The effect of oxygenated fuel properties on diesel spray combustion and soot formation

Wonah Park^{ab}, Seunghyun Park^a, Rolf D. Reitz^a, and Eric Kurtz^c*

^a Engine Research Center, University of Wisconsin-Madison, Madison, WI 53706, United States

^b Korea Institute of Machinery & Materials, Daejeon, 305-343, South Korea (Present)

^c Ford Motor Company, Dearborn, MI 48126, United States

*** Corresponding Author**

E-mail : wpark@kimm.re.kr

Phone : +82-42-868-7053

Address : 156 Gajeongbuk-Ro, Yuseong-Gu, Daejeon 34103, South Korea

ABSTRACT

Diesel engines have advantages due to their potential for high fuel conversion efficiency. However, it is necessary to reduce pollutant emissions, particularly NO_x and soot to meet emission mandates. Many studies have shown that oxygenated fuel additives can effectively reduce soot emissions. In this research, to investigate the effect of oxygenated fuel properties on combustion and soot emission, CFD simulations were carried out using newly developed

chemical mechanisms for various oxygenated fuels such as tri-propylene glycol methyl ether, methyl decanoate, and dimethyl ether. The results show that the formation of soot precursors decreases with increased oxygen content and decreased number of C–C bonds in the fuel. The fuel molecular structure strongly affects soot formation in addition to fuel-air mixing. Comparisons of fuel blends (oxygenated fuels with n-hexadecane) including methyl decanoate, which have the same fuel oxygen ratio, show that the effects of the ignition delay and lift-off length control soot formation for fuels with similar fuel oxygen ratio and number of C-C bonds.

KEYWORDS

oxygenated fuel, diesel spray combustion, soot emission, tri-propylene glycol methyl ether (TPGME), methyl decanoate (MD), dimethyl ether (DME)

1. INTRODUCTION

Current engine research is focused on reducing exhaust emissions and improving fuel economy. This is motivated by increased environmental concerns, strict government regulations on exhaust emission standards. Direct injection diesel engines have advantages for reducing fuel consumption and greenhouse gas emissions due to the potential of high fuel conversion efficiency (a measure of how effectively fuel is transformed into usable energy) [1]. However, it is necessary to reduce emissions, particularly nitrogen oxides (NO_x) and soot to meet the emission regulations.

1
2
3
4 Among the various methods to reduce soot emissions in diesel engines, many studies have
5
6 shown that oxygenated fuel additives can effectively reduce soot emissions [2-8]. Miyamoto et
7
8 al. [2] showed experimentally that soot can be significantly reduced by adding oxygenated
9
10 species to the fuel. Westbrook et al. [3] found that the presence of oxygen in the fuel reduces
11
12 soot and soot precursors during combustion. Mixtures of these additives to a base hydrocarbon
13
14 fuel reduces soot formation by decreasing the overall equivalence ratio, producing higher
15
16 temperatures, and providing the necessary oxygen radical species to consume more soot
17
18 precursor species. Recently, Manin et al. [4] studied the effects of oxygenated fuels on
19
20 combustion and soot formation using optical diagnostics to monitor ignition, combustion, and
21
22 soot formation processes from spray flames in a constant-volume combustion vessel. They
23
24 compared various oxygenated fuels and fuel blends to identify and understand those fuel
25
26 properties that inherently extend the operating range for leaner lifted-flame combustion
27
28 requirements.
29
30
31
32
33
34
35
36

37 The present research focuses on investigating the combustion and soot formation characteristics
38
39 of oxygenated fuels. To address the effects of oxygenated fuels on combustion and emissions,
40
41 three different oxygenated fuels, including tri-propylene glycol methyl ether (TPGME), methyl
42
43 decanoate (MD), and dimethyl ether (DME), were considered and compared with n-hexadecane.
44
45 At first, new reduced MD mechanism was developed to match both measured shock tube and
46
47 spray ignition delays. Oxygenated fuel mechanisms, including MD were validated based on
48
49 experimental data, and then applied to CFD simulations to provide guidelines for improving
50
51 engine soot emissions by accounting for the characteristics of oxygenated fuel properties over
52
53 various conditions. Then, simulations were performed to compare the oxygenated fuels and to
54
55 give more insights between soot formation and an oxygenated fuel's molecular structure, which
56
57
58
59
60
61
62
63
64
65

could not be explained by the experiments. Last, simulations using fuel blends (TPGME/n-hexadecane and DME/n-hexadecane), which have the exactly same fuel oxygen ratio as MD, were also performed to investigate soot formation under the same fuel oxygen ratio [9] condition.

