

CHEMICAL ADDITIVES FOR MAXIMIZING FUEL REACTIVITY

Phase I Report

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Prepared by:

Vladimir M. Zamansky, Vitali V. Lissianski, Mark S. Sheldon, and Eric L. Petersen

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18 Mason, Irvine, CA 92618

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**Vladimir M. Zamansky, Vitali V. Lissianski, Mark S. Sheldon
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Report developed under SBIR contract for topic AF99-221. The objective of the project is to demonstrate the feasibility of a modeling based search for chemical additives which can reduce soot formation in fuel systems of interest to the Air Force. Several mechanisms of soot reduction in the presence of additives were considered by kinetic modeling. Modeling identified homogeneous catalysis as the most effective mechanism of soot suppression. Modeling showed that under optimum conditions, soot could be reduced by 95+% when the amount of additive is 5% of fuel. A series of shock tube experiments were performed to validate modeling predictions. Three potential soot-reducing additives were tested: isopropyl nitrate, methanol, and sodium carbonate. The experiments confirmed that additives acting through the mechanism of homogeneous catalysis significantly suppress soot formation.

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1.0 INTRODUCTION

1.1 Soot Emissions from Combustion Sources

Under ideal conditions, the combustion of hydrocarbons leads to carbon dioxide and water. However, nonidealities such as locally insufficient oxygen exist in practical combustion devices, resulting in partial fuel conversion and products of incomplete combustion. The fuel-oxidizer mixing time, the species-formation time, and the species-oxidation time determine the appearance of these unwanted products in the exhaust of the combustion device. Examples of unwanted emissions include carbon monoxide (CO), oxides of nitrogen (NO_x), particulates (soot), and unburned hydrocarbons (UHC). Of these emissions, particulates are emphasized in the present proposal, and of particular concern is the emission of soot from aircraft gas turbine engines.

In addition to the threat of increased detection by adversaries, soot emissions from aircraft turbines are dangerous for human health. Studies (*George and Burlin, 1960; Megonnell, 1971*) show that although the overall contribution to air pollution by aircraft in metropolitan areas is only 1 or 2 percent of the total, it is usually responsible for around 10% of the total in the immediate vicinity of the airport. Although soot is not the most abundant pollutant when compared with CO, NO_x, and UHC, it may be one of the most hazardous since soot particles are of the proper size (50 to 2000 Å) to penetrate deep into the lungs.

Soot also negatively affects overall cycle performance. The increased emissivity and higher radiative heat transfer caused by soot formation in the combustor can cause engine overheating and damage, and excessive quantities of soot particles can erode turbine blades and cause carbonaceous deposits. In military applications requiring high-altitude relight, a fuel-rich primary combustion zone is desirable since it improves the engine's relight capability, but the resulting sooty exhaust is equally undesirable for signature reasons.

Soot emission is also a serious problem in diesel engines. Although diesel engines offer improved fuel efficiency over gasoline engines, they have higher emissions of NO_x and particulate matter. Reducing emissions of these two regulated pollutants is confounded by the fact that engine operating conditions leading to reduced particulate matter result in higher NO_x emissions, and vice versa.

One common method of enhancing fuel performance involves the use of additives, where some additives designed to enhance some property of the fuel can also affect soot emissions. For example, additives are often employed to increase reactivity, improve thermal stability, enhance a fuel's heat sink ability, or improve a fuel's low-temperature properties. For example, JP-8+100 jet fuel contains a number of additives that suppress pyrolytic and oxidative deposits at elevated temperatures and reduce corrosion and the formation of carbon on metal surfaces in the turbine. Some additives, unfortunately, may also increase soot formation, while others may enhance soot suppression. (The former problem will become even more serious with any trend toward a more aromatic fuel.) From the standpoint of the present proposal, an ideal additive would be one that decreases the formation of soot without negatively impacting other fuel properties.

Gas turbine and diesel engine design modifications are the most economical long-term approach to reduce soot emissions, but they may not be possible in all cases. The use of fuel additives is another solution that calls for attention.

