

Development of multi-component diesel surrogate fuel models – Part II:Validation of the integrated mechanisms in 0-D kinetic and 2-D CFD spray combustion simulations

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- 1 Development of Multi-Component Diesel Surrogate Fuel Models Part II: Validation of
- 2 the Integrated Mechanisms in 0-D Kinetic and 2-D CFD Spray Combustion Simulations
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## 12 Abstract

The aim of this study is to develop compact yet comprehensive multi-component diesel 13 surrogate fuel models for computational fluid dynamics (CFD) spray combustion modelling 14 studies. The fuel constituent reduced mechanisms including n-hexadecane (HXN), 15 2,2,4,4,6,8,8-heptamethylnonane (HMN), cyclohexane (CHX) and toluene developed in Part 16 I are applied in this work. They are combined to produce two different versions of multi-17 component diesel surrogate models in the form of MCDS1 (HXN + HMN) and MCDS2 18 (HXN + HMN + toluene + CHX). The integrated mechanisms are then comprehensively 19 20 validated in zero-dimensional chemical kinetic simulations under a wide range of shock tube and jet stirred reactor conditions. Subsequently, the fidelity of the surrogate models is further 21 22 evaluated in two-dimensional CFD spray combustion simulations. Simulation results show that ignition delay (ID) prediction corresponds well to the change of fuel constituent mass 23 fraction which is calculated to match the cetane number (CN). In addition, comparisons of the 24 simulation results to the experimental data of #2 diesel fuel (D2) in a constant volume 25

26 combustion chamber show that IDs and lift-off lengths are reasonably well replicated by the models. The MCDS2 model is also found to perform better in the soot formation prediction in 27 D2 fuel combustion as the model contains aromatic and cyclo-alkane components which 28 29 provide an additional pathway to the formation of rich species such as  $C_2H_2$  and  $C_6H_6$ . Implementation of MCDS2 predicts an increase of maximum local soot volume fraction by a 30 factor of 2.1 when the ambient temperature increases from 900K to 1000K, while the 31 prediction by MCDS1 is lower at 1.6. This trend qualitatively agrees with the experimental 32 observation. This work demonstrates that MCDS1 serves as a potential surrogate fuel model 33 34 for diesel fuels with CN values ranging from 15 to 100. It also shows that MCDS2 is a more appropriate surrogate model for fuels with aromatics and cyclo-paraffinic contents, 35 particularly when soot calculation is of main interest. 36

Keywords: multi-component diesel surrogate, CFD simulations, spray combustion, chemical kineticmechanism, soot formation.

### 39 1. Introduction

In multi-dimensional computational fluid dynamics (CFD) modelling studies [1-6], n-40 heptane has been widely utilised as a single-component diesel surrogate fuel model owing to 41 its cetane number (CN) of 55, which is comparable to those of the actual diesel fuels which 42 43 range between 40 to 56 [7]. Nonetheless, actual diesel fuels generally consist of long carbon 44 chain structure with 10 to 25 carbon atoms [7]. Fuels with long-chain n-alkanes exhibit higher reactivity at low temperatures as compared to those with short carbon chains. This is 45 46 due to the higher ratio of secondary to primary hydrogen atoms which then increases the Hatom abstraction rate during the initiation phase of the oxidation of alkanes [8]. As a 47 consequence, the combustion of long-chain hydrocarbons particularly n-hexadecane (HXN) 48 49 [9] has become the centre of attention in many current research works [10–13]. HXN is the

50 primary reference fuel and it has a CN of 100. Surrogate fuel models with different CN values can hence be produced when HXN is blended with other fuels such as 1-51 methylnaphthalene with a CN of 0 and 2,2,4,4,6,8,8-heptamethylnonane (HMN) with a CN of 52 53 15. Therefore, HXN has been identified as a promising component for diesel fuel surrogate model in recent works [12-14]. Nonetheless, it is evident that the Hydrogen/Carbon Molar 54 Ratio (H/C) of HXN is different from that of the actual diesel fuels, on top of the difference 55 56 in CN. H/C ratio is a key property in simulation studies in order to replicate combustion properties such as heat of reaction, local air/fuel stoichiometric location, flame temperature 57 58 and flame speed [15]. It is important to note that similar restriction is expected to hold for any other single-component diesel surrogate fuels [16,17]. 59

Apart from that, the Polycyclic Aromatic Hydrocarbons (PAH) formation in diesel fuel 60 combustion is not well described by a single-component diesel surrogate fuel model [7]. In 61 62 the experiment carried out by Kook and Pickett [18], soot formation of a surrogate fuel comprising 23% m-xylene and 77% n-dodecane (by volume) was studied and the sooting 63 64 tendency was subsequently compared to a conventional jet fuel under diesel-engine like conditions. Their planar laser induced incandescence (PLII) measurement revealed that the 65 soot level produced by the n-dodecane/m-xylene surrogate fuel is higher than that of the 66 67 conventional jet fuel. For the combustion of fuels that do not contain aromatic compounds, the maximum local soot volume fraction (SVF) increases by a factor of approximately two 68 when the ambient temperature rises from 900K to 1000K. On the other hand, the maximum 69 SVF increases by a factor of at least five for the combustion of fuels which consist of 70 aromatic volume of 23% to 27%. This corresponds with the reported experimental studies 71 [19–22] where the sooting tendency of a single-component surrogate model is comparatively 72 less significant than an alkane/aromatic mixture. Single component diesel surrogate models 73

which do not contain PAH chemistry in its original fuel composition are hence debatablesince actual diesel fuels contain 20% to 30% of aromatic compounds [23].

