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*H.J. Curran, E. Fisher, P.-A. Glaude, N.M. Marinov, W.J.  
Pitz, C.K. Westbrook*

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# **Detailed Chemical Kinetic Modeling of Diesel Combustion with Oxygenated Fuels**

H. J. Curran, E. Fisher\*, P.-A. Glaude, N. M. Marinov,  
W. J. Pitz and C. K. Westbrook

Lawrence Livermore National Laboratory  
P. O. Box 808  
Livermore, CA 94551

\* Sibley School of Mechanical and Aerospace Engineering  
Cornell University  
Ithaca, New York 14853

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## **Abstract**

The influence of oxygenated hydrocarbons as additives to diesel fuels on ignition, NO<sub>x</sub> emissions and soot production has been examined using a detailed chemical kinetic reaction mechanism. N-heptane was used as a representative diesel fuel, and methanol, ethanol, dimethyl ether and dimethoxymethane were used as oxygenated fuel additives. It was found that addition of oxygenated hydrocarbons reduced NO<sub>x</sub> levels and reduced the production of soot precursors. When the overall oxygen content in the fuel reached approximately 25% by mass, production of soot precursors fell effectively to zero, in agreement with experimental studies. The kinetic factors responsible for these observations are discussed.

## **Introduction**

Emission standards for diesel engines used in vehicles have been steadily reduced in recent years, and a great deal of research and development effort has been focused on reducing particulate and nitrogen oxide emissions, as shown in Figure 1. One promising approach to reducing emissions involves the addition of oxygen to the fuel, generally by adding an oxygenated compound to the normal diesel fuel. Miyamoto et al. [1] have shown that particulate levels can be

significantly reduced by adding oxygenated species to the fuel. They found the Bosch smoke number (a measure of the particulate or soot levels in diesel exhaust) falls from about 55% for conventional diesel fuel to less than 1% when the oxygen content of the fuel is above about 25% by mass.

Addition of oxygenates to automotive fuel, including both diesel fuel as well as gasoline, clearly reduces NO<sub>x</sub> and CO emissions by reducing flame temperatures. This is the basis for addition of oxygenates to produce reformulated gasoline in selected portions of the country. Of course, this is also accompanied by a slight reduction in fuel economy.

Recently, a new overall picture of diesel combustion has been developed [2], in which a series of laser and other diagnostic studies identified several stages in diesel combustion that had not previously been recognized. These stages are shown in Figures 2 and 3. In Fig. 2 the time evolution of the diesel spray is shown, beginning as a liquid jet that vaporizes and entrains hot air in the combustion chamber, leading eventually to ignition. The relatively steady period of jet combustion is shown in Fig. 3, which continues as long as fuel is being injected. In particular, Dec has shown that the fuel spray vaporizes and mixes with air and products of earlier combustion to provide a fuel-rich region in which a gas phase, premixed rich burn occurs. The products of this ignition are then observed experimentally to lead rapidly to formation of soot particles, which subsequently are consumed in a diffusion flame.

Recently, Flynn et al. [3] used a chemical kinetic model to study the premixed, rich ignition process. Using n-heptane as the representative diesel fuel, they showed that addition of methanol to the fuel reduced the concentrations of a number of hydrocarbon species in the products of the rich ignition. Specifically, methanol addition reduced the total concentrations of acetylene, ethylene and 1,3-butadiene, as well as propargyl and vinyl radicals, in the ignition products. These are the same species shown in a number of studies [4-6] to be responsible for formation of aromatic and polycyclic aromatic species in flames, species which lead eventually to production of soot.

At least two hypotheses have been advanced to explain the role that oxygenated species play in diesel ignition and the reduction in the concentrations of these species. The first is that the additive, methanol in the case of Flynn et al., does not contain any C – C bonds and cannot then produce significant levels of the species such as acetylene, ethylene or the unsaturated radicals which are known to lead to aromatic species. The second hypothesis is that the product distribution changes very naturally as oxygen is added and the overall equivalence ratio is reduced. In the present study, we repeat the ignition

calculations of Flynn et al. and add a number of other oxygenated species to determine which of these theories is more applicable to this model.

## **Chemical Kinetic Model**

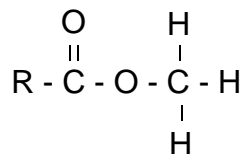
As done by Flynn et al., we focus on the zero-dimensional ignition of a mixture of hydrocarbons with air. As shown in Figure 3, the liquid fuel jet has entrained considerable amounts of hot, compressed air, as well as hot combustion products from the diffusion flame. The cooler vaporized fuel is heated as its equivalence ratio is reduced, and this continuous mixing of fuel, air and reaction products is treated by the model as a stirred reactor in which the fuel vapor is steadily modified by the air and reaction products. Eventually, the fuel/air/product mixture burns, and the model indicates that this occurs at a local equivalence ratio of approximately 3 – 4, or very fuel-rich. In the present study, we assume that the rate of mixing and the temperatures of the air and reaction products are all the same as in the baseline case and do not vary from one oxygenate to another. All that is changed in the modeling calculations is the composition, and therefore the kinetics, of the oxygenated additive.

