

MODELLING STUDY OF THE EFFECT OF CHEMICAL ADDITIVES ON SOOT PRECURSORS REDUCTION

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ABSTRACT—The effect of chemical additives, such as dimethyl ether (DME), ethanol, carbon disulfide on the soot formation were examined numerically. In this study, the Frenklach soot mechanism was used as a base mechanism to predict the soot formation in the ethane flame. The combination of Westbrook's DME mechanism, Marinov's ethanol mechanism, and chemical kinetic mechanism for hydrogen sulfide and carbon disulfide flames was made with the base mechanism because the DME, ethanol, CS₂ additives are added into the ethane fuel. CHEMKIN code was used as a numerical analysis software to simulate the effect of chemical additives on reduction of the polycyclic aromatic hydrocarbons (PAH's) which are soot precursors. From the numerical results it is observed that addition of DME, ethanol and CS₂ into ethane fuel can reduce PAH species significantly. That means these additives can reduce soot formation significantly. Results also strongly suggest suppression of soot formation by these additives to be mainly a chemical effect. H and OH radicals may be the key species to the reduction of PAH species for additives.

KEY WORDS : Soot, Chemical additives, Polycyclic aromatic hydrocarbon (PAH), Dimethyl ether (DME), Ethanol, Carbon disulfide

1. INTRODUCTION

Diesel engines have been known as the most efficient internal combustion engine since it was invented in the late 19th century by Rudolf Diesel. On the other hand, diesel engines have disadvantages such as noise, nitrogen oxides (NO_x), particulate matter (PM) emission. Diesel engines are still looked upon as the main engines for the transportation in the near future with the energy crisis and global warming.

Newly developed common-rail injection systems allow for the higher injection pressure and pilot injection, which help reduce the pollutant emissions and engine noise. Higher injection pressure causes faster combustion which results in the higher in-cylinder gas temperature compared to the conventional low pressure injection system. Although this increases the NO_x emission slightly, considerable soot reduction occurs. Multiple and split injection strategies can reduce the PM without increasing the NO_x emission (<http://www.dieselnet.com>).

These methods are difficult to be applied to the existing engine already made. But, modification to the fuel can reduce the emission without the major change in the existing engine. One of the practical approaches to soot reduction is to blend additives into the Diesel fuel, so

as to alter the soot nucleation and growth processes or to enhance soot oxidation.

Although the effect of various additives on soot formation has been observed by numerous researchers, relatively little is known about the mechanisms involved in soot suppression. Phenomenological theories have been suggested to explain the influence of additives on the formation of soot particles. For example, modest reductions in soot loading by adding of inert species such as Ar and N₂ have largely been attributed to lower flame temperatures and decreased fuel concentrations (dilution) (Schug *et al.*, 1980). Such effects are believed to significantly decrease the reaction rates of processes leading to soot formation. However, large reductions in soot formation by additives are explained by chemical mechanisms.

Frenklach and Yuan (1987), in the studies of the effects of methanol and ethanol addition to benzene on soot formation, observed that the decomposition of ethanol decreased the degree of hydrogen atom super-equilibrium compared to methanol, thus allowing ethanol to have a stronger suppressing effect than methanol. Overall, they attributed the suppression of soot formation to the enhanced oxidation of soot and soot precursors by OH generated from alcohol pyrolysis and to the removal of H atoms by alcohol and water molecules.

The most effective gaseous soot suppression additives appear to be sulfur compounds, such as H₂S, SF₆, and

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CS₂. Ni *et al.* (1994) and Park *et al.* (2002), using one-dimensional laser-induced incandescence (LII) and fluorescence measurement, demonstrated that the addition of methanol and CS₂ into the ethene diffusion flames can significantly reduce the formation of soot particle. Also they suggested that chemical interaction may play an important role in the suppression of soot formation of methanol and CS₂.

The works by Litzinger *et al.* (2000) have evaluated the effects on soot emissions of alcohols and ethers as additives to diesel fuel in a direct-injection diesel engine.

While there have been some suggestions regarding the mechanism of soot formation and the effect of chemical additives, it is typically difficult to elucidate these mechanisms in an experimental study. Hence, in this study numerical simulations using Frenklach mechanism were carried out to examine the importance of chemical effects on the reduction of Polycyclic Aromatic Hydrocarbons (PAH) which are known to be precursors to soot and are possible source of mass for soot growth when soot-suppressant additives, such as ethanol, DME and carbon disulfide are added.

