# A Comprehensive and Compact Mechanism for the Oxidation of *methyl*-Decanoate

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## **1** Introduction

Methyl-decanoate (MD) is an important surrogate fuel component representing the methyl-ester fraction in biodiesel. In recent years different experimental studies using MD as fuel were reported; detailed as well as reduced mechanisms were developed for both improving our kinetic understanding and engineering applications. Jet stirred reactor (JSR) experiments were performed by Dagaut et al. (2007) [1] with rapeseed oil at 1 and 10 atm, 800 to 1400 K with 0.25 to 1.5 s residence times. These experiments were simulated using n-hexadecane as reference fuel. A general similarity was noticed for major species (such as  $C_2$  to  $C_6$  olefins). The early formation of  $CO_2$  caused by the methyl-ester group was not captured by the model.

The first detailed oxidation mechanism for MD was developed by Herbinet et al. [2]. It is based on oxidation reaction rules by Curran and co-workers [3] with an extension to cover the methyl-ester group, this MD oxidation model can predict the early  $CO_2$  formation in the rapeseed oil JSR experiment [1].

Seshadri and co-workers [4] used the direct relation graph (DRG) method to reduce Herbinet's detailed mechanism to a skeleton level with 713 elementary reactions and 125 species. The skeleton mechanism predicted experimental extinction and ignition of MD in opposed-flow diffusion flames. Their results indicate that low temperature chemistry is of minor importance for this configuration. Hence the skeleton mechanism covers mainly the high temperature oxidation pathways.

Sarathy et al. (2009) [5] investigated the MD flame in an opposed-flow diffusion burner. Their results indicate that MD is mainly consumed via abstraction of hydrogen atoms and the ester moiety in MD leads to the formation of low molecular weight oxygenated compounds such as CO<sub>2</sub>, CH<sub>2</sub>O and ketenes. In their work a skeletal mechanism with 648 species, 2998 reactions was derived from the detailed mechanism by Herbinet et al. [2]

Glaude et al. (2010) [6] studied MD oxidation in a JSR experiment. The authors performed a modelling study of methyl-decanoate, methyl-heptanoate and methyl-hexanoate. 30 species including olefins, unsaturated esters and cyclic ethers were quantified and successfully simulated in this work. Based on the calculations it was concluded that the ester group has very little influence on the reactivity of large esters, and in the low temperature region the oxidation of methyl esters is similar to that of n-alkanes. This finding is supported by the shock tube study of Wang and Oehlschlaeger (2011) of the autoignition of MD [7]. Their work revealed ignition characteristics very similar to n-alkanes: at high temperatures the ignition delay times and at low temperature the NTC behaviour was found to be similar to n-alkanes. The finding was explained with the importance of the long alkyl chain controlling the overall reactivity of MD and a minor role of the methyl-ester group which, however, inhibits the low temperature reactivity. Also the methyl-ester flame study by Wang et al. (2011) [8] showed similar flame speeds and extinction strain rates of n-decane/air and methyl-decanoate/air flames.

Dievart et al. (2012) [9] developed an oxidation mechanism for MD strictly through the extension of the chemical kinetic and thermochemical parameters of methyl-butanoate.

Ranzi and co-workers (2012) [10] built the oxidation mechanism of MD as an extension of the lumped model of methyl-butanoate. It was shown that these two consistent models can be applied to simulate the combustion behaviour of intermediate methyl esters by using the lever rule between the two reference components.

Table 1 summarizes published MD models which include both low and high temperature oxidation pathways. Among these models, the most compact mechanism is from Grana et al. with 350 species. In the present work we propose a more compact MD mechanism model with comprehensive validations over a wide pressure and temperature range.

Author	Mechanism size
Herbinet et al. (2008)	3012 species, 8820 reactions
Sarathy et al. (2011)	648 species, 2998 reactions
Glaude et al. (2010)	1251 species, 7171 reactions
Dievart et al. (2012)	2276 species, 7086 reactions (detailed)
Grana et al. (2012)	350 species, 10000 reactions

Table 1: Published MD models with low and high temperature oxidation pathways

In a first step a detailed MD mechanism is developed and compared against experimental ignition delay times, flame speeds and the speciation in a JSR and a counter-flow flame. Additionally the model is further validated for a broad subset of  $C_1$ - $C_4$  fuels covering the complete set of typical combustion conditions. Finally, a compact mechanism is derived by using the chemistry guided reduction approach (CGR). This compact MD oxidation mechanism is suitable for the direct applications in engine simulations.

## 2 Chemical modelling

## **Detailed mechanism**

The  $C_1$ - $C_4$  chemistry by Schenk et al. [11] is used as base mechanism in this work. This mechanism is broadly validated for  $C_1$ - $C_4$  chemistry, including butane an butene isomers, and the combustion of toluene.