The calculations are carried out using the HCT code [7], which solves the conservation equations of mass, momentum, energy, and each chemical species. This code has been used in a wide range of computational studies of combustion in laminar flames, flow reactors, static reactors, stirred reactors, shock tubes, and other environments. The key to the model is the reaction mechanism for the fuels being examined.

The basic diesel fuel is represented by n-heptane, which has a cetane number consistent with most realistic diesel fuels. The reaction mechanism for n-heptane has been developed and tested through extensive comparisons between computed and experimental data [8], and all of the chemical processes important in diesel ignition have been validated for this fuel. The reaction mechanisms for the oxygenated additives have similarly been tested through comparisons with experimental data for methanol [9,10], ethanol [11], and dimethyl ether (DME) [12]. Another oxygenated fuel, dimethoxy methane (DMM), has also been included in this work. The reaction mechanism for DMM has been developed using the same thermochemical and kinetic principles as used to develop the other fuel reaction mechanisms, although the available experimental data are not really sufficient to fully validate the mechanism.

Finally, we have included a few modeling calculations in which the fuel was methyl butanoate, a small example of a large family of so-called biodiesel fuels,

consisting of methyl esters. These fuels generally have long alkyl chains with as many as 15 – 20 carbon atoms:



However, for our preliminary modeling calculations, we have treated only the case for methyl butanoate, for which R = n-propyl. Experimental studies [13] indicate that this is the smallest methyl ester whose ignition displays a negative temperature coefficient at relatively low temperatures, as noted for many purely hydrocarbon fuels [14] in diesel and spark ignition conditions.

Each of these fuels demonstrates a combination of high temperature reactivity and a low temperature peroxide chemistry mechanism [14]. Modeling studies have shown how these mechanisms contribute to ignition behavior, and the reaction mechanisms for all of the fuels in this study, with the exception of methyl butanoate, have been thoroughly validated through comparisons between experimental and computed ignition and combustion events. The mechanism for methyl butanoate is currently being developed and tested.

## Ignition Modeling

As noted above, ignition of a fuel spray in a diesel engine is quite complex. Fuel is introduced into the combustion chamber as a liquid jet into a high temperature, highly compressed air charge that has been compressed by the engine piston. The jet vaporizes and mixes with hot compressed air, as well as with hot products of rich ignition, and eventually it ignites. However, unlike a conventional ignition, this ignition is limited by the lack of oxygen, to completely burn its fuel to CO<sub>2</sub> and H<sub>2</sub>O. Instead, this ignition, which occurs at a local equivalence ratio of between  $\phi = 3$  and 4, yields a variety of products; the work of Dec [2,3] has shown that these products lead immediately to soot formation in the diesel engine chamber.

The work of Flynn et al. [3] suggests very strongly that the products of this rich premixed ignition consist of soot precursors, and that the variation in the concentrations of these soot precursors produces the variability in soot production for different fuels. As diesel fuel is steadily replaced by oxygenated species, the post-ignition gases contain reduced concentrations of those species which lead to soot production, and less soot is ultimately produced.

## Computed Results

We have carried out rich, premixed ignition delay calculations for mixtures of n-heptane and oxygenates including methanol, ethanol, DMM and DME over a range of initial oxygenate fractions. A limited number of calculations were also carried out for a simple biodiesel molecule methyl butanoate, but these are not reliable until the reaction submechanism for that oxygenated compound is independently validated. We have assumed that the mixing of fuel, air and reaction products is the same in all of the computed cases. In each case the computed results yield a computed ignition delay time and concentrations of selected species that are produced by the rich premixed ignition.

Addition of each of the oxygenated species in this study retarded ignition by a time interval between 0.1 and 0.5 ms. Also, in nearly every case, addition of oxygenated species also reduced the concentrations of the important stable and radical intermediate species. For example, Figure 4 shows the concentrations of ethene during the ignition of n-heptane and of mixtures of n-heptane with each of the major oxygenated additives examined in this study. Addition of extensive fractions of each oxygenate reduces the ethene concentrations by about a factor of 50% as well as delaying the ignition. Similar time histories of other selected radical and stable intermediate species are shown in Figures 5-9.

We have summed the concentrations of soot precursors including ethylene, acetylene, and propargyl radicals, and the results are shown in Figure 10. It is clear from these results that the reduction in precursor concentrations is very similar for all of these oxygenated fuel additives. This result is in agreement with the experimental work of Miyamoto et al. [1] who included results for a variety of oxygenated additives.

Note that the results for ethanol addition (ethanol has one C – C bond) follow the same trend as the oxygenated species that do not contain C – C bonds, indicating that the presence or absence of C – C bonds in the oxygenate has no discernable influence on the product distribution for diesel ignition, at least for the fuels in this study.