2. CHEMICAL KINETIC MECHANISM

2.1. Mechanism of Soot Formation

The carbonaceous particulates that form from gas-phase processes are generally referred to as soot. The identical chemical character of the soot formed from different combustion systems seems to suggest a commonality in the chemical mechanism of soot formation. It has been seen that there is an underlying fuel-independent general mechanism that is modified only with respect to the alternative routes to intermediates (Glassman, 1996).

Most of the mass of soot and associated heavy hydrocarbons is thought to come from acetylene (C₂H₂). The reactions of C₂H₂ leading to soot are said to proceed in two ways: by reactive addition of C₂H₂ to growing and coalescing polycyclic aromatic hydrocarbons (PAH) and by the direct reactive addition of C₂H₂ to the surface of growing soot particles (Wang and Frenklach, 1997; Xu and Faeth, 2000). These PAH species get conjugated so that they are resonanced-stabilized at the high temperature in which they grow. Eventually, the aromatic structure reach a large enough size to develop into particle nuclei (Glassman, 1996). Oxidation of PAH and soot particles is a process that competes with the formation of these species. It decreases the mass of PAH formed through its conversion into CO and CO₂. Depending upon the type of combustion system, oxidation may occur simultaneously with formation as in premixed aromatic flames and well-mixed combustors, or it may occur subsequent to formation as in diffusion flames or staged combustors. The main oxidants are OH, H, O and

O₂; with OH being the largest contributor under fuel-rich conditions and O₂ under fuel lean conditions (Richter and Howard, 2000).

The comprehensive mechanism proposed by Frenklach *et al.* (1997) and Appel *et al.* (2000) is widely accepted and is believed to successfully model soot formation in premixed flames. This model begins with fuel pyrolysis, followed by the formation of polycyclic aromatic hydrocarbons, their planar growth and coagulation into spherical particles, and finally surface growth and oxidation of the particles. Studies with this model have revealed a dominant kinetic pattern of aromatic-ring growth: Hydrogen Abstraction Carbon Addition (HACA). This reaction scheme has been adopted to describe surface growth of soot particle. This group has subjected the reaction steps comprising HACA to theoretical scrutiny and their efforts have produced a self-consistent set of reaction rate coefficients, thermodynamic data, and transport properties for PAH compounds. A data-based kinetic model has been developed which has been shown to reproduce the concentration profiles of major, intermediate, and aromatic species in several experimental studies of laminar premixed acetylene and ethylene flames.

2.2. Combination of Mechanisms

To investigate the effects of DME, ethanol and CS₂ additives on the soot reduction, the kinetic oxidation model of DME, ethanol and carbon disulfide should be combined with the base mechanism. The base mechanism in this combination was Frenklach's soot mechanism, which included a fuel oxidation mechanism of ethane. Subsets of DME mechanism Curran *et al.* (1998) ethanol mechanism Marinov (1998) were combined into the base mechanism for DME and ethanol addition cases. Also, the selected reactions from the kinetic oxidation mechanisms of hydrogen sulfide (H-S-O) and carbon disulfide (C-S-O) system (Basevich *et al.*, 1995) were combined into the base mechanism for CS₂ addition case. The mechanisms were combined such that duplicate reactions, if any, were removed from the overall mechanism. When adding reactions, care was taken to include all the reactions involved in the additive's breakdown into smaller species, some of which were already present in the base mechanism. The thermodynamic data were also combined to provide for the entire data set.

3. NUMERICAL ANALYSIS

The numerical analysis software used for this study was CHEMKIN code (1991), which is a software package whose purpose is to facilitate the formation, solution, and interpretation of problems involving elementary gas-phase

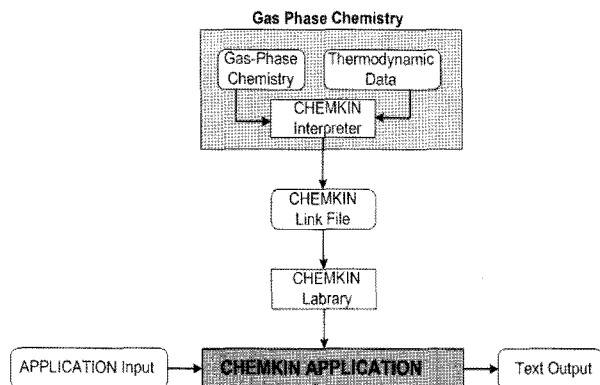


Figure 1. Schematic diagram showing the structure of the CHEMKIN package and its relation to an application program.

chemical kinetics. It provides a flexible and powerful tool for incorporating complex chemical kinetics into simulations of fluid dynamics. The general structure of the CHEMKIN package is shown in Figure 1. To apply CHEMKIN to a problem, one selects an application from the CHEMKIN collection that best describes a particular reactor geometry or set of flow conditions.