1.2 Use of Additives to Reduce Soot Emissions

Many compounds affect the chemistry of soot formation. The effect of additives on soot formation in flames has been studied extensively (for example, see the literature cited in *Haynes and Wagner, 1981*). In diffusion flames, the simple dilution of fuel by inert gases generally decreases the tendency to produce soot. The addition of hydrogen to the fuel also suppresses soot emission, although the effect is only slightly greater than that of inert dilution. When CO_2 or H_2O is added to the fuel, there is a considerable reduction in soot-forming tendency. It was suggested (*McLintock, 1968*) that the influence of CO_2 and H_2O is exerted primarily in the soot-oxidation zone, where these species presumably promote soot burnout. A similar mechanism has been proposed for SO_2 , which is even more effective in opposing soot formation than either CO_2 or H_2O . However, a more recent study (*Schug et al., 1980*) has shown that, in general, reductions in sooting tendency are brought about thermally. Thus, additives such as He, Ar, N_2 , H_2O , CO_2 and SO_2 are all equally effective when considered on the basis of their heat capacities.

Conversely, the effect of oxygen addition to the fuel is more complex, where small additions of O_2 result (counter-intuitively) in increased soot emissions. It has been suggested that the presence of oxygen accelerates the pyrolysis without altering significantly the product distribution.

The most striking effects of additives are those exhibited by various metals (*Haynes and Wagner, 1981*), some of which are used commercially as smoke suppressants in liquid-fuel combustion (Ba is widely used as a diesel smoke suppressant and is added in the amount 0.5% by weight of the fuel). Alkali and alkaline earth metals, manganese, iron and other transition metals such as nickel, cobalt and copper can also reduce smoke.

A number of smoke-suppressant additives have been tested and shown to reduce smoke formation in diesel engines (*Shih, 1998; Maricq et al., 1998*). It was shown (*Shih, 1998*) that EHM (2-ethylhexyl nitrate), DTBP (di-*t*-butyl peroxide), MTBE (methyl tertiary butyl ether), DMC ($\text{C}_3\text{H}_6\text{O}_3$), diglyme, monoglyme, and ethanol reduce soot formation when added in the amount of 5-20% by weight. DMM (dimethoxy methane) was also found (*Maricq et al., 1998*) to reduce particulate mass coming from diesel engines. The effect of these additives is mostly due to dilution and the improved supply of oxygen in the soot-formation zone.

MMT (methylcyclopentadienyl manganese) has proven to be effective in the reduction of soot emissions from diesel and gas turbine engines. However, MMT as well as products of its combustion are toxic. It also contributes to plugging in catalytic converters when used in diesel engines.

Existing soot-suppressing additives are not very effective or are toxic. New additives are needed both for military and civilian applications. These additives have to be effective when added in small amounts and should not negatively affect other fuel properties. They also should be environmentally friendly.

2.0 PHASE I TECHNICAL APPROACH AND OBJECTIVES

2.1 Modeling Assisted Search for Additives

As was mentioned in the previous section, a number of additives for soot suppression have been suggested in the past. The choice of additives was mostly based on the consideration that the supply of additional oxygen to the soot-formation zone reduces soot formation. Thus, many tested additives contain oxygen. Some other additives contain metal atoms that were found in flame tests to reduce soot formation. While an "empirical" search for soot suppressing additives was the only available option up to one decade ago due to the lack of knowledge of the combustion chemistry of complex fuels, it covered only a few of the several possible mechanisms of soot suppression. Progress in the understanding of combustion chemistry and the mechanism of soot formation, coupled with the development of advanced codes for combustion modeling during last decade, make it possible to use kinetic modeling in a search for soot-suppressing additives.

Understanding of the combustion chemistry of complex fuels has significantly improved in recent years. A number of detailed mechanisms (Chevalier, 1992; Callahan *et al.*, 1996; Maurice, 1996; Roberts *et al.*, 1996; Held *et al.*, 1997; Curran *et al.*, 1998) describing hydrocarbon fuels up to cetane ($n\text{-C}_{16}\text{H}_{34}$) have been suggested. Some of these mechanisms (for example, Chevalier, 1992) include up to 7,000 reactions of 1,200 species and closely describe many combustion properties of complex fuels. Significant progress (Tan and Frank, 1996; Zhang and McKinnon, 1995) has also been achieved in the understanding of benzene oxidation, an important component of aviation fuel. A detailed review of mechanisms of complex fuels is presented in Lissianski *et al.*, 1999.

