

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

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## Introduction

Emission standards for diesel engines 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. 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] showed experimentally 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, as shown in Figure 1.

It has been well established that addition of oxygenates to automotive fuel, including both diesel fuel as well as gasoline, 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.

A new overall picture of diesel combustion has been developed by Dec [2], in which laser diagnostic studies identified stages in diesel combustion that had not previously been recognized. These stages are summarized in Figure 2. The evolution of the diesel spray is shown, starting as a liquid jet that vaporizes and entrains hot air from the combustion chamber. This relatively steady process continues as long as fuel is being injected. In particular, Dec showed that the fuel spray vaporizes and mixes with air and products of earlier combustion to provide a region in which a gas phase, premixed fuel-rich ignition and 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 and mixing model to study the premixed, rich ignition process. Using n-heptane as a representative diesel fuel, they showed that addition of an oxygenated additive, 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. Flynn et al. did not, however, examine the kinetic processes responsible for the computed reduction in production of soot precursor species.

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 include a number of other oxygenated species to determine which of these theories is more applicable to this model.

## Physical Mixing and Ignition

A model developed by Naber and Siebers [7] was used to estimate the mixing of the fuel jet with the entrained air. The start of fuel injection takes place about 10 degrees before Top Dead Center (TDC) in this engine, so the compressed air already has a relatively high temperature and pressure. The cold fuel and hot air are mixed steadily until the mixture reaches a temperature of about 760K, where the kinetic model indicates that the overall reaction begins to occur. The fuel used for these mixing calculations is n-heptane, which has ignition properties which are typical of diesel fuel, with a cetane number of 56. At this mixed temperature, the fuel/air equivalence ratio  $\phi$  is approximately 4.0. Previous kinetic modeling studies [8,9] have shown that at these temperatures and pressures, fuel-rich mixtures actually react more rapidly than stoichiometric or fuel-lean mixtures, so the kinetic modeling calculations are begun at this point. The calculations are carried out under the assumption of homogeneous, constant pressure conditions, and no additional mixing with hot air is included. Additional mixing with air would tend to accelerate ignition by a relatively minor amount. With these starting conditions, the chemical kinetic model indicates that ignition occurs in slightly less than 1 ms, generally consistent with Dec's observations in the diesel engine, which indicate ignition in less than 1 ms.

In subsequent model calculations, in which selected fractions of diesel fuel (i.e., n-heptane) are replaced by oxygenated species, it is assumed that the same amounts of air and fuel are mixed as in the baseline case above, reaching the same starting conditions for the kinetics calculations. However, since some of the n-heptane has been replaced by an additive containing O atoms, the overall

O/C atom atom ratio has effectively been reduced and the equivalence ratio has been reduced, although all of these mixtures still remain very fuel-rich overall.

The nature of this fuel-rich burn is different from conventional ignition in that, due to the very rich composition, very little production of carbon dioxide or water occurs. Instead, the products consist primarily of CO, hydrogen, and many small hydrocarbon fragments containing 2-4 carbon atoms, such as acetylene and ethylene. In addition, the products include many radical species such as vinyl, propargyl, allyl and methyl allyl radicals as will be discussed below. The temperature rise during this premixed burn stage is approximately 800 – 900K, so the products reach a temperature of 1600 – 1700K.

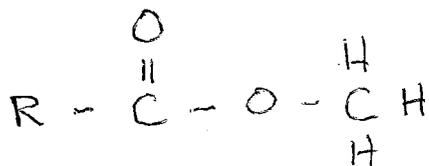
### **Chemical Kinetic Model**

The calculations are carried out using the HCT code [10], 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 of 56, consistent with 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 kinetic processes important in engine combustion and 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 [11,12],

ethanol [13], and dimethyl ether (DME) [14]. Another oxygenated fuel, dimethoxy methane (DMM), has also been included in this work. The reaction mechanism for DMM has been developed [15] using the same thermochemical and kinetic principles as used to develop the other fuel reaction mechanisms, although the available experimental data are not yet sufficient to fully validate the mechanism.

Finally, a few modeling calculations were carried out in which the consisted of either methyl formate or methyl butanoate, a smaller 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:



For the present preliminary modeling calculations, only the case for methyl butanoate, for which R = n-propyl, was included. Experimental studies [16] 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 [17] in diesel and spark ignition conditions.