Recognizing the limitation of single-component diesel surrogate fuel models, development of 76 surrogate models with matching fuel compositions as the actual diesel fuels is necessary. 77 Consequently, multi-component diesel surrogate models with blends of various fuel 78 components have been proposed [7,24–30]. The details of the surrogate mechanisms, together 79 with their respective constitutional components are provided in Table 1. In the earlier years, 80 the number of components in a surrogate model was limited owing to the complexity in 81 solving the stiff ordinary differential equations and the associated high computational cost. 82 Besides, huge quantity of work was required to develop the database and mechanistic 83 understanding of the surrogate components for diesel fuels [7]. Fuel blends which are 84 commonly employed in numerical simulations of diesel combustion are Integrated Diesel 85 86 European Action (IDEA) mechanism [27,28,31], Primary Reference Fuels (PRF) mechanism [32-35] and Diesel Oil Surrogate (DOS) mechanism [36]. With rapid advancement in 87 88 chemical kinetics as well as computing power, surrogate models with greater number of fuel 89 components are established such as PRF+1 mechanism [24] and Toluene Reference Fuel/PAH (TRF-PAH) mechanism [25]. Nonetheless, PRF, PRF+1 and TRF-PAH surrogate 90 models are predominantly developed for homogeneous charge compression ignition (HCCI) 91 applications. In these chemical models, n-heptane is mainly employed to represent the n-92 alkane component. Although the component mass fraction in these fuel blends can be 93 adjusted to generate diesel surrogate models with different CN, the maximum boundary of 94 the CN range is constrained by the CN of n-heptane. Thus, they are not suitable to be used as 95 surrogate models for fuels with higher CN such as a paraffinic diesel reference fuel blend 96 97 [37] with a CN of 80. More recently, POLIMI\_Diesel\_201 mechanism has been developed by Ranzi et al. [38] which consists of toluene, xylene, methylnaphthalene and n-alkanes up to 98

99 HXN. The mechanism was well validated in chemical kinetic simulations through comparison of the ignition delay (ID) predictions with experimental measurements of a 100 binary diesel surrogate mixture under auto-ignition condition [39]. On the other hand, Chang 101 102 et al. [29] have also formulated a diesel surrogate fuel model comprising toluene, n-decane, iso-octane and methylcyclohexane. These hydrocarbons are selected to represent the 103 104 aromatics, straight-, branched- and cyclo-alkane components in the actual diesel fuels, respectively. The integrated mechanism was comprehensively validated against the 105 experimental data for each fuel constituent and blends, as well as for practical diesel fuel 106 107 under wide-ranging operating conditions. However, the performance of these two surrogate models [29,38] is yet to be tested in multi-dimensional CFD modelling studies. 108

Set against this background, this study aims to develop appropriate multi-component diesel 109 surrogate models which account for both diesel fuel ignition and combustion across wider 110 111 CN range of actual diesel fuels. The reduced models of surrogate components for diesel fuels including HXN, HMN, cyclohexane (CHX) and toluene generated in Part I are applied here. 112 113 Two combinations of multi-component diesel surrogate models with different fuel 114 compositions and components are developed and first validated in zero-dimensional (0-D) chemical kinetic simulations. The first model consists of straight- and branched-alkanes while 115 the second consists of aromatics, straight-, branched- and cyclo-alkanes. The fidelity of the 116 multi-component models is further appraised through the comparisons made between 117 measurements of a constant volume combustion chamber and the numerical results of two-118 dimensional (2-D) CFD spray combustion simulations. The study also examines the 119 performance of the surrogate models in predicting soot formation with and without the 120 inclusion of aromatics/cyclo-alkane components. 121

#### 122 2

## 2. Development and Validations of Multi-Component Diesel Surrogate Fuel Models

5

In this section, a sequential procedure is applied to formulate the multi-component diesel 123 surrogate models, as illustrated in Fig. 1. The procedure is similar to the model construction 124 scheme of Slavinskaya et al. [40]. Here, a 'reduced-then-combined' model construction 125 126 strategy is employed where the reduced models for each of the fuel components are first derived from the respective detailed models and are subsequently combined together to 127 generate the multi-component diesel surrogate models. As such, the reduced models for each 128 129 of the components are constructed and may be used for other applications. This strategy also limits errors and complications generated from reducing the combined, detailed surrogate 130 131 models with more than 3,500 species.

The target applications of this work focus on chemical composition match as well as mimicking the combustion and soot precursor formation behaviours of real diesel fuels such as #2 diesel fuel (D2). In this work, the reduced mechanism of HXN is designated as the base mechanism as it is the most abundant and largest hydrocarbon among the fuel constituents. Subsequently, the reduced mechanisms for other surrogate fuel components are added to the base mechanism to generate two combinations of multi-component diesel surrogate models:

138 (a) Multi-Component Diesel Surrogate No. 1 (MCDS1): HXN + HMN;

139 (b) Multi-Component Diesel Surrogate No. 2 (MCDS2): HXN + HMN + toluene + CHX.

The reduced mechanisms of HXN, HMN and CHX generated in Part I are employed. It is noted that the base chemistries of the fuel constituents are essentially similar as the reactions mechanisms are constructed based on the hierarchical nature of hydrocarbon–oxygen systems [9,41,42] in order to ensure that the results may not be affected when the based model is replaced by different models. The approach is similar to the model construction of the detailed mechanisms of n-heptane and iso-octane by Curran et al. [43,44].

146 The CN of MCDS1 is calculated using Equation (1):

6

148 F<sub>HXN</sub> is the mass fraction of HXN and F<sub>HMN</sub> is the mass fraction of HMN. The CN and compositions of MCDS1 are determined based on those of Diesel Primary Reference Fuel 149 (DPRF58) [45]. DPRF58 is a fuel mixture of 42% HXN and 58% HMN by mass, 150 corresponding to a CN of 50.7. It was found to yield the same ID timings as the D2 fuel 151 experimentally [46,47]. However, Equation (1) is not applicable for fuel model which 152 considers other components. The compositions of MCDS2 are hence determined based on 153 those of the D2 fuel. The composition of toluene is fixed at 28% which is close to the 154 aromatic composition of D2 provided in the study by Kook and Pickett [48] and it is also 155 approximately the average value of the aromatic composition of typical North American 156 diesel fuels [7]. Subsequently, mass fractions of the remaining fuel components such as 157 HXN, HMN and CHX are iterated to match the IDs of D2. The properties of D2, MCDS1 and 158 159 MCDS2 surrogate models as well as size of the surrogate models are presented in Table 2.