2. METHODOLOGY

2.1 Fuel Models

Six different fuels were used to help understand which fuel properties affect soot formation.

Three oxygenated fuels, TPGME, DME, and MD, which have different fuel oxygen contents and molecular structures were considered. G60 and M60 are blends of TPGME and n-hexadecane, and DME and n-hexadecane, respectively, which have the same fuel oxygen ratio as MD. The blending ratios (by mole) of G60 and M60 are listed in Table 1. A sixth fuel was a neat n-alkane without oxygenate: n-hexadecane; this fuel served as the baseline reference fuel. The specific properties of each fuel, such as its oxygen content, C-C bond number per molecule, molecular weight, fuel oxygen ratio, lower heating value, and cetane number are listed in Table 1. The number of C-C bonds is obtained from the fuel molecular structure, which is described in Figure 1.

The fuel oxygen ratio [9] is given by

$$\Omega_f = \frac{\sum_j a_j n_{O,j}}{\sum_m a_m (2n_{C,m} + \frac{1}{2}n_{H,m})}$$

Where a is the number of moles, n is the number of atoms, j is fuel, k is oxidizer, m is sum of fuel and oxidizer, O is oxygen, C is carbon, and H is hydrogen.

For the simulations, new reduced TPGME and MD mechanisms were used. A detailed TPGME mechanism [13] (552 species and 2712 reactions) was reduced to a skeletal TPGME mechanism with 85 species and 478 reactions [14]. Several pre-exponential factors were adjusted to within an order of magnitude to capture constant volume vessel ignition delays of the detailed TPGME mechanism at an initial pressure of 40 bar, and the predictions from the skeletal mechanism showed good agreement with those of the detailed one.

An existing MD mechanism [15] showed good agreement with measured trends for the homogeneous low pressure ignition condition. However, it predicted longer ignition delays than measurements (by Manin et al. [4]) and it did not predict ignition below 1000 K under high pressure constant volume chamber conditions. As there are uncertainties in spray models, unlike under the shock tube test condition, various attempts were performed to validate constant volume spray results using the previous MD mechanism by adjusting the spray sub-model constants. However, the simulation results were not able to agree with the experimental data by using the existing MD mechanism and adjusting the spray models. Therefore, a new reduced MD mechanism was developed to match both shock tube and spray ignition delays. Additional ketohydroperoxide isomers and related reactions from MD detailed mechanism [16] were added to the new mechanism by following steps as shown in Figure 2. Table 2 lists comparison of existing and new MD mechanisms and the new MD mechanism has 79 species and 235 reactions. The detailed reactions and their rate constants are listed in Table A-1 in Appendix A and thermodynamic data is in Appendix B.

For DME, the MultiChem mechanism [17], which consists of 113 species and 487 reactions, was used. To consider the fuel blends, the TPGME and DME mechanisms were combined with a reduced n-hexadecane mechanism which consists of 67 species and 319 reactions [18]. Among the n-hexadecane mechanism, 28 species and 112 reactions were extracted from the n-hexadecane mechanism and combined by excluding species and reactions in common with the TPGME and DME mechanisms.

2.2 Soot Model

A multi-step soot model was applied to predict soot formation and oxidation processes [19-20]. In this modeling approach soot is considered to be formed from pyrene, whose concentration is predicted by a PAH formation mechanism. Then the soot particle undergoes C_2H_2 assisted surface growth, coagulation, and is oxidized by O_2 and OH radicals, and PAH condensation is considered on the soot particle surface. The reduced PAH mechanism with 20 species and 132 reactions was added to the fuel mechanisms.

2.3 Other Computational Models

The developed fuel surrogate models were implemented in the KIVA-ERC code to predict the combustion and emission characteristics. The SpeedCHEM code [21] was coupled to the KIVA code to reduce the computational time of the multi-component reaction mechanisms. For the spray calculations, the KH-RT model [22] was used, and the vaporization of the spray was modeled by using a discrete multi-component (DMC) model [23].

3. MODEL VALIDATION

Shock tube ignition delay predictions using the fuel mechanisms were validated using available experimental data. The calculations were performed with the SENKIN code [24] under constant volume conditions.

