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Abstract

A combined experimental and kinetic modeling study of soot formation in diesel engine combustion has been used to study the addition of oxygenated species to diesel fuel to reduce soot emissions. This work indicates that the primary role of oxygen atoms in the fuel mixture is to reduce the levels of carbon atoms available for soot formation by fixing them in the form of CO or CO_2. When the structure of the oxygenate leads to prompt and direct formation of CO_2, the oxygenate is less effective in reducing soot production than in cases when all fuel-bound O atoms produce only CO. The kinetic and molecular structure principles leading to this conclusion are described.

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Introduction

Recent experimental studies have demonstrated that oxygen-containing compounds ("oxygenates") can be blended with diesel fuel to reduce soot emissions from diesel engines. In many of these cases, particularly with small oxygenated molecules such as methanol or ethanol with only one or two oxygen atoms in the additive, the reduction in soot emission has been found to be proportional to the amount of oxygen added to the diesel fuel [1-4] and independent of the specific oxygenate being used. However, when multiple oxygen atoms are present in the additive, the rate of soot reduction sometimes shows a different behavior [3-6], suggesting that the effectiveness of the additive may depend on the molecular structure of the specific oxygenate being used.

Kinetic modeling studies have addressed the role of oxygenated additives in reducing soot production in diesel combustion [7-10], generally confirming the experimental observations for small oxygenates. Specifically, for oxygenates that contain one or two oxygen atoms, including methanol, ethanol, dimethyl ether, and dimethoxy methane, predicted soot production is reduced at the same rate by each oxygenate, proportional to the fraction of oxygen atoms present in the fuel/oxygenate mixture. The chemical kinetic models have shown that the primary effect of these small oxygenates is to displace carbon atoms in the diesel fuel with carbon atoms from the oxygenate that are already bonded to oxygen atoms. Carbon atoms already bonded to oxygen are not available for subsequent soot-producing reactions, so this displacement results in lower levels of species that can produce soot. The purpose of the present study is to extend the same type of analysis to diesel oxygenates with multiple oxygen atoms in each molecule and understand the role, if any, that molecular structure of the oxygenated fuel components plays in soot production.

Conceptual Model of Diesel Engine Combustion

These kinetic models of soot production and the influence of oxygenates are all based on the conceptual model of diesel combustion developed by Dec [11] and extended by Siebers and Higgins [12]. In this model, illustrated in Fig. 1, the liquid fuel jet vaporizes and entrains compressed, heated air. While the fuel/air mixture is still fuel rich ($2 \leq \phi \leq 4$), it reaches an ignition temperature of about 850 K, reacting rapidly until all of the available oxygen in the air is consumed. The products of this rich, premixed ignition contain large amounts of small, unsaturated hydrocarbon species including acetylene, ethylene, and propylene, as well as radicals such as vinyl, propargyl and other similar species, exactly the species that are particularly effective in starting the reactions that lead to soot [13], and soot is then produced in the extended region immediately following the

rich premixed ignition zone. Kinetic models are used to compute the products of the premixed, rich ignition event, and the levels of products that lead preferentially to soot are tabulated and correlated with trends in experimentally observed sooting. While not providing a direct simulation of diesel combustion, this approach has been able to provide useful insights into the fuel-dependent factors involved.
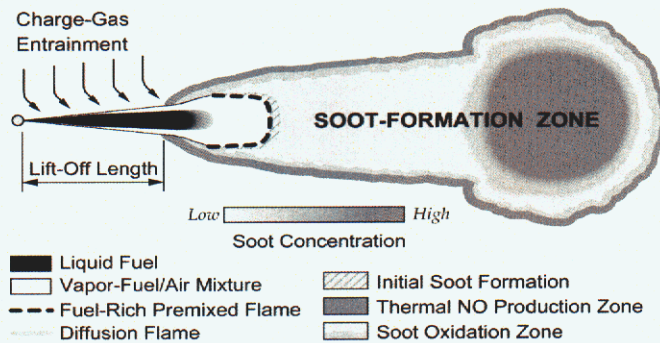
Figure 1. Schematic of a DI diesel jet during the quasi-steady period of combustion (adapted from Refs. [2,11]). Products of the fuel-rich premixed flame are typically > 1100 K and contain insufficient oxygen for complete combustion, an environment that is conducive to soot formation.