## Discussion

Close examination of the computed histories of each of these ignition histories shows that, when oxygenated hydrocarbons are added to the fuel, the oxygen remains permanently connected to a carbon atom. No elementary reactions are able to break this bond, so the carbon atom is unable to participate in any of the

reactions of the small unsaturated species that have been identified as leading to aromatic compounds and soot.

The key to understanding this phenomenon is to realize exactly how much additive is required to provide an oxygen fraction of 25%. In the case of a surrogate diesel fuel such as n-heptane, the molecular weight is 100 (7 carbon atoms and 16 hydrogen atoms), while the molecular weight of methanol is only 32. Thus for a mixture with 25% oxygen by weight, there would have to be approximately 76% methanol and only 24% heptane. If we postulate, based on the kinetic modeling evidence, that none of the carbon atoms in the oxygenated additive are available to participate in aromatic ring formation or growth reactions, largely because they are strongly bonded to O atoms, then the amounts of aromatic precursors should be reduced by about a factor of 4. In actuality, this reduction is not realized in full, as indicated by the species histories in the figures, but the general trend towards reduction in these radical and stable species levels is clear from the computed results.

## **Conclusions**

The model of diesel combustion developed by Dec [2] suggests that some of the products of the rich, premixed ignition are species that lead preferentially to soot production. The present model calculations generally confirm this view, although a great deal of further work is necessary to provide a satisfactory chemical description of soot formation under these conditions. However, current theories and models have been quite successful in understanding the reaction paths for the early parts of this process, namely the cyclization of the smaller fragments into aromatic hydrocarbons with one, two and three rings. The subsequent production of real soot remains a subject for continued study. The present model indicates that when significant fractions of diesel fuel are replaced by oxygenated species, the carbon atoms already bonded to oxygen atoms cannot provide soot precursors, and this process is responsible for the observed results.

## **Acknowledgment**

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## References

1. Miyamoto, N., Ogawa, H., Nurun, N.M., Obata, K., Arima, T., "Smokeless, Low NO<sub>x</sub>, High Thermal Efficiency, and Low Noise Diesel Combustion with Oxygenated Agents as Main Fuel", Society of Automotive Engineers publication SAE-980506, 1998.
2. Dec, J.E., "A Conceptual Model of DI Diesel Combustion Based on Laser-Sheet Imaging", Society of Automotive Engineers publication SAE-970873, 1997.
3. 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", Society of Automotive Engineers publication SAE 1999-01-0509, 1999.
4. Frenklach, M., and Wang, H., "Detailed Modelling of Soot Particle Nucleation and Growth", Twenty-Third Symposium (International) on Combustion, pp. 1559-1566, The Combustion Institute, Pittsburgh, 1990.
5. Marinov, N.M., Pitz, W.J., Westbrook, C.K., Vincitore, A.M., Castaldi, M.J., Senkan, S.M., and Melius, C.F., "Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Laminar Premixed n-Butane Flame", *Combustion and Flame* 114, 192-213 (1998).
6. Harris, S.J., Weiner, A.M., Blint, R.J., and Goldsmith, J.E.M., "Concentration Profiles in Rich and Sooting Ethylene Flames", Twenty-First Symposium (International) on Combustion, pp. 1033-1045, The Combustion Institute, Pittsburgh, 1986.
7. Lund, C.M., "HCT – A General Computer Program for Calculating Time-Dependent Phenomena Involving One-Dimensional Hydrodynamics, Transport, and Detailed Chemical Kinetics", Lawrence Livermore National Laboratory report UCRL-52504 (1978).
8. Curran, H.J., Gaffuri, P., Pitz, W.J., and Westbrook, C.K., "A Comprehensive Modeling Study of n-Heptane Oxidation", *Combustion and Flame* 114, 149-177 (1998).

9. Westbrook, C.K., and Dryer, F.L., "A Comprehensive Mechanism for Methanol Oxidation," *Combustion Science and Technology* 20, 125-140 (1979).
10. Westbrook, C. K., and Dryer, F. L., "Prediction of Laminar Flame Properties of Methanol-Air Mixtures," *Combustion and Flame* 37, 171-192 (1980).
11. Marinov, N.M., "A Detailed Chemical Kinetic Model for High Temperature Ethanol Oxidation", *International Journal of Chemical Kinetics* 31, 183-220 (1999).
12. Curran, H. J., Pitz, W. J., Marinov, N. M., Westbrook, C. K., Dagaut, P., Boettner, J.-C., and Cathonnet, M., "A Wide Range Modeling Study of Dimethyl Ether Oxidation," *International Journal of Chemical Kinetics* 30, 229-241 (1998).
13. Parsons, B.I., and Hinshelwood, C., "The Oxidation of Hydrocarbons and Their Derivatives. Part II. Structural Effects in the Ester Series." *J. Chemical Society* pp.1799-1803 (1956).
14. Westbrook, C. K., Pitz, W. J., and Leppard, W. R., "The Autoignition Chemistry of Paraffinic Fuels and Pro-Knock and Anti-Knock Additives: A Detailed Chemical Kinetic Study", Society of Automotive Engineers publication SAE-912314 (1991).