160 Upon the construction of the multi-component diesel surrogate models, the relative 161 contribution of each reaction pathway to the net production rate of each species has altered as compared with that of the respective single-component model. The reaction pathways of each 162 fuel species in the multi-component diesel surrogate mechanisms are hence reassessed using 163 reaction pathway analysis. It is observed that there are certain species which can be removed 164 from the mechanisms owing to their insignificant effect on the predictions of fuel oxidation 165 166 process upon integration. One of the examples of the eliminated species is the alkyl radical of HMN, namely HMN-R1. It is formed mainly through H-atom abstraction and alkyl radical 167 decomposition from the fuel species. During the reduction of the detailed HMN mechanism, 168 two isomers of HMN are retained during chain-branching process such as HMN-R8 and 169 HMN-R1. However, when HMN is combined with other fuel components in the MCDS1 and 170 171 MCDS2 surrogate mechanisms, influence of HMN-R1 onto the formation of intermediate

species during chain branching process has become less significant. Therefore, HMN-R1,
together with its corresponding reactions and connected species are removed from the
mechanism. The species and reaction elimination process is performed in the following steps:

(i) Reaction path analysis is carried out for all test conditions. Here, the species for H2/CO 175 and small hydrocarbon oxidations are not taken into consideration as these pools of 176 species are shared by the fuel constituents in the integrated models. The normalised 177 temperature A-factor sensitivities (as defined in Part I) for all reactions involving the 178 potential eliminable species are calculated. If the sensitivity coefficient values for all the 179 corresponding reactions are lower than the user-specified threshold value (i.e. 0.05) 180 181 across all the test conditions, the species is then selected for the subsequent elimination 182 procedure.

- (ii) The model accuracy in ID and species profile predictions is selected as the criterion for
  the species elimination procedure upon model integration. Hence, the 0-D simulations
  across all the test conditions are repeated whenever a species is eliminated from the
  mechanism along with its corresponding elementary reactions so that the model
  predictions are not affected. The maximum relative error tolerance between the model
  predictions before and after elimination procedure is retained to within 5%. Sizes of the
- final, reduced multi-component diesel surrogate models are provided in Table 2.

Subsequently, mechanism validations in 0-D simulations are performed using the MCDS1and MCDS2 diesel surrogate models for:

i) ID timing of each diesel fuel component (Fig. A1 in Appendix A);

- ii) species concentration profiles of each diesel fuel component under auto-ignition (Fig. A2
  in Appendix A) and JSR conditions (Fig. A3 in Appendix A);
- 195 iii) species concentration profiles of each diesel fuel component in a JSR (Fig. 2); and
- iv) ID timing of DPRF58 [45] and n-dodecane  $(n-C_{12}H_{26})$  [9]. (Fig. 3)

197 The test conditions applied here are described in part I. It is noteworthy that the 198 computational results generated by both multi-component diesel models are plotted together 199 with those predicted by each fuel constituent model. The purpose here is to demonstrate that 200 the performance in predicting the ID timings and species concentrations retains after 201 mechanism integration is carried out.

202 In Fig. A1, the computed IDs for HXN and HMN oxidations using MCDS1 and MCDS2 surrogate models are similar as the elementary reactions for HXN and HMN in these two 203 mechanisms are the same. Comparison of ID timings and species profiles with those of CHX 204 detailed mechanism is only performed using MCDS2 as MCDS1 does not contain elementary 205 206 reactions for CHX. It is observed that the predicted ID timings for each surrogate model agree reasonably well with those of the surrogate components. In addition, trend of the 207 species concentration profiles for both auto-ignition and JSR conditions is retained using both 208 209 the multi-component surrogate models in comparison with those of each individual diesel fuel component, as shown in Fig. A2 and Fig. A3, respectively. The results for MCDS1 are 210 comparable with those of MCDS2 with only about  $\pm 5\%$  deviations. Apart from that, the 211 species concentration profiles in a JSR for each surrogate component are reproduced using 212 the MCDS2 surrogate model. This is demonstrated in Fig. 2. The deviations in the species 213 214 concentration predictions between the multi-component surrogate models and the individual detailed models for each fuel constituents can be attributed to the influence of kinetic 215 reactions of other fuel components upon model integration. Despite the apparent difference in 216 217 the absolute values, the relative trends of the species profiles computed by the detailed models are reasonably reproduced by the multi-component surrogate models. 218

219 Comparisons of the ID timing predictions between the surrogate models and DPRF58 are 220 shown in Fig. 3(a). Agreement is achieved between the multi-component surrogate and 221 DPRF58 mechanisms in ID predictions throughout the test conditions. Largest deviation is observed for initial temperature of 850K and  $\Phi$  of 1, which is recorded at 33%. The maximum deviations between the computations by the detailed and reduced models are successfully maintained to within an error tolerance of 40%, which is reasonable for largescale mechanism reduction [51–54]. Apart from that, it is found that MCDS2 with compositions of  $F_{HXN}$ : $F_{HMN}$ : $F_{C7H8}$ : $F_{CHX}$  set to 0.42:0.20:0.28:0.10 yields similar ID timing predictions as DPRF58. In other words, its ignition behaviour is compatible with that of D2.

Moreover, the multi-component diesel surrogate mechanisms are further validated in closed homogeneous batch reactor simulations by varying their CN. ID timing predictions are compared in Fig. 3(b) with respect to the detailed n-dodecane mechanism (CN of 87). Composition of  $F_{HXN}$ : $F_{HMN}$  is set to 0.85:0.15 for MCDS1, corresponding to a CN of 87.25. On the other hand, the fuel composition for MCDS2 is fixed at 0.85:0.15:0:0 for  $F_{HXN}$ : $F_{HMN}$ : $F_{C7H8}$ : $F_{CHX}$ . It is observed that the projected ID timings are well replicated using both MCDS1 and MCDS2 diesel surrogate models.