For example, the top portion of Fig. 2 shows experimental results from Miyamoto *et al.* [1], with observed soot emissions being reduced as the oxygenate level is increased, until no soot is observed when oxygen levels in the fuel exceed about 25-30%. The legend in this figure lists the oxygenates used, di-n-butyl ether (DBE), 2-ethylhexyl acetate (EHA), ethylene glycol mono-n-butyl ether (ENB), and diethylene glycol dimethyl ether (DGM). In the bottom portion of Fig. 2, computed results are shown in which n-heptane is used to represent the diesel fuel and methanol is used as the oxygenate. The soot precursors are computed by summing the concentrations of acetylene, ethylene and propargyl radicals in the products of the premixed rich ignition calculations. The similarity in the computed and experimental results suggests that the computed trends can be used to simulate the experimental results.

This approach was first used by Flynn *et al.* [8] and uses a rather simple model for mixing the fuel and entrained air until it reaches an ignition temperature. Mueller *et al.* [14] have developed a much more detailed mixing treatment that considers variable enthalpies of vaporization and a more accurate fuel jet entrainment model, but the simpler model provides very similar results and is used in the present simulations. Many other factors can affect soot production, including injection timing and jet impingement on engine walls and piston surfaces, so the present approach is necessarily limited to situations in which these additional factors are either held fixed or do not contribute.
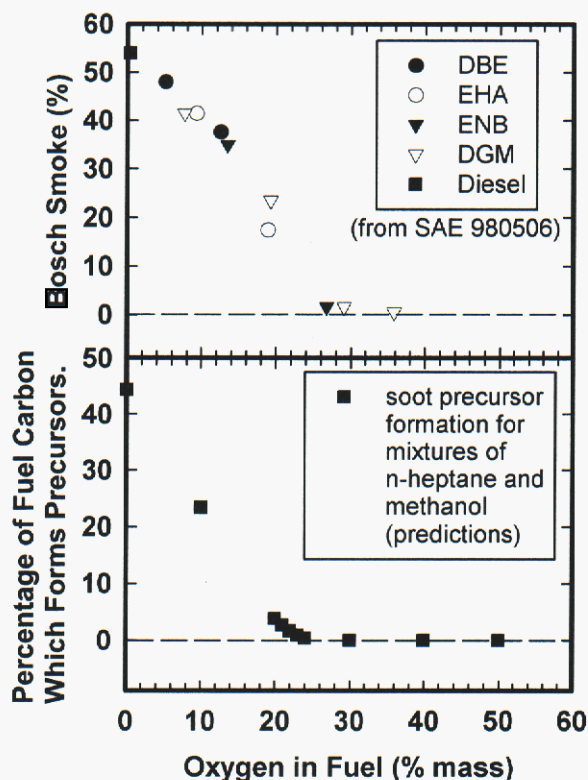
Figure 2. Smoke emissions and particulate precursor formation rates [1,8].

Chemical Kinetic Mechanisms

Following previous kinetic studies of diesel ignition [7-10], n-heptane is used to represent a typical diesel fuel. This is the most realistic species for which a detailed chemical kinetic reaction mechanism, with both high and low temperature reaction submechanisms, has been developed [15]. In addition, n-heptane has a cetane rating of 56, which is representative of many practical diesel fuels, and its combustion leads to intermediate products very similar to those seen in normal diesel combustion. In previous studies of oxygenate addition, detailed reaction mechanisms for methanol, ethanol, dimethyl ether [16,17] and dimethoxy methane [7,10] were developed and used for soot reduction simulations.

The two oxygenates selected for this study are tri-propylene glycol methyl ether (TPGME) and di-butyl maleate (DBM). The overall composition of TPGME is $C_{10}H_{22}O_4$ and that for DBM is $C_{12}H_{20}O_4$. The structures of these molecules are indicated in Fig. 3. The O atoms in TPGME are well dispersed, and there are no double bonds between any of the C atoms, while the O atoms are less well dispersed in DBM and there is a C=C double bond at the middle of the molecule. Detailed chemical kinetic reaction mechanisms were developed for these