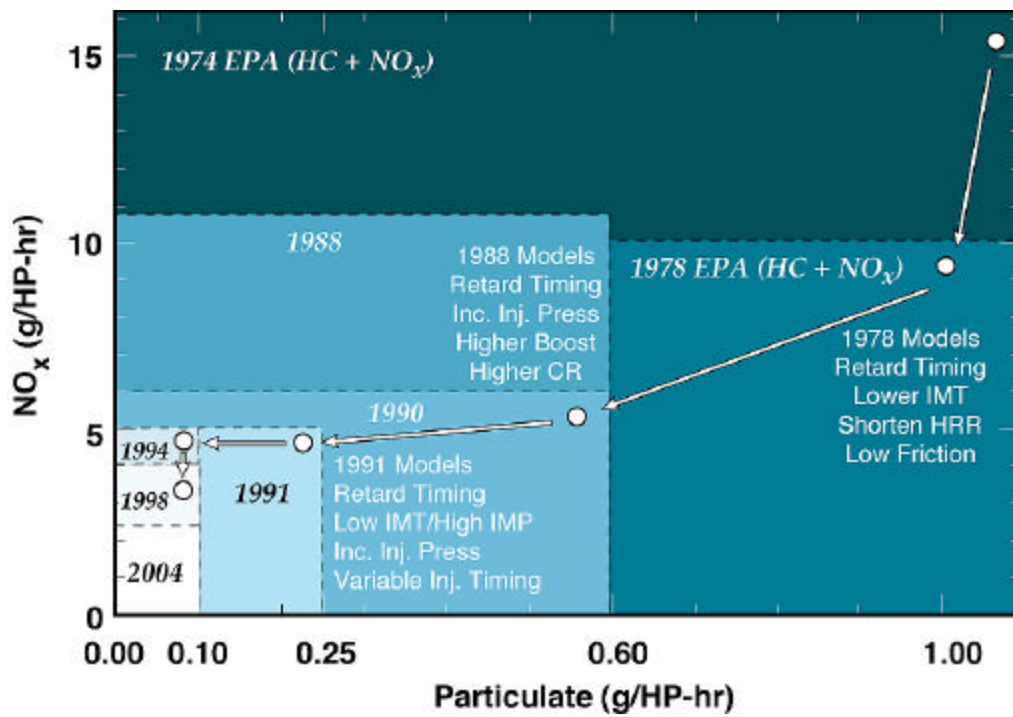


Figure 1: Particulate and NO<sub>x</sub> emission standards for heavy-duty diesel engines in the United States (Courtesy of John Dec).