For the present study, the constant pressure adiabatic model of SENKIN was chosen as an Application Program. This model computes the time evolution of species mole fractions and temperature of a homogeneous reacting gas mixture in a closed system.

4. RESULTS AND DISCUSSIONS

4.1. DME and Ethanol Addition

The idea of using oxygenates to produce cleaner burning diesel fuels is half a century old. Since that time, numerous researchers have reported adding a variety of oxygenated compounds to diesel fuel. This includes ethanol, various alcohols, dimethyl and diethyl carbonates, dimethyl ether and other ethers (Choi and Reitz, 1999; Stoner and Sitzinger, 1999; Liotta and Montalvo, 1993). Here ethanol and DME additives were considered in this numerical study.

The effects of DME and ethanol additives on the PAH which is known as the precursors to soot were investigated numerically by using the Frenklach-DME-Ethanol mechanism which was obtained by combining the Frenklach's mechanism with Westbrook's DME and Ethanol mechanism. The Frenklach mechanism has been verified with ethane, ethene, ethylene as fuels. The ethane was used as a base fuel for our study because the Frenklach soot mechanism does not include the chemical kinetic mechanism of N-heptane or dodecane which can represent the diesel fuel. In all cases, total carbon in the system was held constant. That is, when additive was added, the fuel

proportion was slightly decreased so that the total carbon input was same as the base case. The equivalence ratio was maintained at 2.0 to simulate rich sooting condition. This model was run for a constant-pressure adiabatic case at 10 atmospheres, with an initial temperature 1100 K. Runs were continued until temperature and species reached steady state.

The PAH species selected as indicators for soot were benzene (A1-1 aromatic ring), naphthalene (A2-2 aromatic rings), phenanthrene (A3-3 aromatic rings), and pyrene (A4-4 aromatic rings). Figures 2 and 3 show the percentage change of peak PAH's when the methanol or DME were added into ethane with 10, 20 weight percent, respectively. The peak PAH is reduced substantially by the addition of ethanol or DME. 20% addition case enhance the effect of additives compared to 10% addition case. But no major difference were seen in the species profiles between the 10% and 20% addition cases.

It was observed that the ethanol or DME addition causes a reduction in the ignition delay as may be seen in Figure 4, where the rapid rise in temperature is an indicator of the ignition times. The fact that combustion occurred at different times for the different cases implies a change in the time evolution of the combustion process. Hence most plots of species mole fractions were taken against temperature. It was observed that the peak concentrations of the species occur more or less at similar temperatures for all the cases as may be seen in Figure 5. It was observed that all the cases converged to more or less similar final temperatures. This suggests that temperature-time effects would not affect these results to a great extent. This observation strongly suggests that a chemical interaction is the dominant effect in soot suppression by ethanol or DME addition.

DME (CH_3OCH_3) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) are isomers and hence between these two cases, the C, H and O ratios are exactly conserved. The DME and ethanol cases were

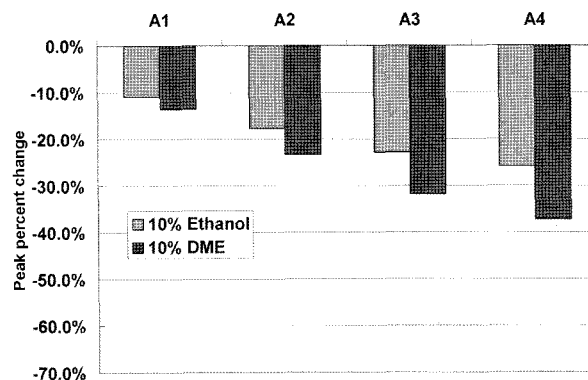


Figure 2. The effect of DME and ethanol additives on the peak changes in the PAH species (P=10 atm; T=1100 K; $\phi=2$; 10% additives by mass).