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oxygenates, based on available bond energies, rates of radical recombination, and available thermochemical data. The resulting submodels for TPGME included 71 new chemical reactions and 25 chemical species, while that for DBM included 103 new chemical reactions and 43 chemical species. Due to lack of kinetic experiments for either fuel, it was not possible to evaluate or test the specific reaction mechanisms. However, the basic kinetic principles upon which they were developed are sound.
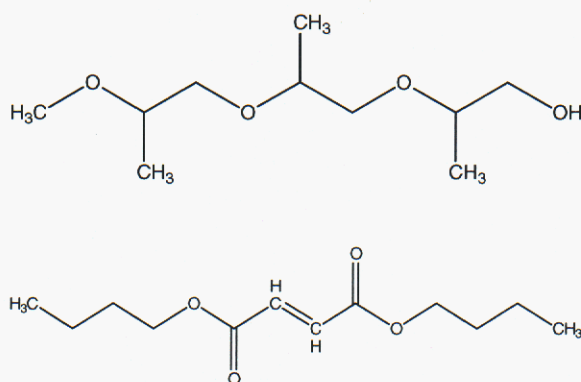
Figure 3. Structural forms for TPGME (top) and DBM (bottom).

For both oxygenates, the reaction submechanisms consisted of unimolecular decomposition of the oxygenate, H atom abstraction from the oxygenate by reactions with O, H, OH, HO$_2$, and CH$_3$, and decomposition of the radicals produced by H atom abstractions. The site-specific rates of the abstraction reactions were estimated from reactions in other hydrocarbon species, and the rates of the decomposition reactions were estimated by using the assumed rates of addition of the decomposition products, combined with computed equilibrium constants.

Summary of Experimental Results

Detailed accounts of the experimental details and facilities are found in Ref. [14], so they will only be summarized briefly here. Two families of experiments were carried out, one in the Sandia/Caterpillar Optical Research Engine (SCORE), a single-cylinder diesel engine based on a Caterpillar C-10 engine that has been modified to provide extensive optical access to the combustion chamber. The second is the Diesel Combustion Simulation Facility (DCSF), an optically accessible constant volume combustion bomb equipped with a fuel injector. The diesel fuel mixture used in the experiments consisted of a mixture of diesel primary reference fuels n-hexadecane (76.5%) and 2,2,4,4,6,8,8-heptamethyl nonane (23.5%) and was denoted CN80. For the mixture with DBM, the fuel

consisted of 7% n-hexadecane, 88% DBM and 5% ethyl-hexyl nitrate and was denoted BM88. The fuel mixture with TPGME consisted of 20% heptamethyl nonane and 80% TPGME, denoted GE80. The ethyl-hexyl nitrate was included in BM88 to ensure that all three fuels had the same ignition delay at the SCORE operating condition. All three fuel mixtures had cetane numbers higher than those typical of current diesel fuels and had short ignition delays (~390 µs) at the given charge-gas conditions. Both BM88 and GE80 fuel mixtures had the same fractional oxygen content at approximately 26% oxygen by weight [5]. Note that both oxygenated fuels consisted of a majority of the oxygenate and only a small fraction consisting of the "diesel fuel" $C_{16}H_{34}$.

The amounts of soot produced in each of the experimental combustion devices were determined by measuring the spatially integrated natural luminosity (SINL), which is assumed to be dominated by incandescence from hot soot in the engine SCORE and DCSF experiments. A significant number of experiments were carried out over a range of operating conditions, and the results are discussed in Refs. [5] and [14]. For purposes of comparing the three fuels of the study, charge-gas conditions of 970 K and 24 kg/m^3 were used. These were the conditions at the end of the premixed burn in the single-cylinder diesel engine and at the time of injection in the constant volume combustion bomb. The soot levels produced in the two devices for the three fuel mixtures (i.e., CN80, BM88, and GE80), as measured by the SINL, are summarized in Fig. 4. These results are normalized by the results with CN80 fuel, and it is very clear that both oxygenates reduce soot production significantly, with the reductions accomplished by TPGME being greater than those achieved by adding DBM. Results measured in the constant volume bomb are similar to those measured in the single-cylinder engine. The discussions in Ref. [14] suggest that the relatively small differences may be due to interactions between the multiple fuel jets in the engine that do not occur in the single fuel jet configuration in the DCSF.
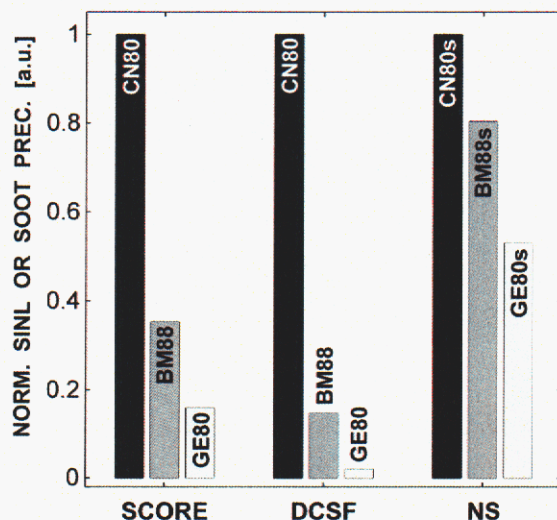
Figure 4. Comparison of soot-reduction data obtained from SCORE and DCSF experiments, as well as numerical simulations (NS). Results are for fixed in-cylinder conditions of 24 kg/m^3 and 970 K. NS results are soot precursor concentrations 1.0 ms after the peak soot precursor concentration was attained.