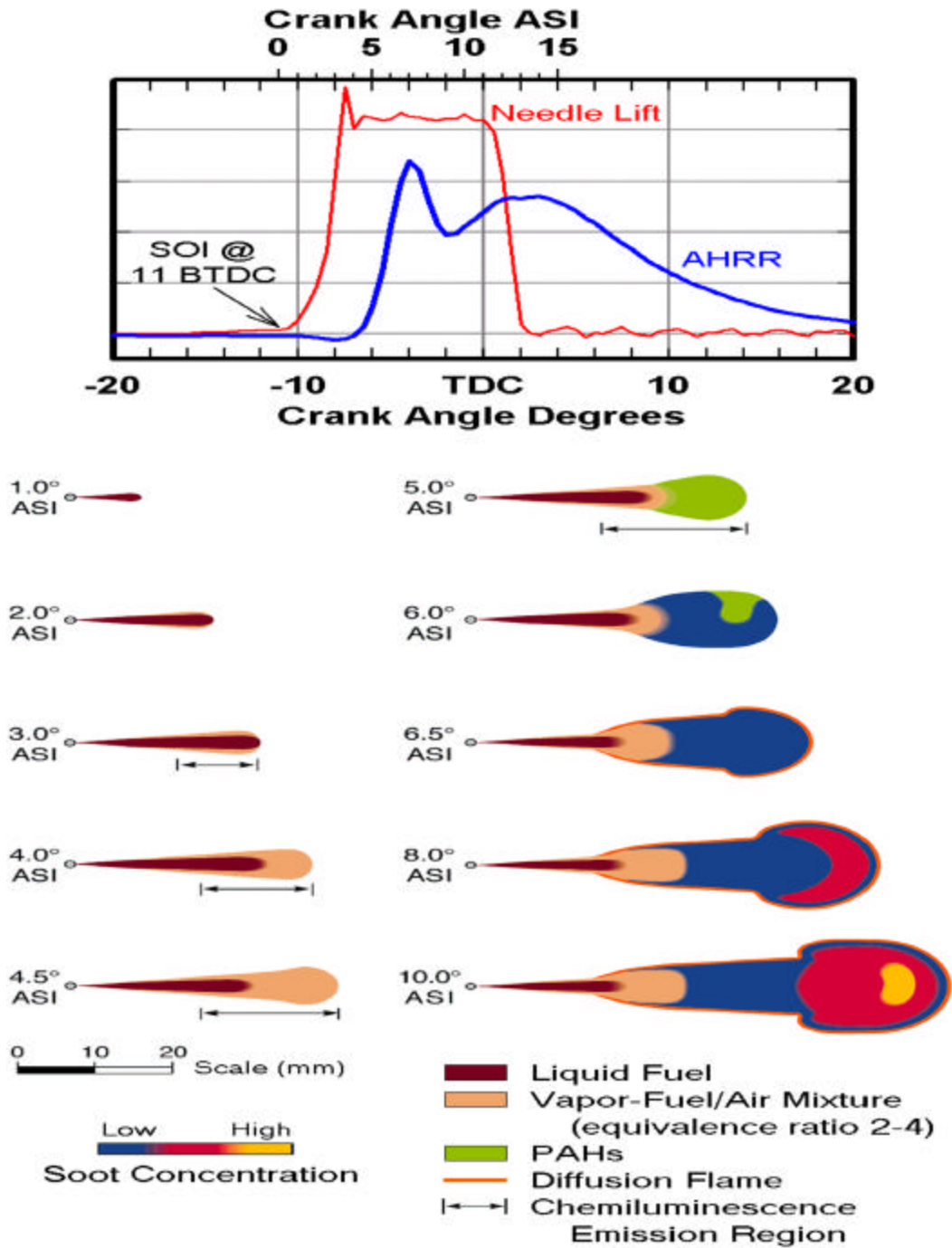


Figure 2: Schematics of early flame images from laser from Flynn et al. [3].

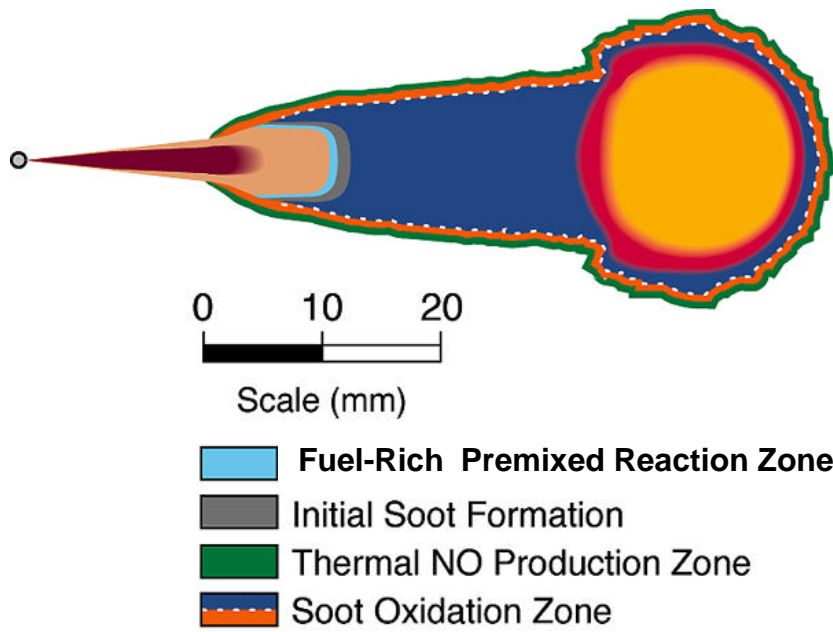


Figure 3: Conceptual picture of direct injection diesel combustion from Dec [2].