The predicted shock tube ignition delay of MD was compared with measured data by Wang et al. [25]. Figure 3 shows comparisons of measured and predicted shock tube ignition delays of MD at $\Phi=1$ and a relatively low pressure 16 bar ambient gas condition. The predicted ignition delay using the new mechanism under predicts the measured data at 700 ~ 900 K ambient temperature conditions. A previous MD mechanism [15], which is described in Figure 3 ('Sim_Old') showed better prediction than the present new MD mechanism ('Sim_New'). However it was not able to predict spray ignition below 1000 K under high pressure constant volume conditions, as discussed later. It is expected that the new MD mechanism shows better agreement than the previous mechanism under high ambient pressure conditions, such as at 40 atm like in the DME results (Figure 4).

For validation of the DME mechanism, shock tube tests by Pfahl et al. [26] were used. In the experiments, ignition delay times of stoichiometric DME/air mixtures were measured at two different initial pressures, one of which is close to engine conditions, and Figure 4 shows the comparisons. The predicted results with the reduced DME mechanism show good agreement with the measured data, especially at the high ambient pressure condition, which is of interest for the present engine applications.

Spray ignition delays and lift-off length data of the fuels from the KIVA-ERC code were compared with the Sandia constant volume spray experiments [4]. Experiments were performed

1
2
3
4 under the ‘Spray A’ standard ambient condition recommended by Engine Combustion Network
5
6 (ECN), which were 900 K ambient temperature, 22.8 kg/m^3 ambient density, and 15 % (vol.)
7
8 oxygen concentration [27]. In addition to the standard condition, the ambient temperature was
9
10 changed from 750 K to 1200 K for a parametric study according to the ECN ignition delay and
11
12 lift-off length guidelines [27]. The fuels were injected by the ‘Spray A’ injector, which has 90
13
14 μm diameter orifice and the injection pressure was 150 MPa. As ignition delay and lift-off length
15
16 were measured using OH chemiluminescence [4], the predicted ignition delay and lift-off length
17
18 were determined using the OH molar concentration and distribution, as shown in Figure 5. The
19
20 predicted ignition delay was determined by the point where OH increased rapidly, and the lift-off
21
22 length was obtained from the OH distribution during the quasi-steady period of the flame.
23
24
25
26
27
28
29

30 The sprays were assumed to be axisymmetric, so a 2-D axisymmetric mesh was used for the
31
32 simulations. The computational grid contained 12,400 cells, 0.9mm in the radial direction for
33
34 half of the computational domain and 1.8mm for the rest of the grid. Extensive studies have been
35
36 performed regarding grid resolution and sensitivities to relevant mesh parameters in previous
37
38 studies [28-30].
39
40
41
42

43 Shock tube ignition delay, spray ignition delay, and lift-off length measurements of TPGME are
44
45 not currently available; so, available results of a 50:50 mixture of TPGME and n-hexadecane by
46
47 volume named G50 [4], were considered. Spray ignition delays and lift-off length data of G50
48
49 from the KIVA-ERC code were compared with the Sandia constant volume spray experiments.
50
51 Figure 6 shows spray ignition delay and lift-off length measurements and predictions for G50.
52
53 Both the ignition delays and lift-off length predicted with the mechanism show good agreement
54
55 with those of the experiments. Figure 7 shows comparisons of soot formation between the
56
57 experiments and the predictions of G50. ‘KL’ is quantitatively related to the soot volume fraction
58
59
60
61
62
63
64
65

1
2
3
4 along the path of the laser using small particle Mie theory [31]. From the simulation results, soot
5
6 volume fraction is obtained and then converted to KL using a conversion equation [27, 31]. The
7
8 amount of soot formed increases with ambient temperature increase, and the soot distributions
9
10 show good qualitative agreement with the experimental results.
11
12
13
14

15 Figure 8 shows validation results of ignition delay and lift-off length for the MD mechanism
16
17 under the ‘Spray A’ conditions. Both the predicted spray ignition delays and lift-off length with
18
19 the new mechanism show good agreement with those of the experiments. Even though the MD
20
21 mechanism by Chang et al. [15] (Figure 8 (‘Sim_Old’)) shows better agreement with the
22
23 measured shock tube data than the new mechanism, the new mechanism shows much better
24
25 performance in predicting high pressure spray ignition delays and lift-off lengths.
26
27
28
29