Upon the model validations under a series of different test conditions in the 0-D kinetic simulations, the proposed MCDS1 and MCDS2 surrogate models are coupled with CFD models in the next section to simulate spray combustion and soot formation under dieselengine like conditions.

#### 239 **3. 2-D Spray Combustion Simulations**

In this section, 2-D multi-dimensional CFD simulations are carried out to simulate spray combustion and soot formation processes using both the multi-component diesel surrogate fuel models. The spray combustion solver in OpenFOAM-2.0.x is used and a multistep soot model is integrated into the solver [55]. The numerical setups for the reacting diesel fuel sprays are described in Table 3(a). Further description of the numerical setups can be found in the former work [12,13]. In this work, the physical properties of the aromatic compounds are represented by those of toluene. On the other hand, the physical properties of the alkanes are represented by the physical properties of n-tetradecane as its physical properties are close to those of real diesel fuels. Thus, the influence of fuel physical properties is isolated and the effect of the chemical kinetics of reaction models can be studied.

Based on the sensitivity study shown in [56], the spatial and temporal evolutions of fourth 250 aromatic ring PAH, pyrene, are similar to those of smaller PAHs or C<sub>2</sub>H<sub>2</sub> when the flame 251 temperature is relatively high (typically under no or low EGR conditions). Hence, 252 implementation of  $C_2H_2$  as soot precursor is usually a good compromise between results 253 accuracy and simplicity when the PAH chemistry is absent [4,57–59]. C<sub>2</sub>H<sub>2</sub> is selected as the 254 255 soot precursor in the numerical simulations using the MCDS1 surrogate model as this mechanism does not contain PAH mechanism. On the other hand, C<sub>6</sub>H<sub>6</sub> is present in the 256 MCDS2 surrogate model when CHX mechanism is integrated into the multi-component 257 258 mechanism during the model development stage. With the presence of the PAH chemistry in the surrogate model, C<sub>6</sub>H<sub>6</sub> is therefore designated as the soot precursor species in the 259 260 respective modelling studies. In order to simulate the mass addition on soot particle surface, C<sub>2</sub>H<sub>2</sub> is consistently used as the soot surface growth species when MCDS1 and MCDS2 are 261 applied. On the other hand, OH and O<sub>2</sub> are set as the soot oxidant species for the calculation 262 263 of soot mass destruction.

In this section, the numerical simulations are separated into two parts. First and foremost, MCDS1 is applied in a sensitivity test to examine its reactivity towards variation in CN. Mass fractions of HXN and HMN as well as the corresponding CN are shown in Table 3(b). It is then followed by the validation of both MCDS1 and MCDS2 using the measurements of D2 fuel [18,48] from constant volume combustion chamber experiments. Mass fraction of each component is varied to mimic the actual fuel properties, which are detailed in Table 2. Operating conditions used for this validation exercise are demonstrated in Table 3(c). 271 Measurements are available for reacting spray test cases at 15% O<sub>2</sub> mole fraction. This condition represents a reactive environment of air diluted with exhaust gas recirculation. The 272 ambient temperature varies from 900K to 1000K while the ambient density is fixed at 273 22.8kg/m<sup>3</sup>. The computed ID, lift-off length (LOL) and SVF are compared to the 274 experimental data. For the simulation results, ID is defined as the maximum dT/dt gradient of 275 the temperature profile. On the other hand, LOL is defined as the distance from the injector to 276 the closest layer where OH mass fraction reaches 2% of its maximum value in the domain. 277 These definitions correspond with those recommended by Engine Combustion Network [50]. 278

#### 279 3.1 Sensitivity Test of the MCDS1 Surrogate Model on CN Variations

The effects of variation in CN on LOL and ID predictions are demonstrated in Fig. 4(a). As the CN increases, it is expected that the ID becomes shorter. Thus, the ignition occurs at a location closer to the injection tip and the associated flame lift-off is hence shorter. The trend is replicated by the model. Based on the results shown in Fig. 4(a), it is observed that the kinetics of MCDS1 surrogate model is sensitive to changes in CN ranging from 15 to 100. MCDS1 serves as a promising surrogate model for diesel fuels with various CN.

In the next section, the MCDS1 model is further validated using the D2 fuel data. Its performance is also compared against that of the counterpart MCDS2 which considers CHX and toluene reactions.

#### 289 3.2 Validation using D2 experimental data

The predicted IDs and LOLs by MCDS1 and MCDS2 surrogate models for D2 fuel combustion at ambient temperatures of 900K and 1000K are demonstrated in Fig. 4(b). It is observed that the predictions follow the overall trend where the calculated ID and LOL decrease with increasing ambient temperature. The maximum deviations in ID and LOL 294 predictions with respect to the experimental measurements retain within 15.4% and 23%, respectively. The IDs calculated using MCDS1 agree well with the measurements in both 295 cases but shorter LOLs are produced. On the other hand, the predicted IDs and LOLs are 296 297 slightly longer in both cases when MCDS2 is applied. This can be attributed to the inclusion of toluene which is difficult to ignite. As it is considered in the initial composition of the 298 MCDS2 model, the resulting ID becomes longer. The flame hence stabilises at a location 299 300 further downstream from the injection tip, yielding a longer LOL. It is noted that the deviations between the experimental and computed LOLs using MCDS2 are less pronounced, 301 302 where deviations of 3.5mm and 2.5mm are recorded for ambient temperatures of 900K and 1000K, respectively. It is worth mentioning that the deviations between the measured and 303 computed LOLs can also be attributed to the absence of turbulence - chemistry interaction 304 (TCI) in the numerical computations. Inclusion of TCI effects has been shown important to 305 improve the prediction of the OH distributions and hence the development of flame lift-off 306 [60-62]. 307