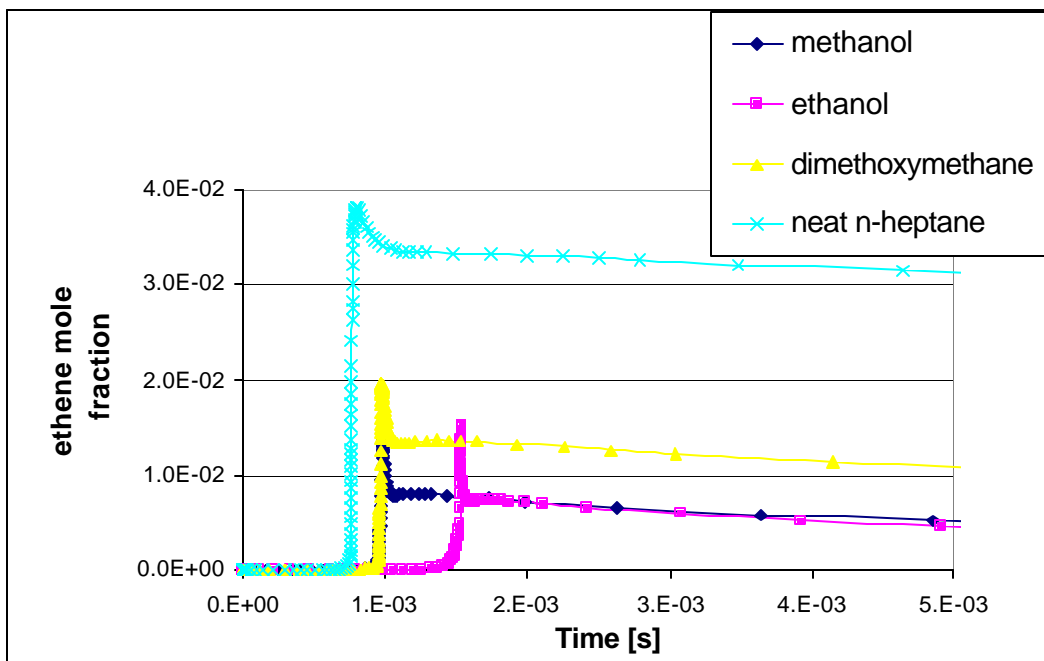


Figure 4: Ethene mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

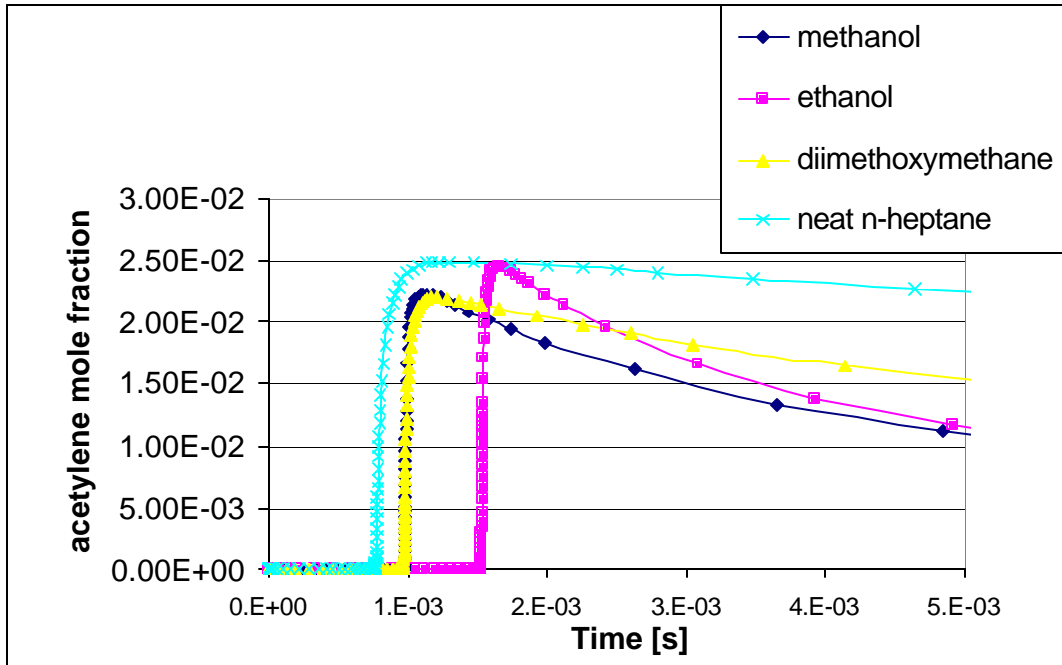


Figure 5: Acetylene mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

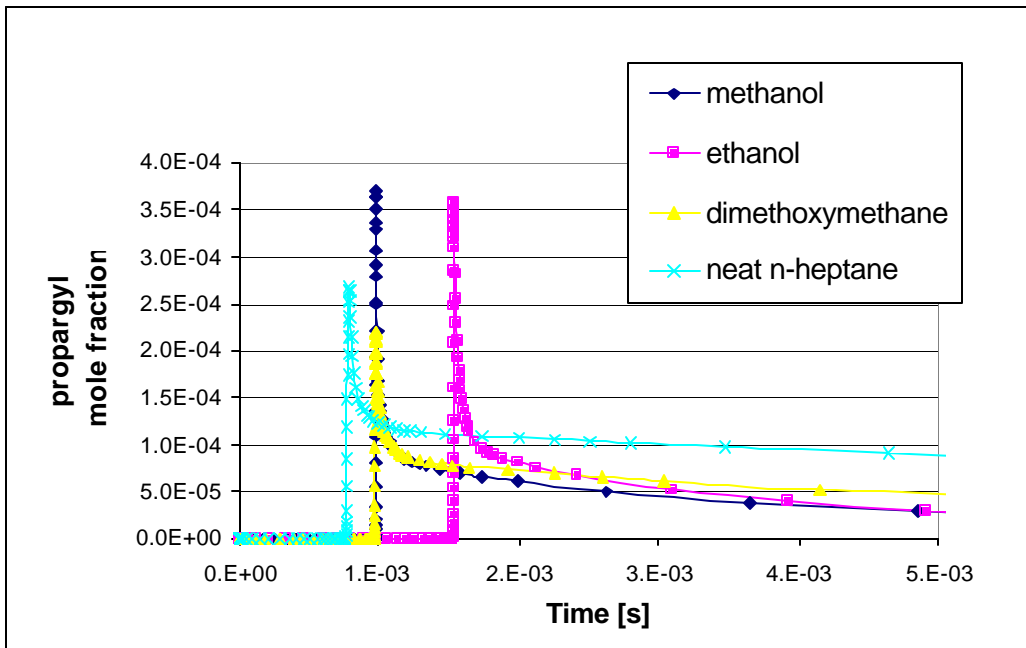


Figure 6: Propargyl radical mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

