay time have been conducted at 15 & 30 bar and equivalence ratio 0.5, 1.0 and 2.0. Another set of experiments measuring laminar burning velocity have also been performed on a heat flux burner at atmospheric pressure over wide range of equivalence ratios. The model developed in this work shows good agreement with ignition data and laminar burning velocity data across the temperature and equivalence ratio range respectively.

Fuel	RON	MON	Density [Kg/m3]	LHV [KJ/Kg]
Methyl acetate	120	120	927.4	17.9
Ethyl acetate	118	120	894.6	21.34

Table 1: Properties of Methyl acetate and Ethyl acetate[4]

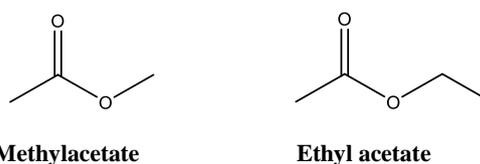**Methylacetate**   **Ethyl acetate**

Figure 1: Structure of Methyl acetate and Ethyl acetate

2 Experiments

In this study methyl and ethyl acetate have been studied in a shock tube facility and heat flux burner for ignition delay time and laminar flame velocity measurements, respectively. The following section discusses the experimental details and measurement procedure for the two facilities.

2.1 High Pressure Shock Tube [HPST]

The high temperature (1000-1400 K) ignition delay data in HPST has been measured behind reflected shock wave at 15 and 30 bar and equivalence ratio 0.5, 1.0, 2.0 as descripted in Table 2. This shock tube is made of 9 m long section of steel with uniform cross-section of 63.5 mm inner diameter. The length of shock tube is divided into three sections; driver section [3 m], driven section [5.7 m] and a section with double diaphragm. This double diaphragm section [30 mm] separates the driver and driven section and enables improved control of the generated

shock wave. In this study helium or mixture of helium and nitrogen is used as driver gas in the shock tube during the experiments.

P/ bar	Phi	MA/mol %	O2/mol %	N2/mol %
	0.5	2.91	20.388	76.699
	1.0	5.65	19.807	74.514
	2.0	10.714	18.75	70.535
15, 30	Phi	EA/mol %	O2/mol %	N2/mol %
	0.5	2.05	20.568	77.375
	1.0	4.03	20.15	75.815
	2.0	7.749	19.373	72.88

Table 2: Details of shock tube experiments of methyl acetate [MA] and ethyl acetate [EA].

During experiments, pressure-time histories are measured using the Kistler 603B pressure transducer mounted on the end wall. The ignition delay in the HPST is defined as the time interval between two sharp pressure rises; one of them due to the shock wave reaching the end-wall and other due to initiation of ignition. The acceptable error for the measured pressures behind the reflected shock wave was ±0.5 bar. The NUI Galway HPST has been further discussed in detail in Nakamura *et al*.[18]

2.2 Heat Flux Burner

Laminar burning velocities of methyl acetate/air and ethyl acetate/air were determined using the heat flux method at Lund University. Measurements were performed at atmospheric pressure, initial gas mixture temperatures 298 and 338 K, and equivalence ratios in the range 0.7-1.4 for methyl acetate and 0.7-1.3 for ethyl acetate. The experimental setup and measurement method have been described in detail by Alekseev et al. [19], and hence it is briefly discussed in this work.

The heat flux method for determination of laminar burning velocities was first presented by de Goey and co-workers [20] in 1993. The method was originally introduced for gaseous fuels and was later extended to liquid fuels. The heat flux method is based on the principle that; at adiabatic burning velocity conditions there is no net heat transfer between the flame and the burner plate and hence temperature of the burner plate remains uniform. One of the advantages this method offers is the measurement of laminar burning velocity in a stretch free flame under adiabatic conditions, hence no corrections for flame stretch are required.

The composition of fuel/oxidizer mixture is metered using Mass Flow Controllers (MFCs) for metering the air, a Cori-Flow liquid mass flow controller for the liquid fuel and a Controlled Evaporator Mixer (CEM) for evaporation of the fuel. Uncertainties in gas mixture composition as well as in the laminar burning velocity is assessed as described by Alekseev *et al*. [19]. However no uncertainty quantification analysis is done in this work.

3 Kinetic Modelling

Detailed chemical kinetic mechanism has been developed for methyl and ethyl acetate based on previous work by Westbrook

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et al [1]. The former mechanism has been updated with additional reaction rates and reaction classes based on theoretical calculations and structurally similar molecules. In present work Aramcomech 2.0 [21] has been used as the base chemistry.