In addition, the SVF predictions of D2 fuel using MCDS1 and MCDS2 are demonstrated in 308 Fig. 5(a). The predictions are compared with the experimental soot clouds [18] obtained at 309 quasi-steady state (4ms after start of injection) for ambient temperatures of 900K and 1000K. 310 These experimental soot images are obtained from the PLII measurement which provides 311 two-dimensional information of SVF distributions for D2 fuel. The red dashed lines on the 312 images indicate the flame LOLs and only qualitative information of soot distribution in the 313 fuel jets is provided based on the images obtained from the experiment. In Fig. 5(a), it is 314 observed that the soot length predicted by MCDS2 is similar to that of the experimental 315 measurements for D2 fuel combustion at ambient temperatures of 900K and 1000K. In 316 contrast, the simulated soot clouds appear to be larger than the soot clouds observed in the 317 experiments for both cases when MCDS1 is employed. In comparison to the predictions of 318

MCDS2, the soot clouds predicted by MCDS1 are formed at further upstream locations closer 319 to the injection tip. This can be attributed to the associated shorter LOLs. Subsequently, 320 quantitative SVF predictions along spray axis at quasi-steady state for D2 fuel combustion 321 322 are demonstrated in Fig. 5(b). Results in Fig. 5(b) shows that the local SVF values produced by MCDS1 and MCDS2 are different. MCDS1 estimates maximum local SVF values of 323 15ppm and 24ppm for the 900K and 1000K test cases, respectively. On the other hand, the 324 maximum local SVF values predicted by MCDS2 for the 900K and 1000K test cases are 325 5.8ppm and 12.2ppm, respectively. It is observed that the local SVF given by MCDS1 is 326 consistently higher than that of MCDS2. This can be attributed to several reasons. First of all, 327 the LOLs predicted by MCDS1 are shorter. The associated amount of air entrained into the 328 fuel rich core region is lesser. Besides this, MCDS1 utilises C<sub>2</sub>H<sub>2</sub> as soot precursor while 329 330 MCDS2 uses  $C_6H_6$ . The mass concentration of  $C_2H_2$  is commonly higher than that of PAH, leading to higher level of soot inception rate and hence soot mass gained. Lastly, as compared 331 to MCDS1, the amount of branched-alkane (i.e. HMN) used in the initial fuel composition of 332 the MCDS2 model is lower. As a consequence, the production rate of C<sub>2</sub>H<sub>2</sub> drops and the 333 soot mass gained through the soot surface growth process decreases correspondingly, 334 yielding lower SVF values. 335

336 The next parameter used to evaluate the performance of the multi-component surrogate models is the soot formation behaviour at different ambient temperatures. The results 337 indicates that the predicted maximum local SVF increases by a factor of 1.6 as the ambient 338 temperature is raised from 900K to 1000K when MCDS1 is applied. The use of MCDS2 339 increases the maximum local SVF by a factor of 2.1. The ratio of increment in maximum 340 SVF from ambient temperature of 900K to 1000K is henceforth represented by ratio<sub>SVF</sub> for 341 brevity. Based on the measurement presented by Kook and Pickett [18], the experimental 342 ratio<sub>SVF</sub> is more than three for D2 fuel combustion. The use of MCDS2 is found to improve 343

the overall simulated  $ratio_{SVF}$ . This can be attributed to the inclusion of aromatic and cycloalkane components in the initial fuel composition in MCDS2. At different ambient temperatures, the production of  $C_2H_2$  is different when the aromatic and cyclo-alkane components are considered and omitted. This is further elaborated in the subsequent section.

348 Numerical analysis of  $C_2H_2$  and  $C_6H_6$  formations is performed at times when temperature

rises by 100K, 200K, 400K, 800K and 1000K from the initial ambient temperatures. The

results are demonstrated in Fig. 6 and the temperature tolerance for this comparison study is

 $\pm 20$ K. Besides these, C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> formations at quasi-steady state are also provided, in

352 which the computed results are obtained at 4ms after the time of injection to ensure that the

353 formation of the selected species in all test cases reaches a quasi-steady state. The

354 observations obtained from the numerical analysis are discussed below:

355 (i) Results in Fig. 6(a) depict that the amount of  $C_2H_2$  produced at the temperature rise of 356 100K from the initial ambient temperatures of 900K and 1000K is lower than  $C_6H_6$  when

both MCDS1 and MCDS2 are applied.  $C_6H_6$  is mainly produced through the breakdowns

of cyclo-paraffin ring as well as toluene via R1 to R4.

359	$CYCHEXENE + OH \Leftrightarrow CYHX1N3J + H_2O$	(R1)
360	CYHX13ENE + H ⇔ CYHX1N3J	(R2)
361	CYHX13ENE $\Leftrightarrow$ C <sub>6</sub> H <sub>6</sub> + H <sub>2</sub>	(R3)
362	$C_6H_5CH_3 \Leftrightarrow C_6H_6 + CH_3$	(R4)

363 (ii) At temperature interval of 200K from the initial ambient temperatures, it is observed that 364 the maximum values of  $C_2H_2$  calculated using MCDS2 are approximately two-fold and 365 five-fold greater than those predicted by MCDS1 in the 900K and 1000K cases, 366 respectively. This is depicted in Fig. 6(b). The apparent differences in the predicted  $C_2H_2$ 367 levels can be attributed to the significant amount of  $C_6H_6$  produced by MCDS2, which