Kinetic Model Results and Discussion

The kinetic model was used to carry out simulated diesel ignition calculations as close to the experimental examples as possible. As noted above, however, n-heptane was used as the surrogate diesel fuel in all three cases; the baseline diesel fuel (denoted as CN80s) was 100% n-heptane, the model version with DBM (denoted as BM88s) had 87.9% DBM and 12.1% n-heptane, and the version with TPGME (denoted as GE80s) had 70.2% TPGME and 29.8% n-heptane. For the same initial conditions as in the experimental cases, the computed results for total soot precursor concentrations at 1 ms following peak precursor concentrations are summarized in Fig. 4. While the computed variations are not quite as sensitive to the amount of oxygenate included as in the experiments, the ordering is the same, again showing that DBM is considerably less effective in reducing soot precursor levels than is TPGME.

The variations in computed soot precursor levels with the amount of oxygen incorporated into the fuel by addition of TPGME and DBM are summarized in Fig. 5. Also included are the same type of computed results for many of the smaller oxygenates used in previous studies [7-9]. In Fig. 5, DMM refers to dimethoxy methane, DME refers to dimethyl ether, and MB refers to methyl butanoate, a smaller surrogate for biodiesel fuel, which will be discussed below. The important result to be obtained from Fig. 5 is that the computed curves for

DMM, DME, methanol and ethanol are effectively the same as that for TPGME. This means that, on the basis of effectiveness *per oxygen atom in the fuel*, TPGME is equally effective as these smaller oxygenates in reducing the soot precursor levels in the numerical simulations. It is also clear from Fig. 5 that DBM is considerably less effective in reducing soot precursors than all of the other oxygenates, consistent with the results summarized in Fig. 4 in which the computed results for TPGME and DBM are combined with the experimental results from the diesel engine and the constant volume combustion bomb. The computed results for methyl butanoate (MB) appear to be slightly less effective at soot reduction than most of the other oxygenates but still more effective than DBM.

The reaction paths of the BM88s and GE80s fuels were traced in the model to provide insight into their respective tendencies to make soot precursors. DBM (in the BM88s fuel) produced large amounts of unsaturated hydrocarbons (ethylene and acetylene). The ethylene resulted from the two butyl groups in DBM and the acetylene resulted from the C=C double bond at the center of the molecule (see Fig. 3 for the molecular structure of DBM). In the case of the GE80s fuel mixtures, TPGME radicals decomposed to produce more aldehydes (mainly acetaldehyde) and fewer unsaturated hydrocarbons (mainly propylene).

Analysis of the reaction paths for DBM shows that a significant fraction of the oxygen in this molecule is underutilized for soot reduction due to the presence of the ester, or –O–(C=O)–, structural groups. It will be shown below that CO_2 can be produced directly from the ester groups in DBM. When CO_2 is produced directly from the fuel, *two oxygen atoms from the fuel are bonded to the same carbon atom in the products*. In general, the combustion products that minimize soot formation are those where *each oxygen atom from the fuel is bonded to a different carbon atom in the products*. This prevents the carbon atom in the products from forming unsaturated species like acetylene and ethylene that lead to soot, because the carbon-oxygen bond does not break at combustion temperatures. When CO_2 is produced directly from the fuel, two oxygen atoms from the fuel are bonded to one carbon in the products and one of the oxygen atoms from the fuel is "wasted" because it is not available to prevent a second carbon atom from forming soot.