30
31 As the ambient pressures of ‘Spray A’ were from 52.3 bar to 78.5 bar and the ambient pressure
32
33 of shock tube was only 16 bar, it is concluded that the new mechanism shows better performance
34
35 under high ambient pressure conditions. Moreover, the new mechanism predicted ignition delays
36
37 and lift-off lengths below 1000 K of ambient temperature, therefore, it can be applied both
38
39 conventional and low temperature combustion (LTC) operating conditions.
40
41
42
43

44 Figure 9 shows comparisons of soot formation between the experiments and predictions. The
45
46 predicted amount of soot formed and the location of soot also show good qualitative agreements
47
48 with the measured data.
49
50
51

52 Since no spray ignition and lift-off length data for DME was available, validation of the DME
53
54 mechanism was carried out using the shock tube ignition data as described above.
55
56
57
58
59
60
61
62
63
64
65

4. RESULTS AND DISCUSSION

In order to investigate the effect of the molecular structure of an oxygenated fuel for spray combustion, the injection velocity was adjusted such that the fuels would have the same injection pressure. The air entrainment into a jet is proportional to ρu^2 , where ρ is injected fuel density and u is the injection velocity [32] and the fuels have different densities. Therefore, adjusting the injection velocity ensures similar oxygen entrainment from the in-cylinder charge gas. All spray combustion simulations were carried out under the ‘Spray A’ ambient conditions which were mentioned above.

4.1 Effect of fuel additive

Constant volume spray simulations were performed using fuel blends (TPGME and n-hexadecane) with varying oxygen content, as shown in Table 3. Figure 10 shows predicted soot distributions at 4 msec after injection and Figure 11 shows the peak soot emission under the constant volume spray conditions. The peak soot emission is the maximum value of soot emission in the domain during the simulation. As can be seen, the amount of soot formed is significantly reduced as the amount of TPGME increases. This result shows the same tendency as the experimental results of Manin et al. [4]. TPGME forms much less soot than n-hexadecane; therefore, the soot emission decreases with increased TPGME in the fuel blend. The effect of fuel molecular structure on soot emission will be discussed next.

4.2 Effect of fuel molecular structure on soot emissions

The oxygenated fuels (TPGME, DME, and MD) and n-hexadecane were compared to give more insights between soot formation and an oxygenated fuel’s molecular structure, which could not

1
2
3
4 be explained by the experiments [4]. Figure 12 shows ignition delay and lift-off length of each
5
6 fuel. Pickett et al. showed that the ignition quality of a fuel affects lift off length. In the case of
7
8 fuels with a big difference in cetane number, fuels with shorter ignition delays generally
9
10 produced shorter lift off lengths [33]. However, fuels with a small difference in cetane number
11
12 and/or containing oxygen do not show the same trend, as shown in Figure 12 and Manin et al.'s
13
14 measurements [4]. It could be different depending on fuel properties, the components of fuel
15
16 blends, mixture ratios, injection velocities or etc. Figure 13 shows comparisons of soot formation
17
18 under 800 K, 900 K, and 1000 K ambient temperature conditions. N-hexadecane shows the
19
20 largest amount of soot formed and MD, TPGME, and DME follow. The oscillations are likely
21
22 due to the competition between soot formation and oxidation. Ignition delay and lift-off length
23
24 determine the amount of fuel-air premixing prior to combustion. Longer ignition delay and lift-
25
26 off length increase fuel-air premixing as a result soot formation decreases. However, these
27
28 oxygenated fuel's behaviors are not correlated with the ignition delay or lift-off length. For
29
30 example, even though MD shows longer ignition delay and lift-off length than TPGME, MD
31
32 forms more soot than TPGME. In the case of TPMGE, TPGME shows shorter ignition delay and
33
34 lift-off length than DME at the 800 K and 900 K ambient temperature conditions. Therefore
35
36 TPGME's higher cetane number could be the explanation that it shows more soot formation than
37
38 DME. However, under the 1000 K condition, TPGME showed almost the same ignition delay as
39
40 DME, but a longer lift-off length than DME. Even though they have the same ignition delay and
41
42 longer lift-off length, TPGME shows more soot formation than DME. These mean there is
43
44 another factor which strongly affects soot formation than fuel-air mixing, and fuel molecular
45
46 structure seems to be one possible factor.
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