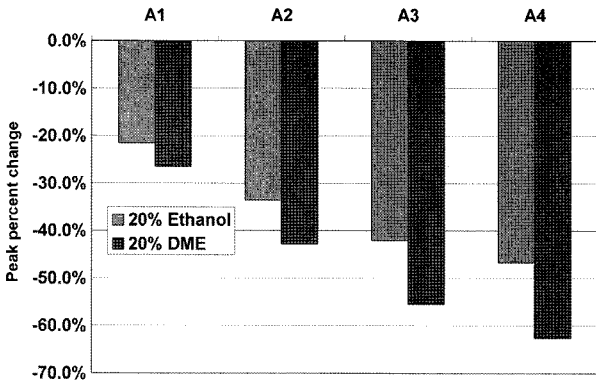


Figure 3. The effect of DME, ethanol additives on the peak percent changes in the PAH species ($P=10$ atm; $T=1100$ K; $\phi=2$; 20% additives by mass).

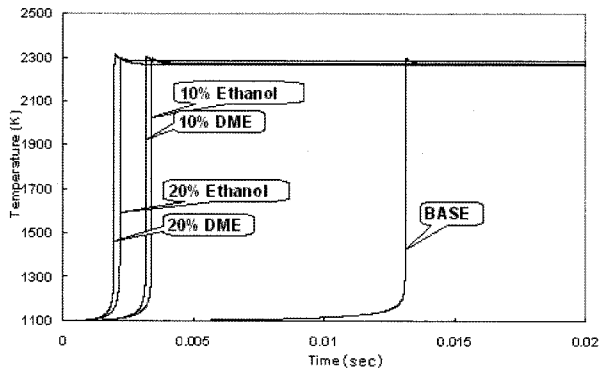


Figure 4. Temperature-time plot for the various additive addition cases.

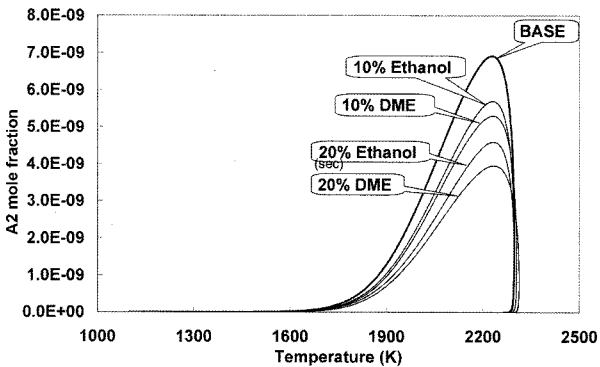


Figure 5. A2 concentration vs. temperature for various additive addition cases.

seen to have nearly similar ignition delay, which are mainly due to the similarity in their octane ratings. Nevertheless, DME showed a pronounced difference in PAH reduction compared to ethanol. This strongly suggests that there is an effect of molecular structure, which distinguishes DME from Ethanol, on the reduction in

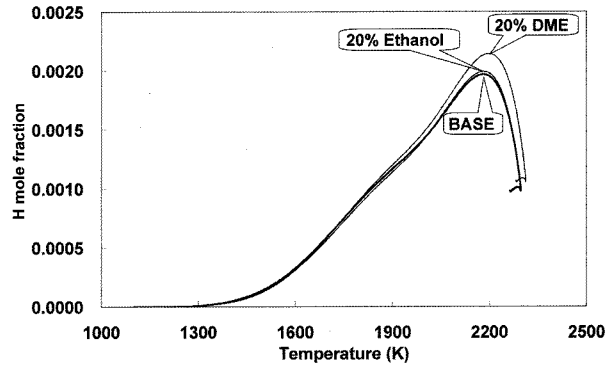


Figure 6. H mole fraction vs. temperature for base, 20% DME, 20% ethanol addition cases.

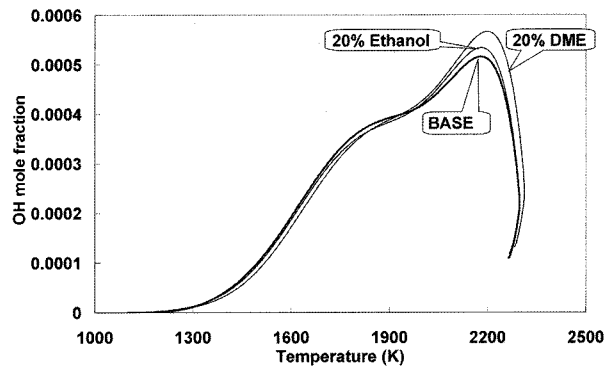


Figure 7. OH mole fraction vs. temperature for base, 20% DME, 20% ethanol addition cases.