As shown in Fig. 6, CO_2 is formed directly from DBM reactions in two ways. First, about 38% of the DBM produces CO_2 directly through Intermediate 1 which also gives Intermediate 2. Then about 90% of Intermediate 2 produces CO_2 directly through Reaction 3. The 90% value is evaluated at 800K and based on calculated barrier heights for reactions analogous to Reaction 1 and 2 [18]. Second, 62% of DBM molecules produce intermediate 2 through DBM radical consumption paths not shown in Fig. 6. Again, 90% of intermediate 2 directly produces CO_2. In summary, 38% of the DBM molecules produce intermediate 1 that eventually gives 1.9 CO_2's and 62% of the DBM produces intermediate 2 that gives 0.9 CO_2. Therefore on average, each DBM molecule directly produces

0.38(1.9)+0.62(0.9)=1.28 CO_2 molecules. Each directly produced CO_2 molecule wastes one oxygen atom. DBM has 4 oxygen atoms, so that 1.28/4= 32% of the oxygen in DBM is "wasted". Thus, DBM is not an optimal molecular structure for an oxygenated fuel with respect to its potential to reduce soot precursors by fully utilizing its O atom loading.
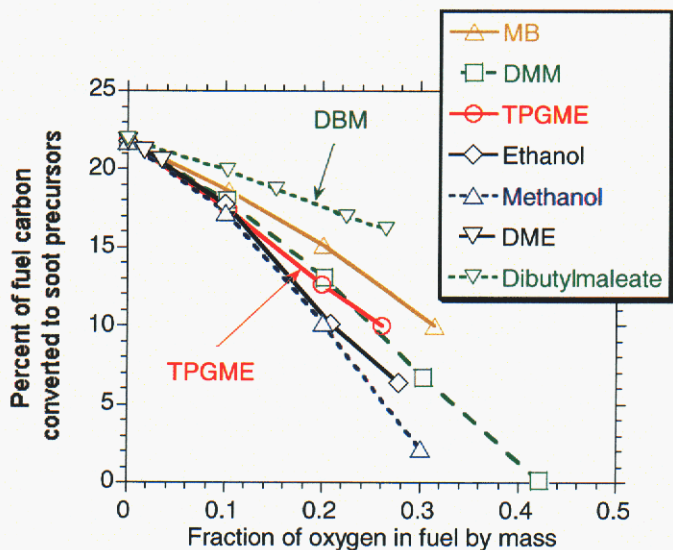

Figure 5. Variation in computed levels of soot precursors with different oxygenated species in n-heptane.
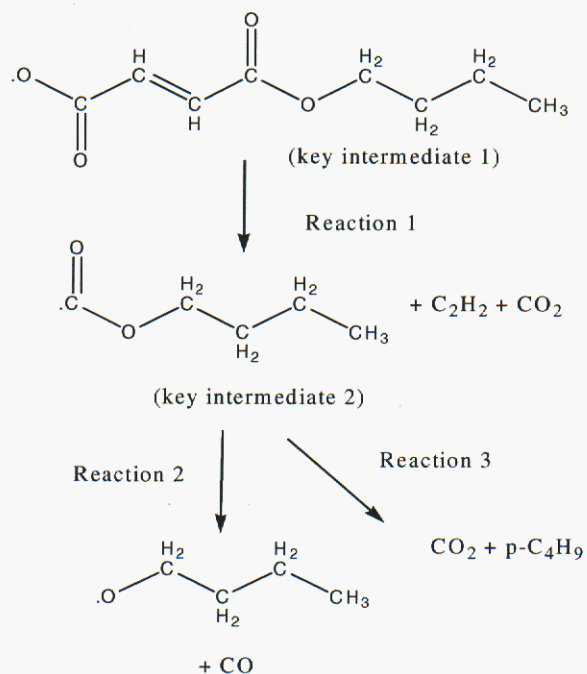

Figure 6. Key reaction intermediates and their products in the detailed reaction mechanism of DBM.