The last two decades have also brought significant progress (Haynes and Wagner, 1981; Colket and Hall, 1994; Wang and Frenklach, 1997) to the understanding of soot formation. It is now a general consensus that the formation of soot during the early stages of the combustion process occurs in radical reactions. The hydrocarbon fuel is degraded during oxidation into small hydrocarbon radicals from which, under fuel-rich conditions, soot precursors are formed. Once formed, aromatic rings grow by a sequential two-step process: H-abstraction which activates the aromatic molecules, and acetylene addition which propagates molecular growth. There are still some uncertainties in understanding how the first aromatic ring in flames of non-aromatic fuels is formed (Miller and Melius, 1992; Wang and Frenklach, 1997). However, current models already are capable of describing the history of soot formation in flames of different fuels, starting from soot precursors to the description of soot yields.

Improved understanding of the combustion chemistry of complex fuels and the chemistry of pollutant formation makes it possible to describe not only the combustion properties of fuels at conditions relevant to gas turbines and diesel engines, but also to describe pollutant formation during this process. For example, the mechanism of Maurice, 1996 has been successfully used to describe kerosene flames and to predict soot formation (Lindstedt and Maurice, 1996) as well as NO_x and CO emissions from the combustion of Jet-A in a well-stirred reactor (Maurice *et al.*, 1999).

These examples demonstrate not only that detailed dynamic modeling is possible for the combustion chemistry of liquid fuels, but also that it provides insight into the underlying chemical process of the combustion of complex fuels including soot formation. This knowledge can assist in the search for new additives that improve the properties of aviation fuels. For example, kinetic modeling can explore different mechanisms of soot suppression and identify the most effective one(s). Individual compounds affecting soot formation through the identified mechanism(s) can be determined based on knowledge of their combustion chemistry. Modeling can also be used to estimate the maximum possible soot suppression effects resulting from the use of known types of soot suppressants. For example, modeling can predict the potential efficiency for supplying a limited amount of oxygen to the soot-formation zone (the mechanism through which most O-containing additives suppress soot formation) and compare it with that of metal-containing compounds.

2.2 Phase I Technical Objectives

The overall objective of the SBIR program is to develop efficient and inexpensive fuel additives for minimizing soot emissions and maximizing combustion efficiency for U.S. Air Force and other applications. The objective of the Phase I work was to demonstrate the feasibility of a modeling based search for soot suppressing additives. The approach in the Phase I work was (1) to identify the most effective mechanisms through which additives can affect soot formation, (2) predict the effect of potential additives via numerical modeling under typical aircraft engine conditions, and (3) confirm the predicted effects via shock tube testing of fuel-air-additive mixtures.

3.0 KINETIC MODELING

The purpose of the kinetic modeling was to identify mechanisms by which additive could reduce soot formation during oxidation of hydrocarbon fuels. The following sections describe efforts to identify the most effective mechanisms of soot reduction and modeling of the effect of several real species on soot formation.

3.1 Mechanisms of Soot Reduction

It was assumed in modeling that additives upon decomposition produce active species that then react with soot precursors and reduce their concentrations. The following mechanisms leading to the formation of active species were considered:

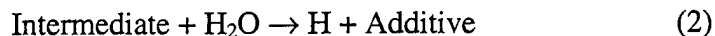
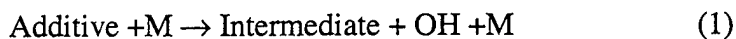
1. Additive N1 $\rightarrow$ H
2. Additive N2 $\rightarrow$ O
3. Additive N3 $\rightarrow$ OH
4. Additive N4 $\rightarrow$ NH₂
5. Additive N5 $\rightarrow$ NH₃
6. Additive N6 $\rightarrow$ NO₂
7. Additive N7 $\rightarrow$ NO₃

8. Additive N8 $\rightarrow$ CH₃
9. Additive N9 $\rightarrow$ CO
10. Additive N10 $\rightarrow$ Homogeneous catalyst (HC)

Additives N1-10 are not real species but rather represent certain groups of compounds with specific chemistry of decomposition. Modeling of the effect of real species on soot formation is more difficult because the mechanism of additive decomposition and oxidation has to be known. For a number of potential additives such modeling is possible with the kinetic mechanism used in this work.

Active species formed as a result of additives N1-9 decomposition are present in the kinetic mechanism and do not require additional reactions (besides the reaction of additive decomposition) to describe their effect on soot formation. The additive N10 is different. It was assumed that additive N10 affects fuel oxidation through the sequence of two reactions in which active species are generated but the additive is not consumed.