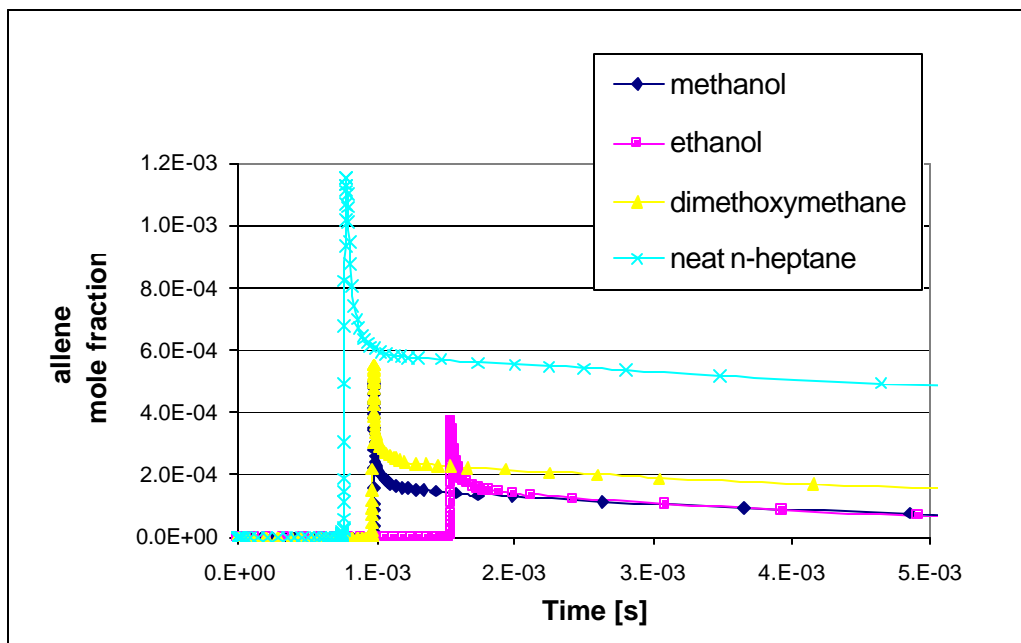


Figure 7: Allene mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

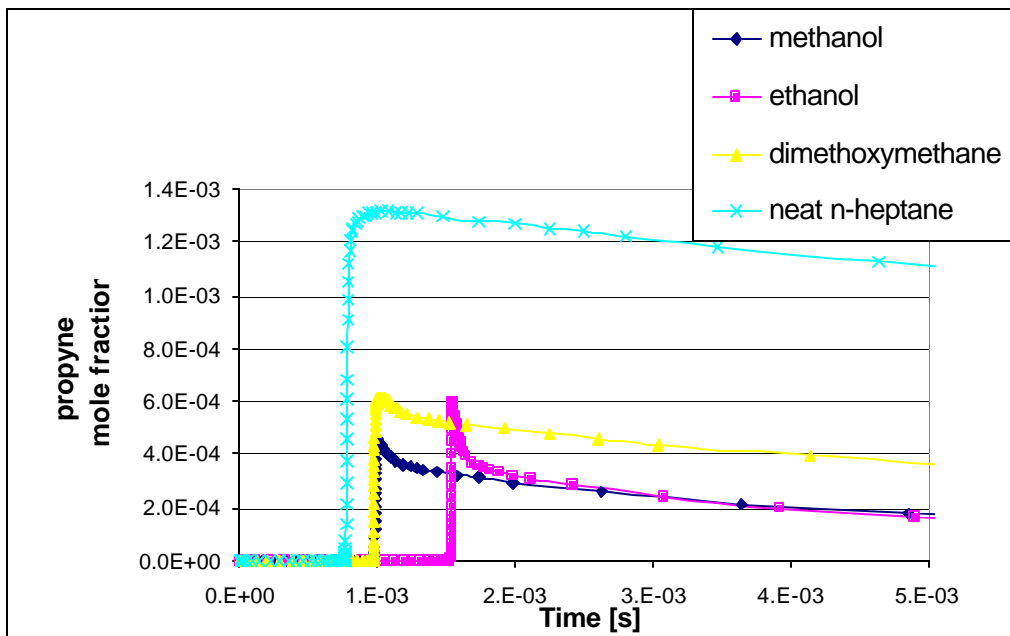


Figure 8: Propyne mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