3.1 Methyl acetate

Kinetic reaction scheme of methyl acetate comprises of H abstraction reactions followed by decomposition of fuel and fuel radical. Rates of H abstraction reaction by OH and HO$_2$ are calculated in this work by Dr. Carlo Cavallotti [politecnico di
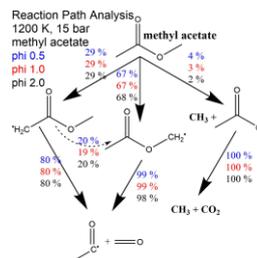

Figure 2: Reaction path analysis of methyl acetate at10% of fuel conversion time. P=15 bar, 1200 K and phi =1.

Milano] at CCSD(T) energy levels. However H abstractions by H, O, CH$_3$ are taken from Tan *et al.* [15]. The fuel decomposition rates are taken from Peukert *et al.* [16] and the fuel radical decomposition reaction rates are from another study by Tan *et al*. [17]. In the reaction scheme the decomposition of fuel and the fuel radicals lead to formation of formaldehyde and some unstable radicals eventually producing CH$_3$, CO and CO$_2$ as shown in Fig.2. Further consumption of formaldehyde and other products has been dealt in the base chemistry reactions.

3.2 Ethyl acetate

The kinetic mechanism of ethyl acetate involves additional reaction pathways as compared to methyl acetate, owing to its relatively larger size. Its oxidation chemistry comprises of unimolecular fuel decomposition and H abstraction reactions by various radicals from fuel. The unimolecular decomposition of ethyl acetate has been studied by Swihart *et al*.[22] using pulsed laser powered homogeneous pyrolysis. They utilized this technique for studying rates of gas phase decomposition reactions. The measurements revealed that the major products of breakdown are acetic acid and ethene. The chemistry of acetic acid involves H atom abstraction followed by fuel radical decomposition. The ethene chemistry is described in detail within the base chemistry and is not discussed here. Some other minor products were also observed as a result of abstraction of primary, secondary H atoms and breakage of methyl, ethyl groups from the fuel molecule. The fuel radicals produced after H atom abstractions along with products of decomposition of C-H bond further undergoes radical decomposition to produce smaller radicals. Figure 3 describes major reaction pathways in
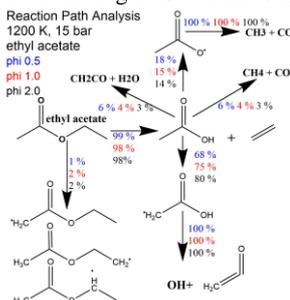

Figure 3: Reaction path analysis of ethyl acetate at 10% of fuel conversion time. P=15 bar, 1200 K and phi =1.

the oxidation chemistry of ethyl acetate. The kinetic mechanism developed in this work only deals with high temperature chemistry as both the experiments discussed in this work are conducted in the high temperature region. The thermodynamic properties are retained from the previous work [1] The transport parameters are recalculated in this work using correlations from Wang *et al*. [23] and Dooley *et al*. [24].

4 Results

The proposed kinetic mechanism has 1958 species and 8098 reactions. Aramcomech 2.0 [21] has been used as base mechanism and all the species with 6 carbon and less have been retained to allow complete account of reactivity. As explained in the experimental sections, ignition and burning velocity data have been acquired at NUI Galway and Lund University, respectively. In this section comparison of developed mechanism is presented with experimental data. The simulations have been performed using Chemkin Pro 18.1. Shock tube simulations were performed with closed homogenous batch reactor model. The ignition delay simulations for methyl acetate and measured data is shown in Fig. 4 and 5. It is evident that the newly proposed model captures the ignition data quite well across all equivalence ratios, pressure and temperature ranges. While the model detailed in [1] under predicts the ignition across all conditions. Comparisons of ignition data and simulations for ethyl acetate is presented in Fig. 6 and 7. Here the old model by Westbrook et al. under predicts the ignition delay at high temperature and over predicts ignition delay at temperatures lower than 1150 K.
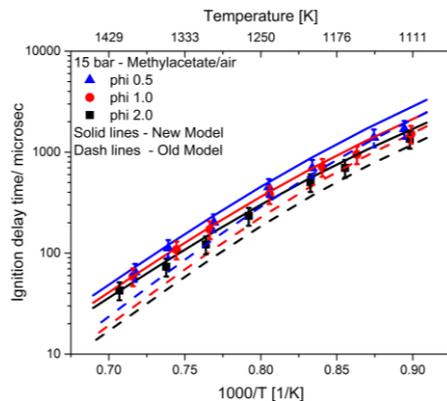

Figure 4: Comparison of methyl acetate ignition delay data with proposed model [solid lines] and model by Westbrook et al. [dash lines] at 15 bar, equivalence ratio = 0.5, 1.0, 2.0.