Each of these fuels demonstrates a combination of high temperature reactivity and a low temperature peroxide chemical kinetic mechanism. 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 mechanisms for methyl butanoate and methyl formate are currently being developed and tested [18].

Formation of soot during hydrocarbon combustion has been the subject of many studies. Although the details of the processes are still not well understood, several features are evident. The major steps seem to consist of (1) production of simple aromatic compounds, (2) growth to multi-ring polycyclic aromatic hydrocarbons (PCAH's), (3) polymerization of PCAH's to produce small particulate compounds, and (4) particulate growth to make soot. In many situations, the fuel itself already contains significant levels of aromatic compounds such as benzene, toluene or xylenes, so step (1) simply provides more of these species. A number of recent soot production studies [4-6] have addressed the problem of formation of small aromatic species when they are not initially present in the fuel.

The chemical kinetic reaction pathways leading to production of aromatic and polycyclic aromatic species were reviewed recently by Miller [19], who identified two major classes of reactions. The first of these has been studied in great detail by Frenklach [4] and is based on reactions of acetylene molecules, such as

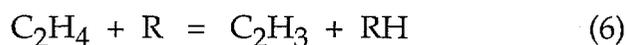


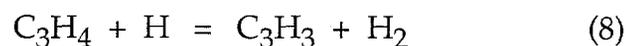
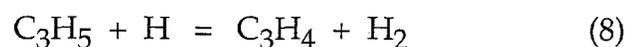
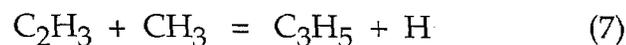
where reactions (2) and (3) produce the aromatic species  $C_6H_6$  (benzene) and  $C_6H_5$  (phenyl radical) via cyclization. Further addition of acetylene and other cyclization reaction steps then lead to larger aromatic compounds and polycyclic aromatic hydrocarbons.

The second class of reactions that create aromatic species are based on reactions involving resonantly stabilized radical species, such as propargyl ( $C_3H_3$ ), allyl ( $C_3H_5$ ) cyclopentadienyl and substituted versions of propargyl and allyl [5,20,21]. As described by Miller, although these species are indeed radicals, their reactivity is considerably lower than the more familiar radicals species such as methyl, hydroxyl and formyl radicals, so their concentrations can build to quite large levels in flames. Their eventual reactions to produce aromatic species include



where both  $C_3H_3$  and  $C_4H_3$  are resonantly stabilized radicals. The  $C_6H_5CH_2$  can then produce toluene by adding one more H atom. Further reactions of resonantly stabilized species with single-ring aromatics can then lead to formation of additional rings and production of polycyclic aromatic species. Ethene is an important part of this reaction sequence in many flames, producing propargyl via





where R is any radical species that can abstract H atoms from ethene.

Both of the reaction pathways above, the first centered on reactions involving acetylene and related species, and the second involving a variety of resonantly stabilized radical species, will take place during combustion of most fuels, especially diesel fuels, although their relative contributions might vary from one fuel to another. Although this kinetic modeling study did not follow the subsequent reactions of the aromatic species, the assumption was made that increasing the concentrations of the key species in these reaction sequences at the appropriate time and location would increase soot production during combustion. Based on the in-cylinder experimental studies of Dec and the resulting model for diesel combustion summarized in Fig. 1, the levels of these species in the products of the premixed, rich burn will be especially important, since the experiments indicate that these products begin immediately to produce soot in the engine. The concentrations of acetylene, propargyl and ethene will be used to try to quantify relative sooting tendencies of different fuels and additives, based on the importance of those species in both reaction sequences leading to production of aromatic and polycyclic aromatic hydrocarbon species.

## Computed Results

Ignition calculations were carried out for rich, premixed mixtures of n-heptane and oxygenates including methanol, ethanol, DMM and DME over a range of initial oxygenate fractions. It was assumed that the mixing of fuel, air and reaction products would be the same in all of the computed cases, as discussed above. In each case the computed results yield an ignition delay time and concentrations of all of the species that are produced by the rich premixed ignition.

The baseline case with n-heptane as the fuel ignited after about 0.8 ms, reaching a final temperature of about 1700K. The concentration variations with time for ethene, acetylene and propargyl radicals in this case are shown in Figures 3-5, labeled "neat n-heptane". The sum of these three soot precursor species just after the ignition accounted for about 22% of the total carbon in the reactant mixture.