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Reaction path analysis shows that TPGME, whose chemistry leads to mostly aldehydes and CO is a much more optimal molecular structure for an oxygenated fuel based on its potential to reduce soot precursors. The major factor responsible for this kinetic behavior of TPGME is that its O atoms are dispersed effectively throughout the molecule so that none of the C atoms are initially bonded to more than one O atom. As a result, no decomposition reaction pathway can immediately produce CO_2, and the consumption of each TPGME species produces 4 fragments with O atoms, therefore eliminating at least 4 C atoms that will not participate in soot formation reactions.

For simple oxygenates with only one O atom, including methanol, ethanol and dimethyl ether, the O atom is already bonded to a C atom. In dimethyl ether, the O atom is initially bonded to two C atoms, and although subsequent reaction invariably breaks one of the C-O bonds, the O atom remains connected to the other C atom, thereby eliminating that C atom from further soot production reaction pathways. In the case of dimethoxy methane, the two O atoms are initially bonded to the central C atom and one of the C atoms in a methoxy group, and subsequent reactions break one of the bonds between the central C atom and one of the O atoms. However, because of the location of the other methoxy group, the O atom broken off still remains bonded to the C atom from the broken-off methoxy group. Therefore, each O atom in these simple oxygenates is able to keep at least one C atom from participating in soot producing reaction pathways.

The purpose of the present work has been to examine the reactivity of two oxygenated species, each of which has 4 oxygen atoms in the molecule. The experimental work shows that the two oxygenates have different impacts on the observed sooting behavior of the fuel mixtures in both the diesel engine and the constant-volume combustion bomb, with DBM reducing the soot precursor production less effectively than does TPGME. The kinetic modeling has shown that TPGME is equal in effectiveness, per oxygen atom in the fuel, to that of the simple oxygenates, which is in turn due to the fact that each O atom in TPGME remains bonded to a different C atom which is therefore unable to contribute to soot production. In contrast, the lesser effectiveness in reducing soot precursors of DBM is due to the specific locations of the O atoms in that molecule, which leads to significant amounts of CO_2 production directly from DBM decomposition. Every time a CO_2 molecule is produced from DBM, the number of C atoms removed from soot production by DBM is less than it would be with TPGME.

One final extrapolation can be made from these computed results. In the results shown above in Fig. 5, computed results for a range of oxygenates were summarized, including the oxygenated species methyl butanoate (MB). This species was used [9] as a surrogate intended to be representative of a wide class of so-called "biodiesel" fuels. Biodiesel species are produced by esterification of a range of vegetable oils, resulting in molecules with long chains of 16 - 18 C atoms, with a methyl ester group at one end of the chain. This

methyl ester or R–O–(C=O)– structural group features a carbon atom bonded to two O atoms in the same way as in DBM (see Fig. 3), and the kinetic model indicates that, just as in DBM consumption, the oxygen in MB is not as effective, *per O atom in the oxygenate*, at preventing C atoms in the fuel from participating in soot-formation reactions. In the same sense as noted above for DBM, some of the oxygen in MB is "wasted" because it produces CO_2 directly, so the two O atoms prevent only one C atom from potentially forming soot in those cases. This therefore suggests that biodiesel fuels, with the methyl ester containing the fuel-bound oxygen, should not be as effective per O atom as TPGME in reducing soot production. This prediction could be confirmed or contradicted by using a suitable biodiesel fuel in engine or constant volume bomb experiments and would constitute a valuable test of the modeling predictions. The present work also suggests that simple analysis of oxygenated fuel species molecular structure could provide a reliable estimate of the relative effectiveness of other, as yet untested, oxygenates as soot-reducing fuel components. Oxygenates with structures that might be expected to produce CO_2 directly would not be likely to be particularly effective in this type of function in diesel engine combustion.

Acknowledgments

References

1. Miyamoto, N., Ogawa, H., Nurun, N., Obata, K., and Arima, T., "Smokeless, Low NOx, High Thermal Efficiency, and Low Noise Diesel Combustion with Oxygenated Agents as Main Fuel," SAE Paper 980506, *SAE Trans.*, Vol. 107, Sect. 4, pp. 171-177, 1998.
2. Musculus, M.P., Dec, J.E., and Tree, D.R., "Effects of Fuel Parameters and Diffusion Flame Lift-Off on Soot Formation in a Heavy-Duty Diesel Engine," SAE Paper 2002-01-0889, 2002.
3. Gonzalez, M.A., Piel, W., Asmus, T., Clark, W., Garbak, J., Liney, E., Natarajan, M., Naegeli, D.W., Yost, D., Frame, E., and Wallace, J.P., "Oxygenates Screening for Advanced Petroleum-Based Diesel Fuels: Part 2. The Effect of Oxygenate Blending Compounds on Exhaust Emissions," SAE Paper 2001-01-3632, 2001.