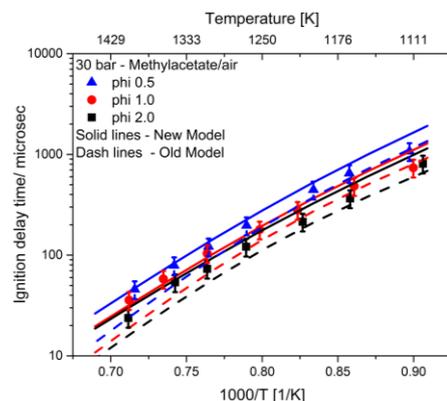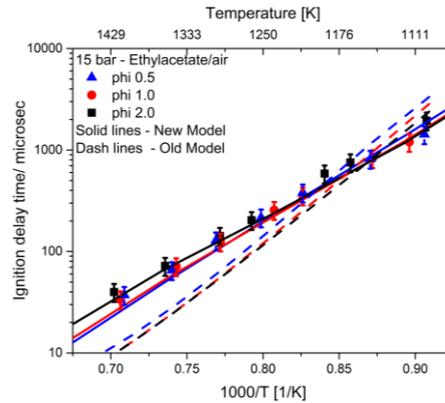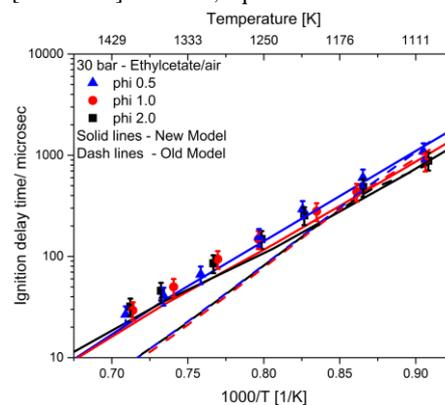

Figure 5: Comparison of methyl acetate ignition delay data with proposed model [solid lines] and model by Westbrook et al.

[dash lines] at 30 bar, equivalence ratio = 0.5, 1.0, 2.0.

Figure 6: Comparison of ethyl acetate ignition delay data with proposed model [solid lines] and model by Westbrook et al. [dash lines] at 15 bar, equivalence ratio = 0.5, 1.0, 2.0.

Figure 7: Comparison of ethyl acetate ignition delay data with proposed model [solid lines] and model by Westbrook et al. [dash lines] at 30 bar, equivalence ratio = 0.5, 1.0, 2.0.

Burning velocity simulations have been conducted at $T_{unburned}$ = 298 K and 338 K and $P_{unburned}$ = 1 atm with premixed laminar flamespeed model in Chemkin Pro 18.1. The comparisons between experimental data and simulations are presented in Figure 8 and 19 for methyl acetate and ethyl acetate, respectively. The Westbrook model over predicts the burning velocity for both the fuels over the entire equivalence ratio range. However the model developed in this study predicts the burning velocity within 10% of measured data at all conditions.
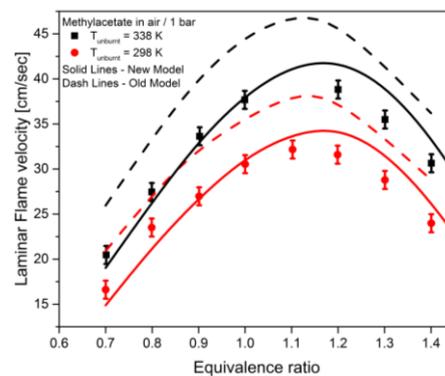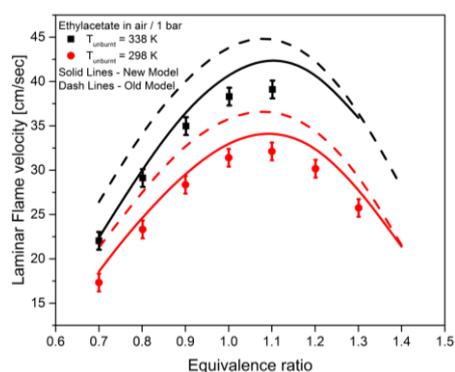

Figure 8: Comparison of methyl acetate burning velocity data with proposed model [solid lines] and model by Westbrook et al. [dash lines] at 1 bar, 298 K, 338 K and equivalence ratio = 0.7 -

1.4.

Figure 9: Comparison of ethyl acetate burning velocity data with proposed model [solid lines] and model by Westbrook et al. [dash lines] at 1 bar, 298 K, 338 K and equivalence ratio = 0.7 - 1.3.

5 Conclusions

A detailed mechanism for small esters, methyl acetate and ethyl acetate has been developed. Experiments were conducted to measure ignition delay time at NUI Galway and laminar burning velocity at Lund University. Comparisons between the model and experimental data is conducted and model was found to agree well with the experimental data over the entire experimental range.

The modifications made in the mechanism could not be presented here due to limitation of space. The corresponding author could be contacted for obtaining the mechanism and thermochemistry data files.

6 Acknowledgment

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