Beginning with this mixture of n-heptane and air at a fuel/air equivalence ratio of 4.0, n-heptane was gradually replaced by selected oxygenated species. For each mixture in the replacement of n-heptane by oxygenated species, the sum of the selected soot precursor concentrations was computed. It was found that the replacement of fuel by oxygenated species produced a systematic reduction in the concentration of post-ignition soot precursor concentrations. These results are summarized in Figure 6. Within the scope of this study, all of the additives seemed to produce the same reductions in concentrations of soot precursors. It is interesting to 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. Extrapolating these results shown in Fig. 6, the model predicts that it would require an oxygen fraction of between 30% and 40% in the fuel to completely reduce the levels of these species to a negligible level. This result can be compared to the experimental results of Miyamoto et al. [1] shown earlier in Fig. 1, which indicates exactly the same trends. In their experiments, all of the additives produced approximately the same effects, as well as an oxygen content of 30% being necessary to reduce the Bosch smoke number to zero.

Comparisons of the production of soot precursor species between the baseline case of n-heptane and mixtures of n-heptane and different oxygenated species is shown in Figs. 3-5. For the mixed fuels, 20% of the total fuel weight consists of oxygen. The reductions in these concentrations is quite pronounced, especially for ethene.

A few calculations were carried out using methyl formate and methyl butanoate as the oxygenated additive. The results were generally consistent with those reported here for the other oxygenates, but the uncertainties in the kinetic mechanisms for these fuels makes it difficult to make any judgments of their relative effectiveness in reducing soot precursor production. However, since these fuels have structural features shared by larger biodiesel fuels, they will be included in future kinetic studies as their reaction mechanisms are refined and validated.

## Discussion

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 that 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 the kinetic features of this problem is to realize exactly how much additive is required to provide an oxygen fraction of 30%. In the present case of a somewhat idealized diesel fuel such as n-heptane, its 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 30% oxygen by weight, there would have to be approximately 82% methanol and only 18% 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 5. In actuality, this reduction is not realized in full, as indicated by the species histories in the Figs. 3-5, but the general trend towards reduction in these radical and stable species levels is clear from the computed results.

For some oxygenates, it is in fact difficult to add enough oxygen to affect the sooting tendency. In Fig. 6, the point labeled "neat DME (gas)" reflects the fact that in DME, oxygen is only 35% of the mass of the molecule. For large

biodiesel fuels with 16 – 18 carbon atoms, oxygen is only about 10% of the fuel mass, so reductions in sooting tendency with these fuels would be noticeable but not extreme. Blends of biodiesel with conventional diesel fuel would be expected to have proportionally smaller effects on soot precursor levels.

Furthermore, the distinction between the two “theories” for explaining the effectiveness of oxygenated species on sooting behavior begins to disappear when it is shown that an oxygenated additive that has multiple C – C bonds and only one or two O atoms will necessarily have a rather small O weight fraction and would not be expected to be very effective in reducing sooting or the production of soot precursor species.

## **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. The species acetylene, ethene and propargyl radicals provide a useful measure of the capacity of the ignition products to produce small aromatic species and eventually to produce soot, although the current study does not address soot production directly. Other combinations of this rich premixed burn might provide even better indications of sooting tendencies.

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. Since the fractions of oxygenates required to completely eliminate soot precursor production are so large, approaching 75-80%, it is probably unrealistic to attempt this degree of fuel modification in actual diesel engine practice, but the insights into the processes leading to soot provided by the model, supported by the excellent qualitative agreement between experimental and model results, can be very valuable in future studies of diesel combustion chemistry.

### **Acknowledgment**

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### Figure captions

1. Smoke emissions from diesel engines with oxygenated additives, from Miyamoto et al. [1].
2. Schematic of quasi-steady burning jet from laser measurements of Dec [2].
3. Ethene mole fractions in ignition of neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.
4. Acetylene mole fractions in ignition of neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.
5. Propargyl mole fractions in ignition of neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.
6. Level of soot precursors as oxygen is added to the simulated diesel fuel.