The dependence of soot emissions on the fuel oxygen content is very strong, and fuels with more C-C bonds per unit carbon number show higher soot formation even with similar oxygen content [5-7]. Therefore, n-hexadecane, with the most C-C bonds and no oxygen in the molecule shows the largest amount of soot formed. Moreover, DME with no C-C bonds shows the least amount of soot, even though it has similar fuel oxygen concentration as TPGME. DME without C-C bonds is oxidized to carbon monoxide and methane before PAH formation starts as the PAH formation reactions are slower than the cracking process of DME. A fuel which has C-C bonds easily loses H atoms and forms soot precursors, such as acetylene (C_2H_2), ethene (C_2H_4), and propargyl (C_3H_3) [5]. Figure 14 shows one of the important soot precursors, acetylene, for the 1000 K ambient temperature condition. N-hexadecane shows the largest amount of acetylene formation and MD, TPGME, and DME follow. This order is proportional to the number of C-C bonds of each fuel and inversely proportional to the fuel oxygen ratio.

4.3 Comparison of fuel blends

Next, the fuel blends, G60 (TPGME + n-hexadecane) and M60 (DME + n-hexadecane), which have the same fuel oxygen ratio as MD were considered so as to be able to isolate the oxygen effect in the fuel molecule. Manin et al. compared G50 and MD as they thought these two fuels have similar fuel oxygen ratios (the fuel oxygen ratio of G50 is 6.5 in the paper [4]). However, our calculation of the fuel oxygen ratio of G50, according to Muller et al.'s description [9], is 5.0. Therefore, the new fuel blends G60 and M60 which have the same fuel oxygen ratio as the MD (6.06) were selected and then compared with MD. The fuel blending ratio and the fuel oxygen ratios of each fuel blend are listed in Table 1.

The predicted spray ignition delays and lift-off lengths of the three fuels are shown in Figure 15. The two fuel blends show similar ignition delays, while MD shows a longer ignition delay than G60 and M60 due to its lower cetane number. For the lift-off length, MD shows the longest lift-off length and G60 and M60 follow. Particularly, the absolute value of ignition delay and lift-off length difference between MD and fuel blends (M60 and G60) is high under the low ambient temperature (800 K and 900 K) conditions.

Figure 16 shows quantitative comparisons of soot formation under the 800 K, 900 K, and 1000 K ambient temperature conditions. In the case of G60 and M60, which have the same fuel oxygen ratio and similar n-hexadecane content, M60 always shows less soot formation than G60 due to its fewer C-C bonds. The soot formation of G60 and MD, which have the same fuel oxygen ratio and similar number of C-C bonds, is affected by the ignition delay and lift-off length. At the 800 K and 900 K conditions, MD shows longer ignition delay and lift-off length; as a result, G60 forms more soot than MD. At the 1000 K condition, the ignition delay and lift-off length differences of the fuels are reduced and MD shows the largest amount of soot formation.

5. CONCLUSIONS

The effect of oxygenated fuel properties on soot formation was investigated. The following conclusions were reached:

1. The effects of the molecular structure of several oxygenated fuels (TPGME, DME, MD, and blends with n-hexadecane) were investigated for spray injections under engine relevant conditions.

1
2
3
4 2. The formation of soot precursors was seen to decrease with increased oxygen content in the
5
6 fuel and with decreased number of C–C bonds in the fuel molecule. N-hexadecane showed the
7
8 largest amount of soot formation due to the fact that there is no oxygen in the fuel and the most
9
10 C-C bonds, while DME showed the smallest amount of soot formation due to its high fuel
11
12 oxygen ratio and no C-C bonds. The results show that fuel molecular structure strongly affects
13
14 soot formation in addition to fuel-air mixing, which was held constant for all cases.
15
16
17
18
19

20 3. Fuel blends, G60 (TPGME + hexadecane) and M60 (DME + hexadecane), which had the
21
22 same fuel oxygen ratio as MD were considered in order to remove the effect of oxygen in the
23
24 fuel molecule. It was found that in this case the effects of the spray ignition delay and lift-off
25
26 length control the soot formation for fuels with similar fuel oxygen ratio and number of C-C
27
28 bonds.
29
30
31
32
33
34
35

36 ACKNOWLEDGMENT

37
38
39

40 This material is based upon work supported by the Department of Energy under Award Number
41
42 DE-EE0005386.
43
44
45
46
47

48 DISCLAIMER

49
50

51 This report was prepared as an account of work sponsored by an agency of the United States
52
53 Government. Neither the United States Government nor any agency thereof, nor any of their
54
55 employees, makes any warranty, express or implied, or assumes any legal liability or
56
57 responsibility for the accuracy, completeness, or usefulness of any information, apparatus,
58
59
60
61
62
63
64
65