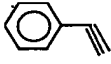
This mechanism is known to be very effective in reduction of ignition delays of hydrocarbon fuels. For example, NO₂-containing additives promote oxidation of hydrocarbon fuels through chain reactions, the total effect of which is generation of active species (OH, H, etc.) while NO₂ is not consumed. Additives of molecular hydrogen promote CO oxidation through a similar mechanism. Metal-containing additives affect oxidation of hydrocarbon fuels through homogeneous catalysis as well. The following reactions were used to describe the effect of additive N10:



When added together, these reactions result in formation of radicals from water $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$. Thus, the net effect of additive N10 is to shift the equilibrium in the reaction of water decomposition to the right. The principal difference in the mechanism of additive N10 from that of other additives is that additive N10 is not consumed in reactions (1) and (2), while concentrations of additives N1-9 decrease during fuel oxidation as a result of their decomposition.

Calculations were conducted with fuel mixture of 90% C₈H₁₈ and 10% C₆H₆. The fuel was premixed with air at equivalence ratio 3.0. The amount of the additive was 5% from the amount of fuel. The modeling was done using EER's ODF kinetic code (*Kau and Tyson, 1987*) at constant temperature 1500 K and pressure 1 atm. The mixture residence time was 100 ms. The kinetic mechanism (*Maurice, 1996*) was updated by the author and included 1,156 reactions of 187 species.

Among many soot precursors, the following species were selected as targets:

- C₃H₃, propargyl radical
- C₆H₆, benzene
- C₇H₈, toluene
- C₈H₆, 
- C₈H₈, 

The selection of targets in the modeling was mainly influenced by the desire to follow the growth of aromatic species starting with benzene and its precursors. The growth of aromatic compounds by addition of acetylene (accepted to be the primary route of soot formation) extends in the mechanism only to C_8H_8 . Modeling showed that the results do not depend significantly on the selection of targets.

Figure 1 shows effects of additives on concentrations of soot precursors. For comparison, the effects of 5% fuel replacement with inert agent (N_2) and O_2 are also shown.

Modeling shows that efficiencies of additives N1-9 increase as the decomposition time of additives decreases. The results presented on Fig. 1 were obtained at 1 μs decomposition time and correspond to the most optimistic scenario.

Modeling demonstrates that partial fuel replacement with inert additive (N_2) results in reduction of concentrations of soot precursors. It also shows that all oxygen-containing additives are only slightly more effective than the inert agent is. Combined effect of two additives (Fig. 2) is predicted to be similar to that of one additive. The strongest effect, however, was observed for the additive N10 (Fig. 1).

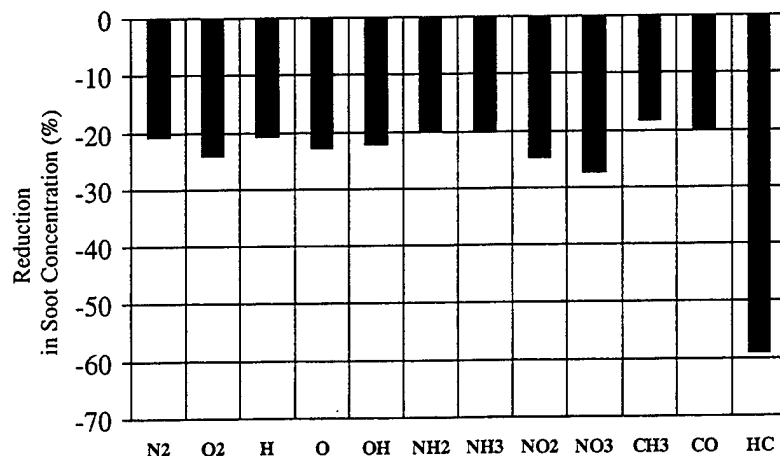


Figure 1. Effect of additives on soot concentration.

Modeling identified homogeneous catalysis as the most effective mechanism to reduce soot formation and predicted that concentrations of soot precursors are reduced by about 50% when homogeneous catalyst is added in the amount 5% of fuel. Modeling results for homogeneous catalysis presented in Fig. 1 were obtained at $k_1 = 4.0 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_2 = 1.0 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which were taken the same as rate coefficients of actual reactions $NaOH + M \rightarrow Na + OH + M$ and $Na + H_2O \rightarrow NaOH + H$. These values of k_1 and k_2 correspond to the case of homogeneous catalysis by Na-containing compounds ($NaOH$, $NaHCO_3$, Na_2CO_3 , etc) and do not necessary represent the optimum kinetic parameters. Sodium hydroxide was selected as a known example of homogeneous catalysts. There is the potential that other compounds, including non-metal substances, can be found in future research. Figure 3 shows the effect of k_2 on concentration of one of the soot precursors, C_8H_8 . Modeling predicts that the additive acting through the