4. Choi, C.Y. and Reitz, R.D., "An Experimental Study on the Effects of Oxygenated Fuel Blends and Multiple Injection Strategies on DI Diesel Engine Emissions," *Fuel*, Vol. 78, pp. 1303-1317, 1999.

5. Mueller, C.J. and Martin, G.C., "Effects of Oxygenated Compounds on Combustion and Soot Evolution in a DI Diesel Engine: Broadband Natural Luminosity Imaging," SAE Paper 2002-01-1631, 2002.

6. Stoner, M. and Litzinger, T.A., "Effects of Structure and Boiling Point of Oxygenated Blending Compounds in Reducing Diesel Emissions," SAE Paper 1999-01-1475, 1999.

7. Curran, H.J., Fisher, E.M., Glaude, P.A., Marinov, N.M., Pitz, W.J., Westbrook, C.K., Layton, D.W., Flynn, P.F., Durrett, R.P., zur Loye, A.O., Akinyemi, O.C., and Dryer, F.L., "Detailed Chemical Kinetic Modeling of Diesel Combustion with Oxygenated Fuels," SAE Paper 2001-01-0653, 2001.

8. Flynn, P.F., Durrett, R.P., Hunter, G.L., zur Loye, A.O., Akinyemi, O.C., Dec, J.E., and Westbrook, C.K., "Diesel Combustion: An Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation," SAE Paper 1999-01-0509, *SAE Trans.*, Vol. 108, Sect. 3, 1999.

9. Fisher, E.M., Pitz, W.J., Curran, H.J., and Westbrook, C.K., "Detailed Chemical Kinetic Mechanisms for Combustion of Oxygenated Fuels," *Proc.Comb.Inst.*, Vol. 28, pp. 1579-1586, 2000.

10. Daly, D.T., and Nag, P., "Combustion Modeling of Soot Reduction in Diesel and Alternative Fuels Using Chemkin", SAE Paper 2001-01-1239, 2001.

11. Dec, J.E., "A Conceptual Model of DI Diesel Combustion Based on Laser-Sheet Imaging," SAE Paper 970873, *SAE Trans.*, Vol. 106, Sect. 3, pp. 1319-1348, 1997.

12. Siebers, D.L. and Higgins, B.S., "Flame Lift-Off on Direct-Injection Diesel Sprays Under Quiescent Conditions," SAE Paper 2001-01-0530, 2001.

13. Appel, J., Bockhorn, H., and Frenklach, M., "Kinetic Modeling of Soot Formation with Detailed Chemistry and Physics: Laminar Premixed Flames of C2 Hydrocarbons", *Combust. Flame* 121, 122-136 (2000), and references cited therein.

14. Mueller, C.J., Pitz, W.J., Pickett, L.M., Martin, G.C., Siebers, D.L., Westbrook, C.K., "Effects of Oxygenates on Soot Processes in DI Diesel Engines: Experiments and Numerical Simulations," SAE Paper 2003-01-1791, 2003.

15. Curran, H.J., Gaffuri, P., Pitz, W.J., and Westbrook, C.K., "A Comprehensive Modeling Study of n-Heptane Oxidation", *Combust. Flame* 114, 149-177 (1998).

16. Fischer, S.L., Dryer, F.L., and Curran, H.J., "The Reaction Kinetics of Dimethyl Ether. I. High-Temperature Pyrolysis and Oxidation in Flow Reactors," *Int.J.Chem.Kinetics*, Vol. 32, pp. 713-740, 2000.

17. Kaiser, E.W., Wallington, T.J., Hurley, M.D., Platz, J., Curran, H.J., Pitz, W.J., and Westbrook, C.K., "Experimental and Modeling Study of Premixed Atmospheric-Pressure Dimethyl Ether-Air Flames," *J.Phys.Chem.*, Vol. A 104, pp. 8194-8206, 2000.

18. Good, D.A., and Francisco, J.S., "Tropospheric Oxidation Mechanism of Dimethyl Ether and Methyl Formate", *J. Phys. Chem. A* 104, 1171-1185 (2000).

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