PAH. This is consistent with the experimental results of Liotta and Montalvo (1993), where ethers were found to be more effective compared to alcohols.

The reason for this quantitative difference between DME and ethanol may be related to the basic reaction mechanism of these two oxygenates. To better understand the mechanism of PAH reduction, the concentration profiles of selected species such as H, OH, CH_2O , H_2O_2 , C_2H_2 were investigated. The H mole fraction for various cases are plotted against temperature in Figure 6. Ethanol addition case shows increases in peak H of about 1.2% while DME addition case shows a substantial increase in peak H of about 7.5%. The OH plot in Figure 7 also shows a similar trend as H. Ethanol shows a change in peak OH of about 3.5% while DME shows substantial increase in peak OH of about 9.8%. The increases in H and OH for ethanol case are not as high as for DME case. The increases in H and OH for DME compared to ethanol may be the causes for the difference of peak PAH's between two cases. Hence as can be seen from the above data, H and OH species may be said to be the key to PAH reductions for the additives.

The formaldehyde plot in Figure 8 shows that there is

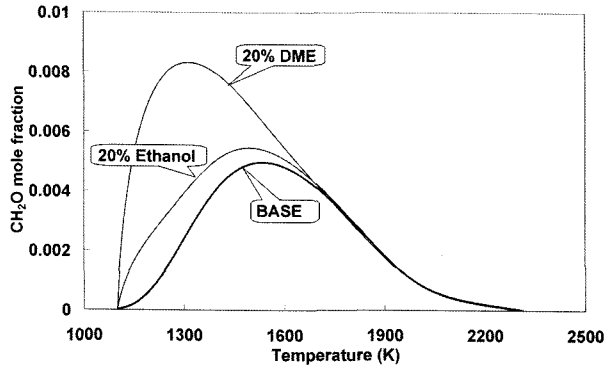


Figure 8. CH_2O mole fraction vs. temperature for base, 20% DME, 20% ethanol addition cases.

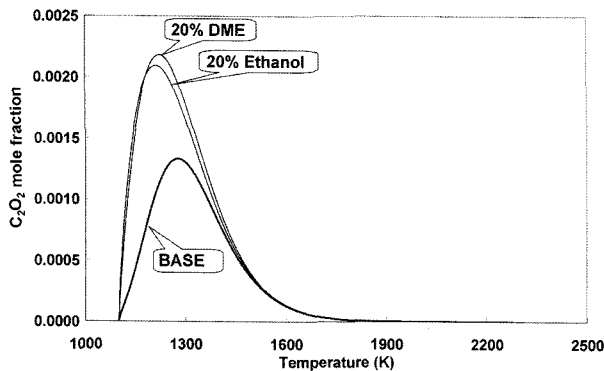


Figure 9. H_2O_2 mole fraction vs. temperature for base, 20% DME, 20% ethanol addition cases.

an early release of CH_2O in both DME and ethanol cases which increases the peak CH_2O concentration considerably as compared to the base case. There is a peak increase of about 9.8% for ethanol and 68% for DME. The increase in CH_2O in ethanol is not as high as in DME. The more rapid conversion of DME into CH_2O compared to ethanol may be the cause for the differences between these two cases. Hydrogen Peroxide also follows a similar trend as CH_2O as seen in Figure 9. There is a considerable amount of H_2O_2 formed from DME and ethanol in the early stages of combustion causing a peak change of 57% and 64% respectively. There seems to be a strong correlation between the peak percent change of PAH species and the fuel breakdown sequence.