mechanism of homogeneous catalysis can provide up to 95% soot reduction. Reduction in C_8H_8 concentration first increases almost linearly with an increase in k_2 , and then levels off. An increase in k_1 results in improvement of process efficiency, especially at $k_2 > 1.0 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This indicates that the efficiency of homogeneous catalysis can be limited by either of reactions (1) or (2).

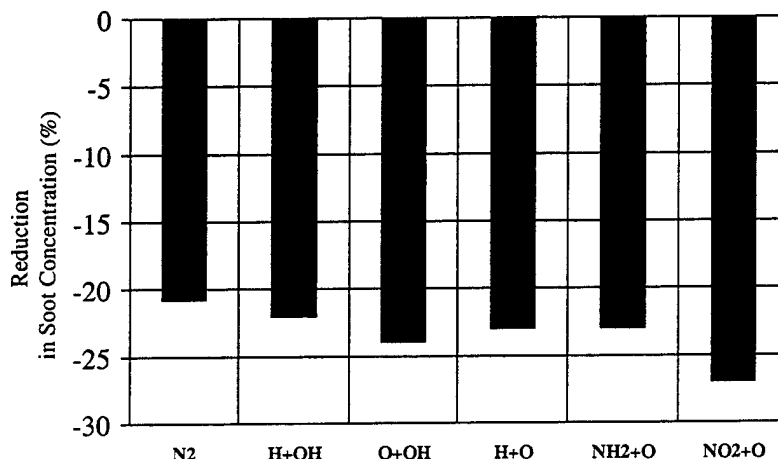
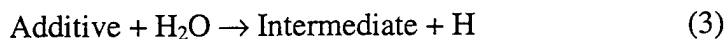


Figure 2. Combined effect of additives on soot concentration.

Thus, modeling predicts very high efficiency of the mechanism of homogeneous catalysis for a certain range of kinetic parameters. The important question, however, is if the identified ranges of k_1 and k_2 correspond to actual values of rate coefficients normally found in kinetic systems for similar reactions. Reaction (1) describes decomposition of *stable* species, while reaction (2) is a reaction between *active* species (for example, a radical or an atom) and H_2O . It is known that decomposition of stable species can occur very quickly at 1500 K. For example, rate coefficient of the first-order reaction of CH_3ONO_2 decomposition at 1500 K is $1.4 \times 10^8 \text{ s}^{-1}$ (Mallard *et al.*, 1998). Reactions of active species with H_2O are also usually fast. For example, rate coefficient of the reaction between CH_3 and H_2O at 1500 K is $3.7 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, while reaction of OH and H_2O has rate coefficient $1.3 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Thus, identified in modeling k_1 and k_2 correspond to the realistic range of rate coefficients for similar reactions.

In a suggested mechanism of homogeneous catalysis the additive first decomposes and produces intermediate species which then react with water and reproduce the additive. The same effect can be achieved if the additive first reacts with water to form H and intermediate species, and then reproduces itself through decomposition of unstable intermediate species:



The net effect of reactions (3) and (4), as of reactions (1) and (2), is formation of radicals from water $H_2O \rightarrow H + OH$.

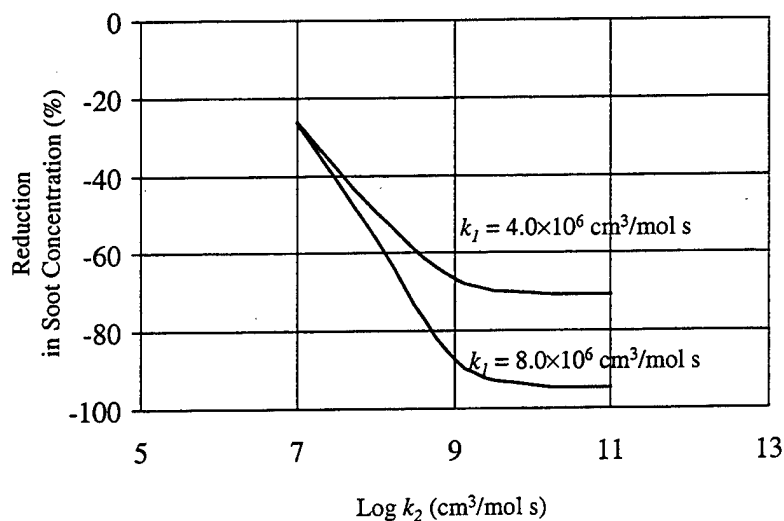


Figure 3. Predicted effect of k_2 on soot concentration.