1
2
3
4 product, or process disclosed, or represents that its use would not infringe privately owned rights.
5
6 Reference herein to any specific commercial product, process, or service by trade name,
7
8 trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement,
9
10 recommendation, or favoring by the United States Government or any agency thereof. The
11
12 views and opinions of authors expressed herein do not necessarily state or reflect those of the
13
14 United States Government or any agency thereof.
15
16
17
18
19
20

21 REFERENCES

- 22
23
24 [1] J. B. Heywood, Internal Combustion Engine Fundamentals, McGraw-hill, New York, 1988.
25
26
27 [2] N. Miyamoto, H. Ogawa, N. M. Nurun, K. Obata, T. Arima, “Smokeless, Low NO_x, High
28
29 Thermal Efficiency, and Low Noise Diesel Combustion with Oxygenated Agents as Main Fuel”,
30
31 SAE technical paper (1998) 980506.
32
33
34
35 [3] C. K. Westbrook, W. J. Pitz, and H. J. Curran, “Chemical kinetic modeling study of the
36
37 effects of oxygenated hydrocarbons on soot emissions from diesel engines”, J. Phys. Chem. A.
38
39 110 (21) (2006) 6912–6922.
40
41
42
43 [4] J. Manin, S. Skeen, L. Pickett, E. Kurtz, J. Anderson, “Effects of Oxygenated Fuels on
44
45 Combustion and Soot Formation/Oxidation Processes”, SAE Int. J. Fuels Lubr. 7(3) (2014) 704-
46
47 717.
48
49
50
51 [5] H. J. Curran, E. M. Fisher, P. A. Glaude, N. M. Marinov, W. J. Pitz, C. K. Westbrook, D. W.
52
53 Layton, P. F. Flynn, R. P. Durrett, A. O. zur Loye and O. C. Akinyemi, F. L. Dryer, “Detailed
54
55 Chemical Kinetic Modeling of Diesel Combustion with Oxygenated Fuels”, SAE technical paper
56
57 (2001) 2001-01-0653.
58
59
60
61
62
63
64
65

- [6] L. Rubino, M. J. Thomson, “The Effect of Oxygenated Additives on Soot Precursor Formation in a Counterflow Diffusion Flame”, SAE technical paper (1999) 1999-01-3589.
- [7] J. Jeong, D. Jung, O. Lim Y. Pyo, Y. Lee, “Influence of Pilot Injection on Combustion Characteristics and Emissions in a DI Diesel Engine Fueled with Diesel and DME”, International Journal of Automotive Technology 15(5) (2014) 861-869.
- [8] C.C. Barrios, C. Martín, A. Domínguez-Sáez, P. Álvarez, M. Pujadas, J. Casanova, “Effects of the addition of oxygenated fuels as additives on combustion characteristics and particle number and size distribution emissions of a TDI diesel engine”, Fuel 132 (2014) 93-100.
- [9] C. Mueller, W. J. Pitz, L. M. Pickett, G. C. Martin, D. L. Siebers, C. K. Westbrook, “ Effects of Oxygenates on Soot Processes in DI Diesel Engines: Experiments and Numerical Simulations”, SAE technical paper (2003) 2003-01-1791.
- [10] T. Fleisch, C. McCarthy, A. Basu, C. Udovich, P. Charbonneau, W. Slodowske, S. Mikkelsen, J. McCandless, “A New Clean Diesel Technology: Demonstration of ULEV Emissions on a Navistar Diesel Engine Fueled with Dimethyl Ether”, SAE technical paper (1995) 950061.
- [11] M. Natarajan, E. A. Frame, D. W. Naegeli, T. Asmus, W. Clark, J. Garbak, A. Manue, D. Gonzales, E. Liney, W. Piel, J. P. Wallace III, “Oxygenates for Advanced Petroleum-Based Diesel Fuels: Part 1. Screening and Selection Methodology for the Oxygenates” SAE technical paper(2001) 2001-01-3631.
- [12] M.J. Murphy, J.D. Taylor, R.L. McCormick, “Compendium of Experimental Cetane Number Data”, National Renewable Energy Laboratory Report, NREL/SR-540-36805, 2004.