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To be able to handle large number of different isomers formed during the oxidation a semi-automatic generator was developed to assist the mechanism generation [13]. The generation rules for the detailed MD mechanism are following the 25 reaction classes of the n-heptane mechanism by Curran et al. [3] and the reaction rates are based on the previous n-heptane study by Ahmed et al [14]. Different from Curran et al., we apply the complete set of reaction classes in the low temperature region to the seed molecule (MD) alone, which greatly reduces the mechanism size. Meanwhile, more detailed submechanisms of olefins has been provided based on the extensive studies of Ranzi and his co-workers [12]. The H atom abstraction reactions from the fuel by highly oxygenated methane derivatives (O<sub>2</sub>CHO) as suggested by Curran [3] were removed. A limited number of reactions are taken from the methyl-decanoate mechanism by Herbinet et al. [2]. The detailed NOx model (thermal and prompt formation pathway) from the GRI mechanism [15] and a reaction mechanism. The detailed oxidation scheme consists of 654 species and 6700 reactions.

#### **3** Mechanism reduction

The CGR approach is based on horizontal chemical lumping and subsequent species removal [17]. Species are removed on the basis of necessity values, which are calculated from the combined reaction flow and sensitivity analysis method [18].

Using the CGR approach the detailed mechanism with 654 species and 6700 reactions is reduced to a skeletal level with 248 species and 2600 reactions (forward and backward are counted as individual reactions) while maintaining its predictive efficiency. This is confirmed by largely unchanged model predictions and sensitivity coefficients for the most sensitive reactions with respect to auto-ignition in the detailed and skeletal model.

For a better understanding of important decomposition pathways during different reaction stages a multi-stage flow analysis has been conducted.

### 4 Validation

### Ignition delay times



Figure 1. Ignition delay times for stoichiometric MD/air mixtures at 16 atm. Symbols: experiments [8]; solid, dashed lines: predictions from detailed, skeletal mechanisms.

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Simulations in this work are performed by using LOGEsoft[19]. The auto-ignition of MD/ air mixtures is simulated at pressures around 16 atm as shown in Fig. 1. The detailed mechanism shows a good agreement with measured ignition delay time except for the very low temperature region. The skeletal mechanism slightly deviates in the negative temperature coefficient region (NTC) when compared with the experiments and the detailed mechanism. This is mainly due to the removal of certain minor pathways.



Figure 2. Ignition delay times for stoichiometric MD/air mixtures at 16 atm. Symbols: experiments [8]; lines: simulations from different MD models.

Fig. 2 shows a comparison of simulated ignition delay times from different MD models against experimental data. The simulations are performed by using constant volume reactor. The model from this study and Herbinet et al. are in good agreement with the experiment while other models show larger deviations.

#### Jet stirred reactor



Figure 3. Species mole fraction in JSR ( $C_{10}H_{22}O_2 = 0.21\%$ ;  $O_2 = 3.255\%$ ; He = 96.535% with  $\tau = 1.5$  s at 1.06 bar). Symbols: experiments [6]; solid, dashed lines: predictions from detailed, skeletal mechanisms.

Fig. 3 compares the calculated major species concentrations in a JSR at 1.06 bar against experimental data from Glaude et al.[6]. The detailed and the skeletal model are in a very good agreement. Compared with the experiment the consumption of the fuel and  $O_2$  is underpredicted in the NTC region. The formation of CO and  $CO_2$  is well predicted at higher temperatures.

#### Laminar flame speed



Figure 4. Laminar flame velocity for MD/air mixtures at T = 403 K, p = 1 atm. Symbols: experiments [8]; solid, dashed lines: model predictions from detailed, skeletal mechanisms.

The predicted flame speeds from the detailed and skeletal mechanisms are compared with experimental data [8] at atmospheric pressure and an initial temperature of 403 K. For equivalence ratios from 0.6 to 1.6 the simulation is in good agreement with experimental data as shown in Fig. 4.

#### **Flame structure**



Figure 5. Species mole fraction in atmospheric pressure diffusion flame (MD = 1.8%; O<sub>2</sub> = 42%; N<sub>2</sub> = 56.2%). Symbols: experiments [5]; solid, dash lines predictions from detailed, skeletal mechanisms.

Fig. 5 compares the predicted species profiles of major species (MD, CO, CO<sub>2</sub>) against the experimental data from the counter-flow flame at atmospheric pressure by Sarathy et al. [5].

#### Conclusions

A detailed *methyl*-decanoate oxidation mechanism including sub models for NOx and soot formation is generated and validated against experiments. With the application of CGR, the detailed mechanism (654 species) is reduced to a skeletal model of 248 species, maintaining its predictivity. Due to its compact size and precise chemical information the skeletal mechanism is suitable for application in engine simulations.

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