The replacement of reactions (1) and (2) with reactions (3) and (4) does not alter modeling predictions since the net effect in both cases is the same. The difference between schemes (1), (2) and (3), (4) is that identified range of optimum kinetic parameters corresponds to different types of chemical reactions. The reaction (3) describes reaction between *stable* species and H_2O . Review of NIST Kinetic Database (Mallard *et al.*, 1998) shows that values of rate coefficients for reactions between H_2O and stable species at 1500 K range several orders of magnitude from $7.5 \times 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction with O_2 to $1.8 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction with BaO . Decomposition of intermediate (reaction (4)), which is assumed in modeling to be *unstable* species, can easily occur with rate coefficient larger than $1.0 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Thus, if homogeneous catalysis occurs through reactions (3) and (4), the identified range of optimum kinetic parameters for reactions (3) and (4) is not out of ordinary and is within the limits of rate coefficients found for similar reactions.

3.2 Effects of Some Real Compounds on Soot Formation

Modeling of the effect of real species on soot formation is possible only for additives with known kinetic mechanism of decomposition and oxidation. Figure 4 shows the predicted effects of CH_3ONO_2 (I, methyl nitrate), $I-C_3H_7ONO_2$ (II, iso-propyl nitrate), $C_3H_7(OH)_3$ (III, glycerol), CH_3OH (IV, methanol), CH_3CHO (V, acetaldehyde) and $NaOH$ (VI) in the amount of 5% of fuel on concentrations of soot precursors. For comparison, the effect of inert additive is also shown (0). The strongest effect on soot reduction is predicted for $NaOH$, which affects fuel oxidation through the mechanism of homogeneous catalysis. Among organic additives, methyl nitrate shows some suppression of soot formation. The effects of iso-propyl nitrate and methanol addition are similar to that of the inert additive. Iso-propyl nitrate, however, has an advantage over other additives because the reduction in fuel heat value as a result of fuel replacement with iso-propyl nitrate is probably one of the smallest among the additives considered.

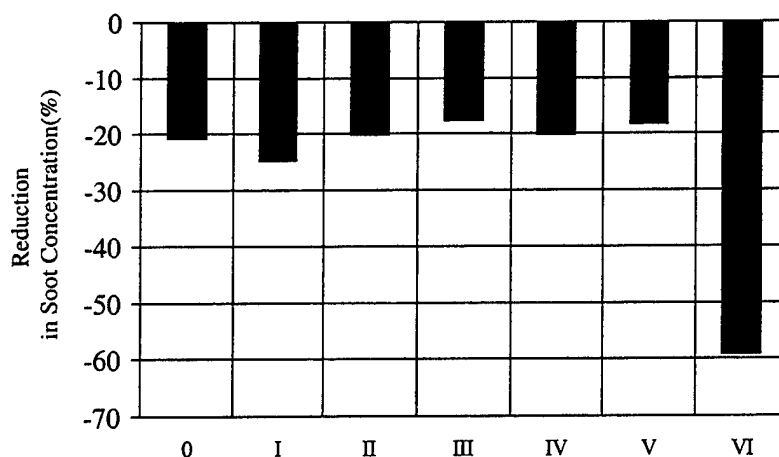


Figure 4. Effect of different compounds on soot concentration.

Figure 5 shows the predicted effect of the CH_3ONO_2 concentration on selected targets. The reduction in concentrations of soot precursors occurs practically linearly with the increase in additive concentration.