368	subsequently leads to higher production rate of $C_2H_2$ as compared to that of $I$	MCDS1.
369	The key formation pathways to $C_2H_2$ from $C_6H_6$ are described by reactions R5 to	R7.
370	$C_6H_6 \Leftrightarrow 2C_3H_3$	(R5)
371	$C_3H_3 + H \Leftrightarrow C_3H_2 + H_2$	(R6)
372	$C_3H_2 + OH \Leftrightarrow C_2H_2 + HCO$	(R7)
373	(iii) In Fig. 6(c), it is observed that the peak mass fractions of $C_2H_2$ in the 1000K of	cases are
374	consistently higher than those in the 900K cases when the initial ambient temp	peratures
375	increase by 400K, disregards the use of MCDS1 and MCDS2. This is due to the	e higher
376	production rate of $C_2H_2$ from the dissociation of $C_6H_6$ by R5 to R7 using MCDS2	2 as well
377	as the consumption of $C_2H_4$ using both MCDS1 and MCDS2 in the 1000K ca	ses. The
378	formation of $C_2H_2$ is significantly dependent on $C_2H_4$ and the main formation p	oathways
379	from $C_2H_4$ to $C_2H_2$ are described by reactions R8 to R10.	
380	$C_2H_4 + M \Leftrightarrow C_2H_2 + H_2 + M$	(R8)
381	$C_2H_4 + OH \Leftrightarrow C_2H_3 + H_2O$	(R9)
382	$C_2H_3 + M \Leftrightarrow C_2H_2 + H + M$	(R10)
383	(iv) At temperature interval of 800K from the initial ambient temperatures, the as	ssociated
384	mass fractions of C <sub>2</sub> H <sub>2</sub> predicted by MCDS1 start to grow significantly and	the peak
385	values match with those produced by MCDS2, as demonstrated in Fig. e	5(d). As
386	discussed in the previous section, MCDS1 contains higher amount of branched-a	alkane in
387	the initial fuel composition. As a result, the production rate of $C_2H_2$ becomes hig	gher than
388	that of MCDS2 which eventually results in the current observation.	
389	(v) Same observation as of Fig. 6(d) persists until approaching ignition points.	
390	(vi) The associated mass fractions of C <sub>2</sub> H <sub>2</sub> continue to rise and eventually those prec	licted by

- 392 state, as illustrated in Fig. 6(f). This corresponds well with the earlier findings in Fig.
- 393

## 5(b), in which SVF predictions by MCDS2 are lower for both 900K and 1000K cases.

The current results suggest that the MCDS1 model is useful for the soot formation 394 simulations where the effect of aromatic chemistry plays a less significant role. For instance, 395 Vishwanathan and Reitz [63] reasonably captured the variation of SVF with respect to the 396 change of injection pressure and injector diameter using a single-component surrogate model, 397 namely n-heptane, showing that the presence of aromatic compounds has less pronounced 398 399 impact on such application. On the other hand, this work demonstrates that the overall soot formation predictions have been improved by considering cyclo-alkane and aromatic 400 compounds. The revised counterpart, MCDS2, is found to predict a higher ratio<sub>SVF</sub> when the 401 ambient temperature varies. Yet, the computed ratio<sub>SVF</sub> is under-predicted as compared to that 402 of the experiment measurement where  $ratio_{SVF} > 3$  is recorded. Further improvement is 403 necessary on the coupled MCDS2-soot model to simulate the complex soot formation 404 phenomenon. 405

The ambient pressure is increased to retain the ambient density of 22.8kg/m<sup>3</sup> as the ambient 406 temperature varies between 900K and 1000K in the current test cases. However, the 407 408 conventional multistep soot model does not capture pressure effects of soot formation [56]. The current soot model assumes that soot particles grow primarily by the addition of gaseous 409  $C_2H_2$ . The use of a pressure dependent surface growth model constant is expected to improve 410 ratio<sub>SVF</sub>. Alternatively, the inclusion of PAH condensation effects on soot formation under 411 such high pressure, high temperature environment may aid to improve the prediction as well. 412 413 Bisetti et al. [64] who implemented Hybrid Method of Moments in their Direct Numerical Simulation of soot formation in the n-heptane/air turbulent non-premixed flame revealed that 414 PAH condensation is significant to the soot mass generation. 415

It is noteworthy that NOx submodel was not included in the multi-component diesel 416 surrogate fuel models. Despite of this, these fuel models are expected to produce reasonable 417 predictions for thermal NOx, which is the major portion of NOx emissions in conventional 418 diesel engines. Thermal NOx formation rate is highly dependent on temperature [65], hence 419 reasonable predictions of the temperature is the pre-requisite for the associated calculation. 420 In the current numerical simulations, the maximum local temperatures calculated by the 421 integrated fuel models are between 2300K and 2400K. These predictions are consistent with 422 those obtained in the study of Pickett et al. [66] for 15% ambient oxygen. Apart from these, it 423 424 is noteworthy that the accurate predictions of OH concentrations are essential for simulating thermal NOx formation. Based on the kinetic studies in the 0-D simulations (as shown in Fig. 425 A2 and A3 in Appendix A), it is observed that the OH mole fractions predicted by the 426 427 integrated models correspond reasonably well with the computations of the detailed models. However, it should also be highlighted that the computation of thermal NOx emissions also 428 depends on the associated Arrhenius rate constants [67]. Hence, the surrogate models can be 429 useful for thermal NOx simulations only when they are integrated with the extended 430 Zeldovich reaction rates which are validated for engine applications. 431

#### 432 **4.** Conclusions

In this study, two multi-component diesel surrogate models namely MCDS1 and MCDS2 433 with different fuel compositions and components have been introduced. MCDS1 model 434 consists of straight- (HXN) and branched- (HMN) alkanes while MCDS2 consists of 435 aromatic hydrocarbon (toluene), straight- (HXN), branched- (HMN) and cyclo- (CHX) 436 alkanes. Surrogate fuel models with CN values ranging from 15 to 100 can be produced 437 through blending of HXN and HMN. In addition, CHX and toluene are incorporated into 438 MCDS2 model to achieve compositional match and to improve soot formation predictions. 439 440 The integrated models are comprehensively validated in 0-D chemical kinetic simulations