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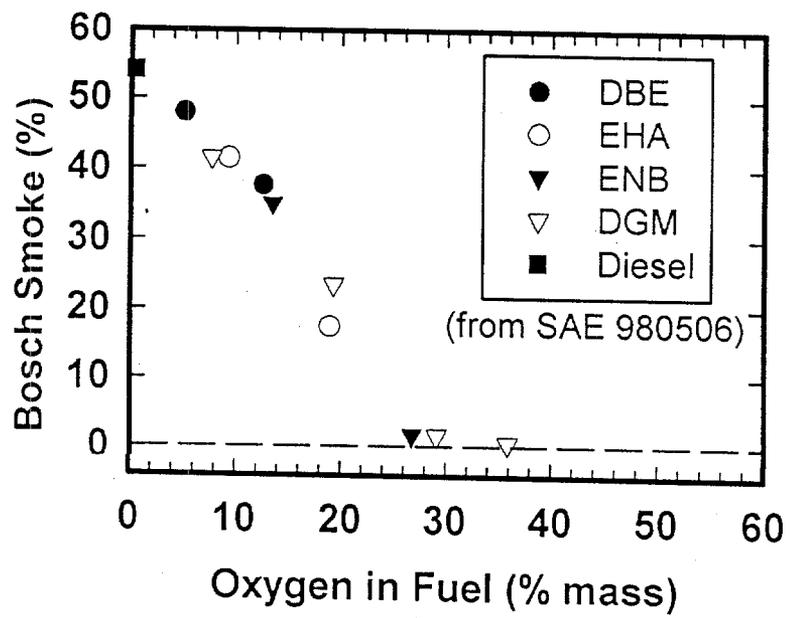


Fig. 1

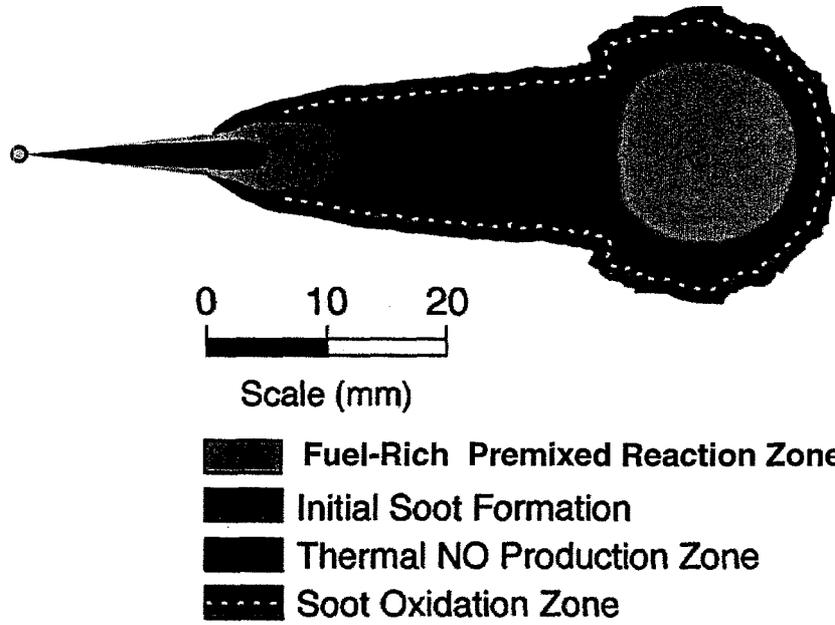


Figure 2: Conceptual picture of direct injection diesel combustion from Dec [2].