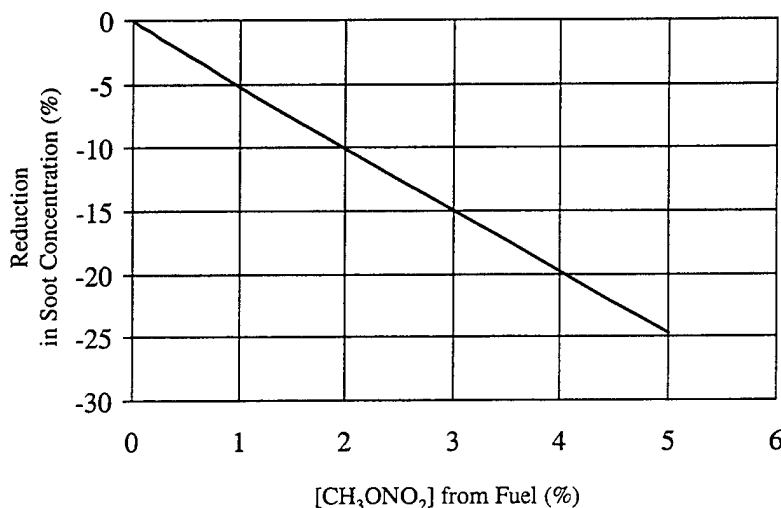


Figure 5. Predicted effect of the CH_3ONO_2 concentration on soot concentration.

Note that the predicted effects of real additives on soot formation derived from modeling are only estimates. Although the kinetic mechanism used in this work is state of the art in modeling the oxidation of large hydrocarbons, it lacks some reactions that can be important when reduction of soot is considered. For example, reactions of aromatic species in the mechanism are limited to reactions with C-H-O species, and no reactions with N-containing species (for example, NO_2 , NO_3 and NH_2) are considered. Review of the NIST Kinetic Database (*Mallard et al., 1998*) shows that kinetic information on such reactions in many cases is not available or limited to room temperature only. Besides, reaction products are not identified. The mechanism of additives reactions is also far from complete. Thus, it can be expected that tests will show higher additive efficiencies than that predicted by modeling.

Modeling shows a significant reducing effect of NaOH on soot formation. However, modeling was done under assumption that all injected Na is present in the gas phase. Under this assumption, the concentration of Na in the gas phase exceeds the equilibrium value. If Na condensation is considered, it can reduce the efficiency of the metal. On the other hand, the heterogeneous reactions on the surface of metal particles can contribute to soot reduction.

4.0 SHOCK TUBE EXPERIMENTS

The ultimate goal of the shock tube experiments is to demonstrate the effectiveness of additives identified in the chemical kinetic modeling. The following sections describe the background literature search, the experimental procedure, the diagnostics setup, and experimental results.

4.1 Background Search

Shock tubes have been employed in the measurement of soot formation in fuel-rich hydrocarbon oxidation and pyrolysis for approximately 25 years. Although not exhaustive, the present search can be summarized in about two dozen publications which cover most of the highlights from specific research groups. In general, previous shock tube measurements of soot formation have been done with gas-phase species highly diluted in argon and (sometimes) nitrogen. Fuels that have been considered include methane (*Lester and Wittig, 1975; Wittig et al., 1990*), acetylene (*Böhm et al., 1998; Cundall et al., 1978; Frenklach et al., 1984a, 1984b; Fussey et al., 1978; Knorre et al., 1996*), ethylene (*Cundall et al., 1978; Fussey et al., 1978*), ethane (*Fussey et al., 1978*), benzene (*Böhm et al., 1998; Frenklach et al., 1984a; Knorre et al., 1996; Simmons and Williams, 1988*), n-heptane (*Kellerer et al., 1996; Kellerer and Wittig, 1997; Yao et al., 1995*), and toluene (*Frenklach et al., 1983, 1984a; Kellerer and Wittig, 1997; Rawlins et al., 1984; Simmons and Williams, 1988; Wang et al., 1981*). Miscellaneous compounds such as phenyl iodide (*Graham and Homer, 1973*), ethylbenzene and cycloheptatriene (*Graham et al., 1975*), allene and 1,3-butadiene (*Frenklach et al., 1984a*), and iron pentacarbonyl (*Tanke et al., 1998*), among others, have also been studied.