441 under a wide range of shock tube and JSR conditions, by comparing the computations to those predicted by each detailed and reduced fuel constituent models. It is found that 442 performance of the surrogate models in ID and species concentration predictions under both 443 auto-ignition and JSR conditions is maintained after mechanism integration. Apart from 444 these, the integrated models are also validated against the JSR experimental results for each 445 diesel fuel constituents. Overall agreement between the computations and measurements is 446 447 achieved with maximum deviations of one order of magnitude on the absolute values. Following that, the fidelity of both multi-component diesel surrogate models is further 448 449 assessed in the 2-D spray combustion simulations. Numerical results reveal that MCDS1 is sensitive to the change of CN. The predicted ID and LOL correspond well with the variation 450 451 of CN. Next, ID, LOL and SVF calculated using MCDS1 and MCDS2 are validated against 452 constant volume combustion chamber experimental data. ID and LOL predictions given by 453 both surrogate models agree reasonably well with the D2 measurements. Besides, it is observed that MCDS2 is able to provide better predictions in soot formation events than 454 MCDS1 due to the inclusion of aromatic and cyclo-alkane components. It is revealed that 455 ratio<sub>SVF</sub> of 1.6 is obtained for D2 fuel combustion when the ambient temperature increases 456 from 900K to 1000K with the absence of aromatic and cyclo-alkane components. The 457 simulated ratio<sub>SVF</sub> increases to 2.1 when both components are incorporated into the base 458 mechanism as the inclusion of these two components provides alternative pathways to form 459 460 rich species such as C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub>. In this work, the effects of including aromatic and cycloalkane components in the surrogate model on soot formation events are highlighted. It is 461 demonstrated that MCDS2 is a potential surrogate model for D2 fuel. Nonetheless, additional 462 463 work is required to improve the coupled MCDS2-soot model in simulating the complex soot formation phenomenon. 464

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656



Fig. 1 Sequential steps to formulate the multi-component diesel surrogate fuel models.



Fig. 2 Computed and experimental species mole fractions obtained from the oxidation of (a) 0.03% HXN (pressure = 1atm,  $\Phi$  = 1.5, residence time = 70ms), (b) 0.07% HMN (pressure = 10atm,  $\Phi$  = 2, residence time = 1s), and (c) 0.1% CHX (pressure = 10atm,  $\Phi$ = 1.5, residence time = 0.5s) under JSR conditions.



Fig. 3 Comparisons of the ID predicted by MCDS1 and MCDS2 surrogate models with the detailed mechanisms of (a) DPRF58<sup>a</sup> [45] and (b) n-dodecane<sup>b</sup> [9] for initial pressure of 40bar,  $\Phi$  of (i) 0.5, (ii) 1 and (iii) 2. [<sup>a</sup>IDs of DPRF58 were computed by Perini et al. [45] using the detailed mechanism of Westbrook et al. [26] in a constant volume vessel using identical initial conditions; <sup>b</sup>The mechanism of n-dodecane was extracted from the detailed mechanism of Westbrook et al. [9] for combustion of n-alkane hydrocarbons from n-octane to HXN.]



Fig. 4 (a) ID (black) and LOL (red) predictions against CN for the sensitivity tests using MCDS1 surrogate model for ambient temperatures of 900K (X) and 1000K (•); (b) ID (black) and LOL (red) predictions using MCDS1 ( $\circ$ ) and MCDS2 (X) surrogate models in comparison with the experimental measurements (•) for D2 fuel combustion for ambient temperatures of 900K and 1000K.



Fig. 5 (a) Qualitative comparisons of predicted SVF contours and experimental soot cloud images at quasi-steady state for D2 fuel combustion in a constant volume chamber using MCDS1 and MCDS2 surrogate models; (b) Comparisons of the computed SVF along spray axis using MCDS1 (black) and MCDS2 (red) surrogate models at ambient temperatures of 900K (...) and 1000K (--).



Fig. 6 Comparisons of  $C_2H_2$  and  $C_6H_6$  mass fractions at temperature intervals of (a) 100K, (b) 200K, (c) 400K, (d) 800K, (e) 1000K and at (f) quasi-steady state for D2 fuel combustion at ambient temperatures of 900K and 1000K using MCDS1 and MCDS2 diesel surrogate models. [\*\*Note: Mass fractions of  $C_6H_6$  at  $\Delta T = 100K$ ,  $\Delta T = 200K$  and  $\Delta T = 400K$  are scaled down by a factor of 20, 10 and 5, respectively.]

Table 1	<b>Details of</b>	the currently	available	multi-com	ponent surre	ogate fuel	models.
						- <b>-</b>	

Surrogate Models	Compositions	$N_S$	$N_R$	Model Descriptions	Year of Publication	Author(s)	Ref.
IDEA	n-decane, 1- methylnaphthalene	118	557	Describe fuel oxidation, soot and NOx formations; Contain low-temperature kinetics for auto-ignition.	1999	Hergart et al.	[31]
PRF	iso-octane, n-heptane	990	4,060	Describe auto-ignition and intermediate product formation at high- pressure conditions; Contain kinetic reactions for low to high temperatures as well as NTC behaviour.	1998	Curran et al.	[32]
		58	120	Describe ignition of PRF in a HCCI engine; Contain kinetic reactions for intermediate and high temperatures.	2007	Kirchen et al.	[33]
		73	296	Describe oxidation of diesel/gasoline; Contain kinetic reactions for low	2013	Wang et al.	[34]
		1,034	4,236	to high temperatures as well as NTC behaviour. Reduced model of Wang et al. [34] is developed based on the LLNL detailed model [35].	-	LLNL	[35]
Diesel PRF	HXN, HMN	2,800	11,000	Contain alkylperoxy radical sub-mechanism and kinetic reactions for low to high temperatures as well as NTC behaviour.	2011	Westbrook et al.	[26]
DOS	n-heptane, toluene	70	305	Describe fuel oxidation, soot and NOx formations; Optimised for engine applications.	2007	Golovitchev et al.	[36]
PRF+1	iso-octane, n-heptane, toluene	469	1,221	Describe fuel oxidation and soot formations; Contain kinetic reactions for low and intermediate temperatures.	2007	Chaos et al.	[24]
TRF-PAH	n-heptane, toluene, PAH	71	360	Describe combustion and PAH formation; Contain kinetic reactions for low to high temperatures.	2013	Wang et al.	[25]
POLIMI_ Diesel_201	HXN , toluene, xylene, methylnaphthalene	201	4,240	Validated under shock-tube (intermediate to high temperatures) and JSR (low to intermediate temperatures) simulations.	2014	Ranzi et al.	[38]
POLIMI_NC12 96 + PAH	n-dodecane, PAH	133	2,275	Contain kinetic reactions for low to high temperatures; Reasonably capture the important characteristics of spray ignition processes.	2015	Frassoldati et al.	[30]
Skeletal Diesel Surrogate Fuel Model	n-decane, iso-octane, methylcyclohexane, toluene	70	220	Validated under shock-tube, JSR, flow reactor and pre-mixed laminar flame simulations.	2015	Chang et al.	[29]