- [13] U. Burke, W. J. Pitz, H. J. Curran, "Experimental and kinetic modeling study of the shock tube ignition of a large oxygenated fuel: Tri-propylene glycol mono-methyl ether", *Combustion and Flame*, 162(7) (2015) 2916-2927.
- [14] S. Park, "Development of Reduced Chemical Kinetic Model for TPGME and Its Application to Enable Lifted Flames for Soot Reduction", MS thesis, University of Wisconsin-Madison, 2014.
- [15] Y. Chang, M. Jia, Y. Li, Y. Zhang, M. Xie, H. Wang, R. D. Reitz, "Development of a Skeletal Oxidation Mechanism for Biodiesel Surrogate", *Proceedings of the Combustion Institute*, 35(3), (2014) 3037-3044.
- [16] O. Herbinet, W. J. Pitz, C. K. Westbrook, "Detailed Chemical Kinetic Oxidation Mechanism for a Biodiesel Surrogate", *Combust. Flame* 154, (2008) 507-528.
- [17] Y. Ra, R. D. Reitz, "A combustion model for IC engine combustion simulations with multi-component fuels", *Combustion and Flame* 158 (2011) 69-90.
- [18] Y. Ra, R. D. Reitz, "A combustion model for multi-component fuels using a physical surrogate group chemistry representation (PSGCR)", *Combustion and Flame* (2015) doi:10.1016/j.combustflame.
- [19] G. Vishwanathan, R. D. Reitz, "Modeling Soot Formation Using Reduced Polycyclic Aromatic Hydrocarbon Chemistry in n-Heptane Lifted Flames with Application to Low Temperature Combustion", *J. Eng. Gas Turbines Power* 131(3) (2009) 032801.
- [20] G. Vishwanathan, "Development and Application of a Practical Soot Modeling Approach for Low Temperature Diesel Combustion", University of Wisconsin Madison, PhD Thesis, 2011.

- [21] F. Perini, K. Anand, Y. Ra, R. D. Reitz “Computationally Efficient Simulation of Multi-Component Fuel Combustion Using a Sparse Analytical Jacobian Chemistry Solver and High-Dimensional Clustering”, Proceedings of the ASME Internal Combustion Engine Division's 2013 Fall Technical Conference ICEF2013, October 13-16, Dearborn, Michigan, USA, 2013.
- [22] J. C. Beal, R. D. Reitz “Modeling spray atomization with the Kelvin-Helmholtz/Rayleigh-Taylor hybrid model”, Atomization and Sprays 9 (1999) 623-650.
- [23] Y. Ra, R. D. Reitz, “A Vaporization Model for Discrete Multi-Component Fuel Sprays”, International Journal of Multiphase Flow 35 (2009) 101-117.
- [24] A. E. Lutz, R. J. Kee, J. A. Miller, “SENKIN: A FORTRAN Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis”, Report No. SAND 87-8248, UC-4, Sandia National Laboratories, Livermore, CA, USA, 1988.
- [25] W. Wang, M. A. Oehlschlaeger, “A shock tube study of methyl decanoate autoignition at elevated pressures”, Combustion and Flame 159 (2012) 476–481.
- [26] U. Pfahl, K. Fieweger, G. Adomeit, “Self-ignition of Diesel-relevant Hydrocarbon-air Mixtures under Engine Comditions” Proc. Combust. Inst. 26 (1996) 781–789.
- [27] Engine Combustion Network website, <http://www.sandia.gov/ecn>.
- [28] N. Abani, A. Munnannur, R. D. Reitz, “Reduction of numerical parameter dependencies in diesel spray models” Journal of Engineering for Gas Turbines and Power 130 (3) (2008) 032809.
- [29] N. Abani, L. S. Kokjohn, S. W. Park, M. Bergin, A. Munnannur, W. Ning, Y. Sun, R. D. Reitz, “An improved Spray Model for Reducing Numerical Parameters Dependencies in Diesel Engine CFD Simulations” SAE technical paper (2008) 2008-01-0970.