One effect that appears to be clear is the direct correlation between the concentration of C_2H_2 and PAH. The trend in the decrease of C_2H_2 matches very closely to the trend in the decrease of PAH species as shown in Figure 10. For example, while peak C_2H_2 decreases by 3.7%, 4.2%, 7.7%, and 8.7% for the 10% ethanol, 10% DME, 20% ethanol, 20% DME cases respectively, the decrease in peak A2 for the corresponding cases were

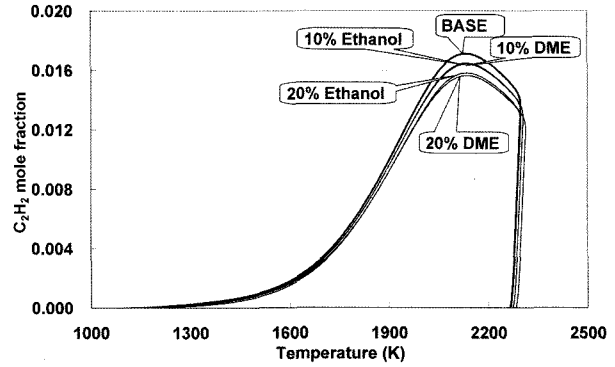


Figure 10. C_2H_2 mole fraction vs. temperature for the various additive addition cases.

18%, 23%, 34% and 43%. This trend agrees with the fact that acetylene is a major intermediate in the production of PAH.

The path of the fuel into PAH formation should be traced to investigate the more detailed chemical effect of the additives.

4.2. Addition of Carbon Disulfide

During the combustion of fuel with carbon disulfide as an additive, a marked decrease in the formation of polycyclic aromatic hydrocarbons, the intermediates for soot particle formation was observed (Ni *et al.*, 1994). In the present work, CS_2 was added to ethane to study numerically the chemical influence of CS_2 on soot formation. For the purpose of comparison, carbon oxide and carbon dioxide were introduced into the ethane.

The effects of CS_2 additives were investigated by using the Frenklach- CS_2 mechanism which was obtained by combining the Frenklach's mechanism with the kinetic oxidation mechanism of hydrogen sulfide and carbon disulfide system. The ethane was used as a base fuel for this study. The effect of CS_2 , CO and CO_2 additives were evaluated from this mechanism. This was run for a constant-pressure adiabatic case at 10 atmospheres, an equivalence ratio of 2.0, with an initial temperature 1100 K. Runs were continued until temperature and species reached steady state.

Figure 11 and 12 show the percentage change of peak PAH's when CS_2 , CO and CO_2 were added into ethane. The peak PAH is reduced by the addition of CS_2 and CO. By contrast, a same amount of CO_2 addition increases peak concentrations in the PAH species compared to the base case. CS_2 addition shows most effective reduction amongst the additives used in this numerical test. 20% addition case enhance the effect of additives compared to 10% addition case. But no major difference were seen in the species profiles between the 10% and 20% addition cases.

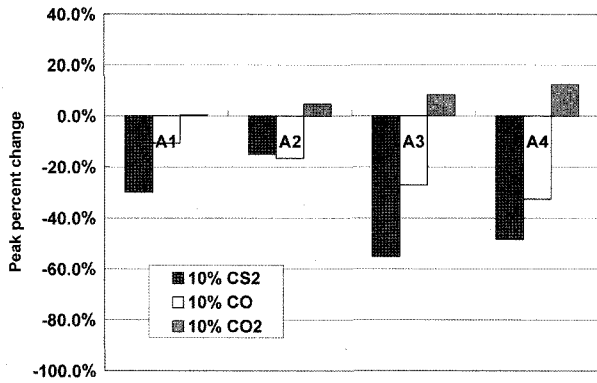


Figure 11. The effect of CS₂, CO and CO₂ on the peak changes in the PAH species (P=10 atm; T=1100 K; $\phi=2$; 10% additives by mass).

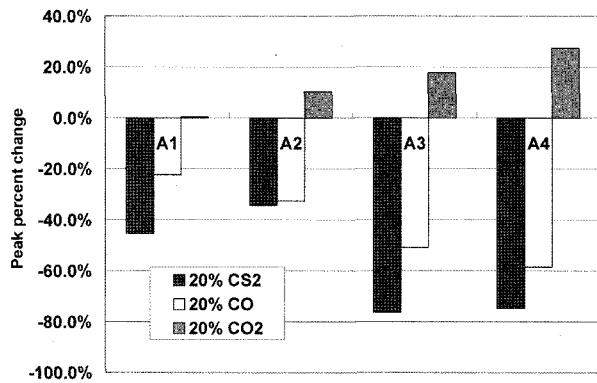


Figure 12. The effect of CS₂, CO and CO₂ on the peak changes in the PAH species (P=10 atm; T=1100 K; $\phi=2$; 10% additives by mass).