 $N_S$  and  $N_R$  denote the number of species and reactions, respectively; NTC is defined as negative temperature coefficient.

# Table 2 Fuel properties [18,48-50] and chemistry sizes of detailed/reduced chemicalmechanism models used in the current work.

Properties	D2	MCDS1	MCDS2
Chemical Formula (mass fraction)	C <sub>3</sub> -C <sub>25</sub>	$F_{HXN}: F_{HMN} = 0.42: 0.58$	$\begin{split} F_{HXN}: F_{HMN}: F_{toluene}: F_{CHX} = \\ 0.42: 0.20: 0.28: 0.10 \end{split}$
Type of Hydrocarbon	33.8% <sup>a</sup> / 27% <sup>b</sup> Aromatics, 65.0% <sup>a</sup> Alkanes, 1.2% <sup>a</sup> Olefins	Straight- and branched-alkanes	Straight-, branched- and cyclo-alkanes, aromatic
CN	46 (40-56)	50.7	-
Molecular Weight [g/mol]	~200.000	226.446	174.612
H/C Ratio	1.800	2.125	1.838
Lower Heating Value [MJ/kg]	42.975	43.900 <sup>c</sup>	42.928 <sup>c</sup>
Boiling Point [°C]	350	287	287
Flash Point [°C]	73.0	111.5 <sup>c</sup>	74.7 <sup>c</sup>
Size of final reduced mechanism $(N_S; N_R)$	-	128; 408 <sup>d</sup> 88; 284 <sup>e</sup>	169; 545 <sup>d</sup> 129; 411 <sup>e</sup>

F denotes mass fraction

<sup>a</sup>Composition of aromatic compounds provided in the study of Pickett and Siebers [37]

<sup>b</sup>Composition of aromatic compounds provided in the study of Kook and Pickett [48]

<sup>c</sup>Volume-averaged properties are given for MCDS1 and MCDS2

<sup>d</sup>Before elimination of unimportant species and reactions upon integration

<sup>e</sup>After elimination of unimportant species and reactions upon integration

Table 3 (a) CFD model setups used for reacting diesel fuel spray simulations; (b) Sensitivity test with various CN using MCDS1 surrogate model; (c) Experimental operating conditions.

(a) Numerical Setups					
Grid	Grading; 0.25mm x 0.25mm (minimum)	, 4mm x 2mm			
Olld	(maximum) in both radial and axial	directions			
Turbulence Model	Standard <i>k</i> - $\varepsilon$ (C <sub>µ</sub> = 0.09 ; C <sub>1</sub> = 1.54 ; C <sub>2</sub> = 1	$.92$ ; $C_3 = -0.33$ ;			
	$\sigma_k = 1$ ; $\sigma_c = 1.3$ )				
Breakup Model	Reitz Diwakar ( $C_{bag} = 6$ ; $C_b = 0.785$ ; $C_{strip}$	Reitz Diwakar ( $C_{bag} = 6$ ; $C_b = 0.785$ ; $C_{strip} = 0.5$ ; $C_s = 12$ )			
Soot Model	Multi-step [55]				
Time Step (s)	5.00E-07				
Number of Parcels	100,000				
Initial k $(m^2/s^2)$	0.735				
Initial $\varepsilon$ (m <sup>2</sup> /s <sup>3</sup> )	3.5				
(b) Sensitivity Test with Various CN					
Tests	<b>Compositions</b> (F <sub>HXN</sub> :F <sub>HMN</sub> )	CN			
1	1:0	100			
2	0.75:0.25 78.75				
3	0.50:0.50	57.5			
4	0.25:0.75	36.25			
5	0:1	15			
(c) Experimental Operating Conditions					
Ambient temperature (K)	900/1000				
Ambient density (kg/m <sup>3</sup> )	22.8				
Ambient Pressure (MPa)	6/6.7				
Orifice diameter (mm) 0.09					
Ambient composition (%) $O_2 = 15\%$ ; $CO_2 = 6.23\%$ ; $H_2O = 3.62\%$ ; $N_2 = 75.15\%$					
Injection duration (ms)	7				

 $\overline{k}$  and  $\varepsilon$  denote the turbulence kinetic energy and turbulence dissipation rate, respectively



**Appendix A: Validation Results for 0-D Chemical Kinetic Simulations** 

Fig. A1 Computed ID of (a) HXN, (b) HMN and (c) CHX calculated by respective detailed and reduced mechanisms as well as MCDS1 and MCDS2 surrogate models, with initial pressure of 60bar and  $\Phi$  of (i) 0.5, (ii) 1.0, (iii) 2.0.



Fig. A2 Computed species profiles for (a) HXN, (b) HMN and (c) CHX combustions under auto-ignition condition, with initial pressure of 60bar, initial temperature of 950K and  $\Phi$  of 1.



Fig. A3 Computed species profiles of (a) HXN, (b) HMN and (c) CHX oxidations under JSR condition as a function of temperature, with initial pressure of 60bar and  $\Phi$  of 1.