- 1
2
3
4 [30] Y. Wang, H. W. Ge, R. D. Reitz, "Validation of Mesh- and Timestep-Independent Spray
5
6 Models for Multidimensional Engine CFD Simulations" SAE Int. J. Fuels Lubr. 3(1) (2010) 277-
7
8 302.
9
- 10
11 [31] M. P. B. Musculus, L. M. Pickett, "Diagnostic considerations for optical laser-extinction
12
13 measurements of soot in high-pressure transient combustion environments" Combustion and
14
15 Flame 141 (2005) 371-391.
16
17
18
19
- 20 [32] F. P. Ricou, D. B. Spalding, "Measurements of entrainment by axisymmetrical turbulent
21
22 jets", Journal of Fluid Mechanics 11 (1) (1961) 21-32.
23
24
25
- 26 [33] L. M. Pickett, D. L. Siebers, C. A. Idicheria, "Relationship Between Ignition Processes and
27
28 the Lift-Off Length of Diesel Fuel Jets" SAE technical paper (2005) 2005-01-3843.
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table lists

Table 1. Fuel properties

Table 2. Comparisons of MD mechanisms (Old: existing MD mechanism [15] and New: New MD mechanism) (o : reaction class included, x : not included)

Table 3. Mixture ratio and fuel oxygen ratio of fuel blends

Figure lists

Figure 1. Molecular structure of the fuel molecules

Figure 2. Processes to develop the new reduced MD mechanism

Figure 3. Comparison of measured [24] and predicted shock tube ignition delays of MD

Figure 4. Comparison of measured [26] and predicted shock tube ignition delays of DME (gray curves: curve fitting lines from measured data)

Figure 5. Determination of ignition delay and lift-off length

Figure 6. Comparisons of measured [4] and predicted spray ignition delay and lift-off length: G50

Figure 7. Comparisons of soot formation of G50: measured [4] (left) and predicted (right).

Figure 8. Comparisons of measured [25] and predicted spray ignition delay and lift-off length: MD

Figure 9. Comparisons of soot formation of MD: measured [4] (left) and predicted (right)

Figure 10. Predicted soot distributions for G15, G33, and G50 at 4 msec after injection for various ambient temperatures.

Figure 11. Peak soot emission predicted for each tested fuel (soot mass [g] divided by injected fuel mass [kg]).

Figure 12. Spray ignition delay (left) and lift-off length (right)

Figure 13. Soot production under various ambient temperatures

Figure 14. Comparison of soot precursor formation at 1000 K ambient temperature

Figure 15. Spray ignition delay (left) and lift-off length (right)

Figure 16. Soot production under various ambient temperature conditions

Table 1. Fuel properties

Fuel		O [#/mol]	C-C Bond [#/mol]	MW [g/mol]	Ω_f [%]	LHV [MJ/kg]	Cetane Number
DME	CH_3OCH_3	1	0	46.1	14.3	28.9	55 [10]
TPGME	$\text{CH}_3\text{OC}_3\text{H}_6(\text{OC}_3\text{H}_6)_2\text{OH}$	4	6	206.3	12.9	28.1	63 [11]
MD	$\text{C}_{11}\text{H}_{22}\text{O}_2$	2	9	118.3	6.06	36.5	53 [12]
n-hexadecane	$\text{C}_{16}\text{H}_{34}$	0	15	226.4	0	44.0	100
G60	TPGME:Hexa = 58:42	2.3	9.75	214.7	6.06	35.1	-
M60	DME:Hexa = 84:16	0.8	2.44	75.3	6.06	36.2	-

Table 2. Comparisons of MD mechanisms (Old: existing MD mechanism [15] and New: New MD mechanism) (o : reaction class included, x : not included)

Reaction Class	Old	New
Uni-molecular initiation	o	o
H-abstractions	o	o
decompositions	o	o
alkyl radical + O ₂ = olefin + ho ₂	x	o
R+O ₂ =RO ₂	o	o
R+R'O ₂ =RO+R'O	x	o
RO ₂ isomerization to qooh	o	o
RO ₂ +HO ₂ =ROOH+O ₂	x	o
RO ₂ +H ₂ O ₂ =ROOH+HO ₂	x	o
RO ₂ +CH ₃ O ₂ =RO+CH ₃ O+O ₂	x	o
RO ₂ +R'O ₂ =RO+R'O+O ₂	x	o
ROOH=RO+OH	x	o
RO decomposition	x	o
decomposition of qooh	x	o

Table 3. Mixture ratio and fuel oxygen ratio of fuel blends

	G15	G33	G50
TPGME : n-hexadecane [vol. %]	15:85	33:67	50:50
Fuel Oxygen Ratio, Ω_f [%]	1.3	3.1	5.0

Figure1

TPGME

MD

Hexadecane

DME

Figure2

Figure3

Figure4

Figure5

(a) Ignition Delay

(b) Lift off length

Figure6

Figure7

Figure8

Figure9

Figure10

Figure11

Figure12

Figure13

Figure14

Figure15

Figure16