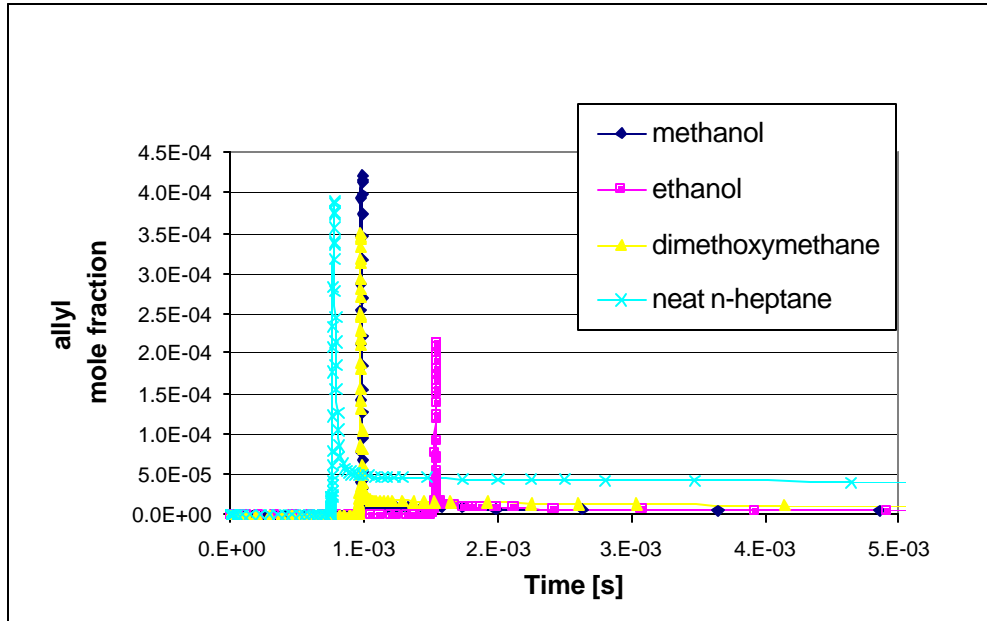


Figure 9: Allyl radical mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.



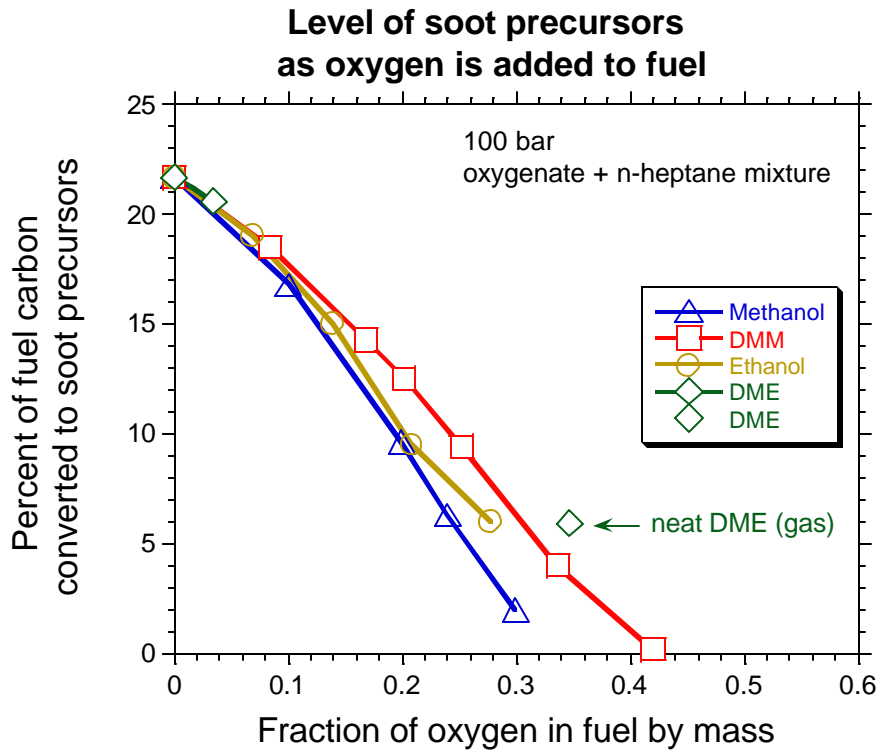


Figure 10: Level of soot precursors as oxygen is added to the simulated diesel fuel.