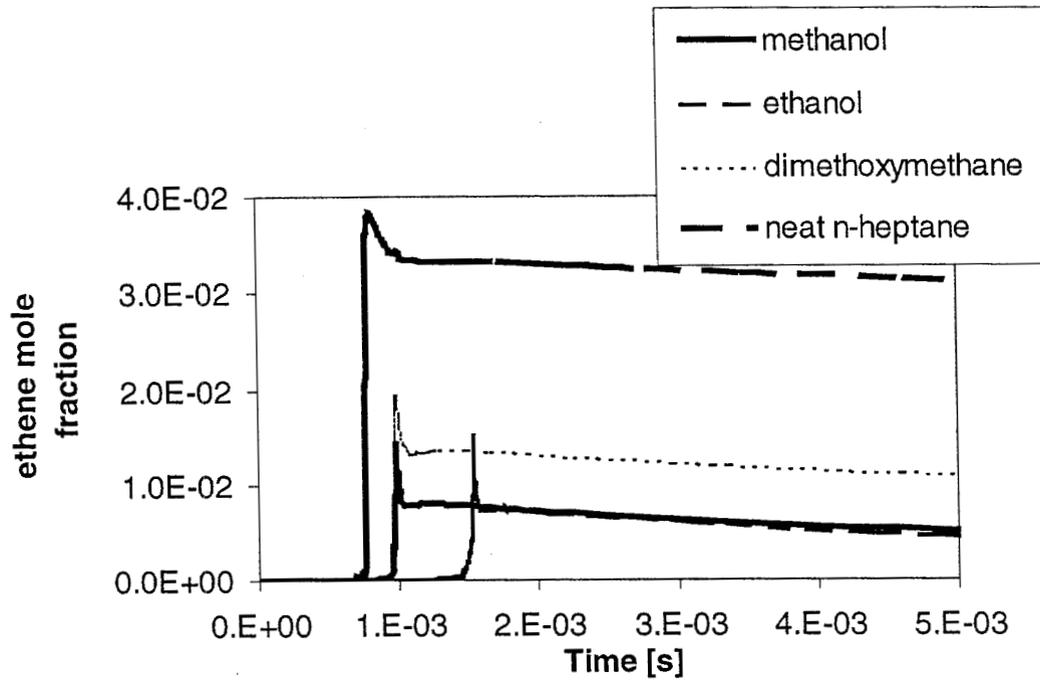


Figure 3: Ethene mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

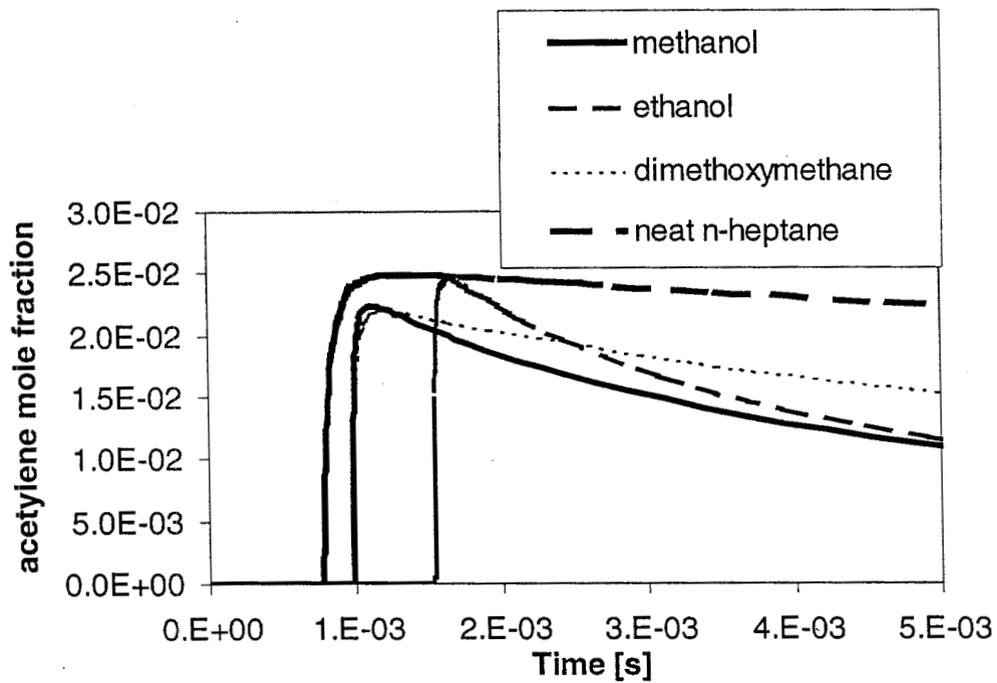


Figure 4: Acetylene mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

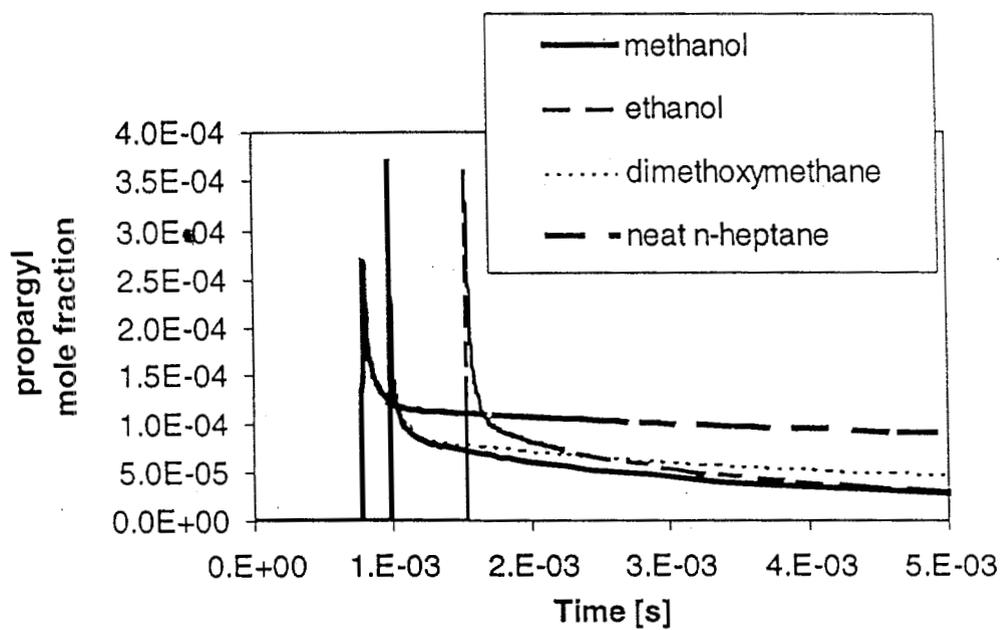