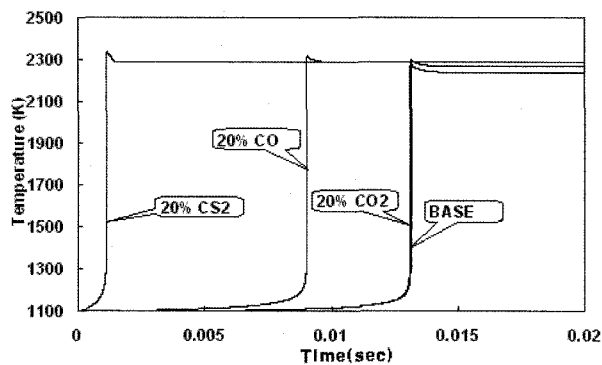


Figure 13. Temperature-time plot for the various additive addition cases.

It is observed that CS₂ cause a reduction in the ignition delay as may be seen in Figure 13, where the rapid rise in temperature is an indicator of the ignition times. CS₂ reduced the ignition time most largely compared to that for the base; CS₂ caused a reduction of 92% and CO of

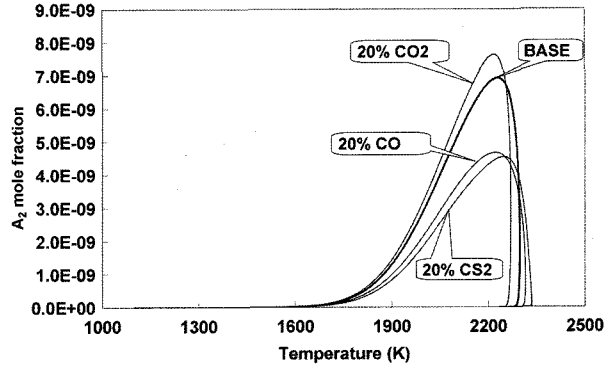


Figure 14. A₂ concentration vs. temperature for various additive addition cases.

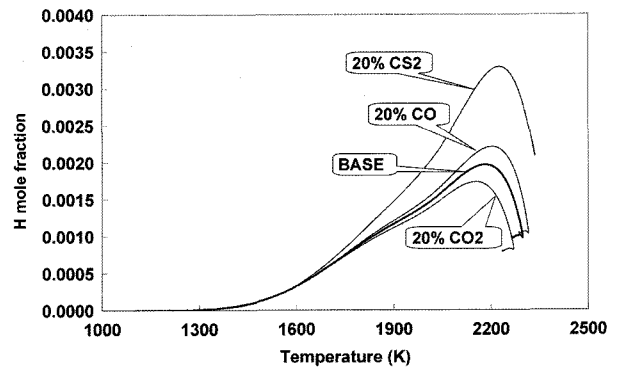


Figure 15. H mole fraction vs. temperature for base, 20% CS₂, 20% CO and 20% CO₂ addition cases.

31%, while the ignition time remained practically unchanged for CO₂ addition. The peak concentrations of PAH species occur more or less at similar temperatures for CS₂, CO and CO₂ cases as shown in Figure 14. This suggest that temperature-time effect would not affect these results to a great extent.

To better understand the mechanism of PAH reduction, the concentration profiles of selected species such as H, OH, CH₂O, H₂O₂ were investigated. The H mole fraction for various cases are plotted against temperature in Figure 15. As can be seen there is an large increase in peak H of about 67% with the addition of CS₂. Adding CO causes an increase in H of about 13%. For the case of CO₂ addition, the peak H concentration decreases by about 12%. This suggests the direct relation of the H radicals to build-up of PAH species. This effect is counter to what may be expected, since an increase in H radicals normally implies an increase in PAH species from previous work (Frenklach and Yuan, 1987; Ni *et al.*, 1994).

A similar correlation is seen with the OH radicals in Figure 16. There is an huge increase of 110% is seen with CS₂ addition. An increase of 15% is seen with CO

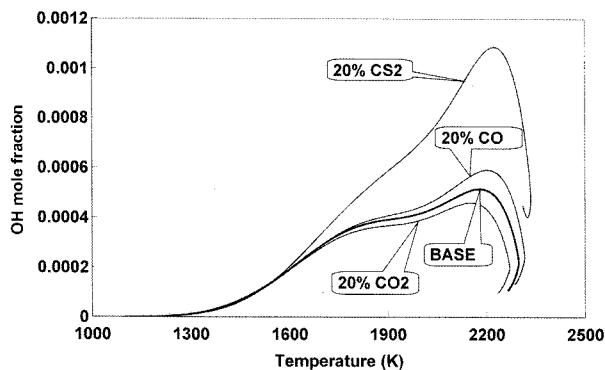


Figure 16. OH mole fraction vs. temperature for base, 20% CS₂, 20% CO and 20% CO₂ addition cases.