Figure 5 Propargyl radical mole fractions for neat n-heptane and for n-heptane /oxygenate mixtures with 20 percent oxygen in the fuel by weight.

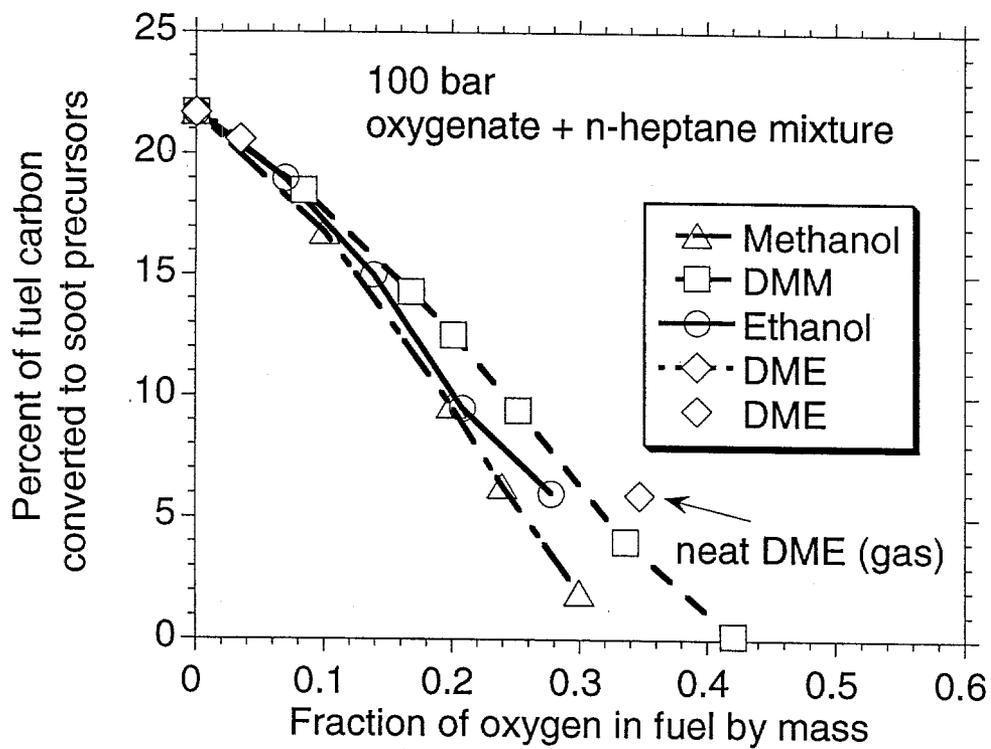


Figure 6: Level of soot precursors as oxygen is added to the simulated diesel fuel.