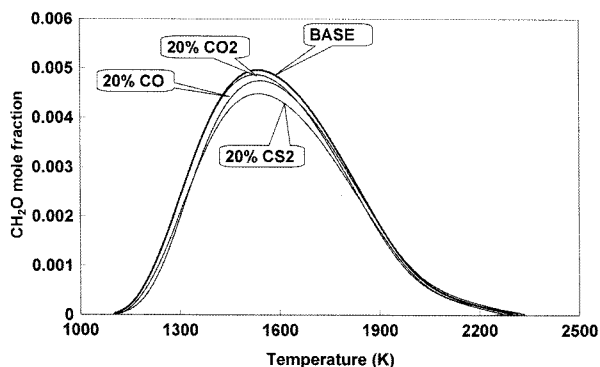


Figure 17. CH₂O mole fraction vs. temperature for base, 20% CS₂, 20% CO and 20% CO₂ addition cases.

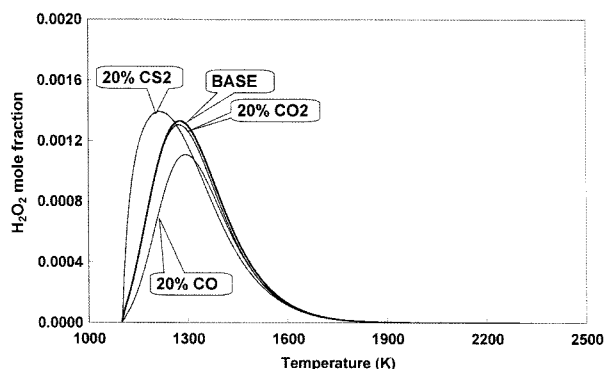


Figure 18. H₂O₂ mole fraction vs. temperature for base, 20% CS₂, 20% CO and 20% CO₂ addition cases.

addition. For CO₂ addition, a decrease of 15% is seen with CO addition. For CO₂ addition, a decrease in OH peak level of about 11% is seen. The concentration of OH radical increases very largely for CS₂ addition. Thus the OH radical seems to have a stronger correlation with the reduction in PAH species compared to H. This may suggest that OH radicals aid in the oxidation of the PAH species. Moreover, OH species may enhance the oxidative

paths for carbon atoms compared to the soot growth paths, which may explain this reduction in PAH. This is consistent with the fact that OH radicals are the chief oxidizing species for soot (Flynn *et al.*, 1999).

The formaldehyde plot in Figure 17 shows that the base, CS₂, CO and CO₂ follows nearly identical trends. Also, Hydrogen peroxide plot in Figure 18 shows that three cases are not distinctly different. Especially, the plots for the base case and CO₂ case are very close to each other for both CH₂O and H₂O₂ concentrations as seen in Figure 17 and 18. Three additives show minor effect on the CH₂O and H₂O₂ concentrations. This would imply that H and OH species may be said to do the more important role to PAH reductions for CS₂, CO additives compared to the DME and ethanol additives.

5. CONCLUSIONS

The effects of chemical additives, such as dimethyl ether (DME), ethanol, carbon disulfide on the soot precursor reduction were examined numerically using a combined Frenklach mechanism. Results obtained are summarized as follows.

- (1) It is observed that the addition of DME, ethanol and CS₂ into ethane fuel can reduce significantly the polycyclic aromatic hydrocarbons which are soot precursor. This means that the formation of soot can be reduced significantly by DME, ethanol and CS₂ addition.
- (2) DME and ethanol are isomers and hence between these two cases, the C, H and O ratios are exactly the same. Nevertheless, DME showed a pronounced difference in PAH reduction compared to ethanol. This strongly suggests that indeed there is an effect of structure on PAH reduction.
- (3) Amongst those tested, CS₂ proved to be most effective. The reason may be explained by the increase in H and OH radical concentration.
- (4) H and OH concentration changes show direct relationship between the reduction in PAH and these species. OH shows a stronger correlation to the PAH species than H.

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