Test temperatures ranged from 1400 to 3500 K, with most experiments being near 2000 K or below. Although the majority of tests were performed at pressures near 1 atm, some reflected-shock experiments have been performed in high-pressure shock tubes at pressures up to 100 atm. These elevated-pressure experiments include the work of *Yao et al. (1995)* and *Kellerer et al. (1996)* for n-heptane, *Kellerer and Wittig (1997)* for toluene, and *Knorre et al. (1996)* for acetylene-based mixtures up to 60 atm,

Laser extinction was the common optical diagnostic for monitoring the formation of soot at high temperatures in the majority of past shock tube experiments. This technique, based on Mie scattering theory for small particles, takes advantage of the fact that the initial soot particles have diameters that are less than the wavelength of most common lasers ($\approx 400\text{-}1000\text{ nm}$). Therefore, scattering is negligible, and extinction of the laser light is equivalent to absorption of the laser light according to Beer's Law:

$$I = I_0 \exp(-K_\lambda cL) = I_0 \exp(-N\pi a^2 QL)$$

where I is the transmitted laser intensity, I_0 is the incident intensity, K_λ is the extinction coefficient for wavelength λ , c is the soot concentration, N is the soot number density, a is the average soot radius, Q is a modified extinction coefficient, and L is the pathlength (Simmons and Williams, 1988). If a single wavelength is used, the value for the extinction coefficient must be known *a priori* and is based on the complex index of refraction of a soot particle, or $(n - ik)$. Measurements for the extinction coefficient of soot particles are available, but there has been much controversy over the proper value (Charalampopoulos and Chang, 1988; Lee and Tien, 1981; Penndorf, 1962; among others). Simmons and Williams (1988) have shown that the Lee and Tien (1981) value is adequate for a wide range of shock tube conditions and fuels.

To avoid estimating the extinction coefficient, the Quotient Dispersion method can be used (Yao *et al.*, 1995). In this technique, two laser wavelengths are passed through the shock tube, and the quotient of the two absorption measurements are taken. Beer's Law above for the two wavelengths then becomes:

$$DQ = \frac{Q_2}{Q_1} = \frac{\ln(I_{20}/I_2)}{\ln(I_{10}/I_1)} = f(a)$$

Hence, the measured dispersion quotient, DQ , is related to the particle size. The particle growth and volume fraction as a function of time can therefore be determined (Kellerer *et al.*, 1996).

Another reason for using multiple wavelengths (with at least one in the infrared region) is the fact that interference absorption from non-soot molecules can occur. At early times in the soot formation process, polyaromatic hydrocarbons (PAHs) are abundant in the reaction zone; these large hydrocarbons tend to absorb light in the visible region of the spectrum, hence biasing extinction measurements at early times (Rawlins *et al.*, 1984; Simmons and Williams, 1988) when visible lasers are used. Most early measurements were done with argon-ion (488, 514 nm) and He-Ne (632.8 nm) lasers and may have associated errors, but recent experiments have shown that an infrared wavelength of 1 μm or more is free of PAH absorption and can be used as an independent check on the visible-laser measurement.

In recent years, heterogeneous shock tube measurements related to soot formation and ignition time have been made (Cadman *et al.*, 1999; Sidhu *et al.*, 1999; Wang *et al.*, 1996). These tests utilize a liquid spray of fuel from an endwall-mounted injector. The reflected shock wave heats up the surrounding gas, leading to a realistic ignition and soot-formation process.

4.2 Experimental Procedure

The baseline fuel for the shock tube experiments was selected to be toluene (C_7H_8). As mentioned above, toluene is a popular soot-formation simulant in shock tubes, particularly at pressures near 1 atm. In contrast, n-heptane is an unfavorable soot-producer at lower pressures, as shown by Simmons and Williams (1988) in n-heptane

pyrolysis at temperatures up to 1900 K (although soot is produced within reasonable test times at higher pressures, as in *Kellerer et al. (1996)* and *Yao et al. (1995)*). However, the vapor pressure of toluene at 298 K is 28.2 torr. This pressure limits argon-diluted mixtures to only about 2% C_7H_8 (for comparison, the vapor pressure of n-heptane is 45.5 torr).

A diagnostic technique based on the extinction/absorption of visible (632 nm) and infrared (1152 nm) laser light was set up for soot measurements. Figure 6 shows a schematic of the measurement technique. A third laser line at 3.39 microns was set up to monitor the presence of toluene prior to running an experiment.

Laser light extinction by soot was chosen as the diagnostic in the present set of experiments for a number of reasons: 1) it is an established technique for monitoring soot formation in shock tubes; 2) it is relatively simple to implement since the lasers are easy to use and come in convenient wavelengths; and, 3) the usage and interpretation of the diagnostic is not labor intensive. Ignition delay time measurements were performed in conjunction with the soot measurements. This was accomplished by observing the emission from CH (431 nm) at the endwall of the shock tube. Pressure measurements were taken at a position 1 cm from the endwall.

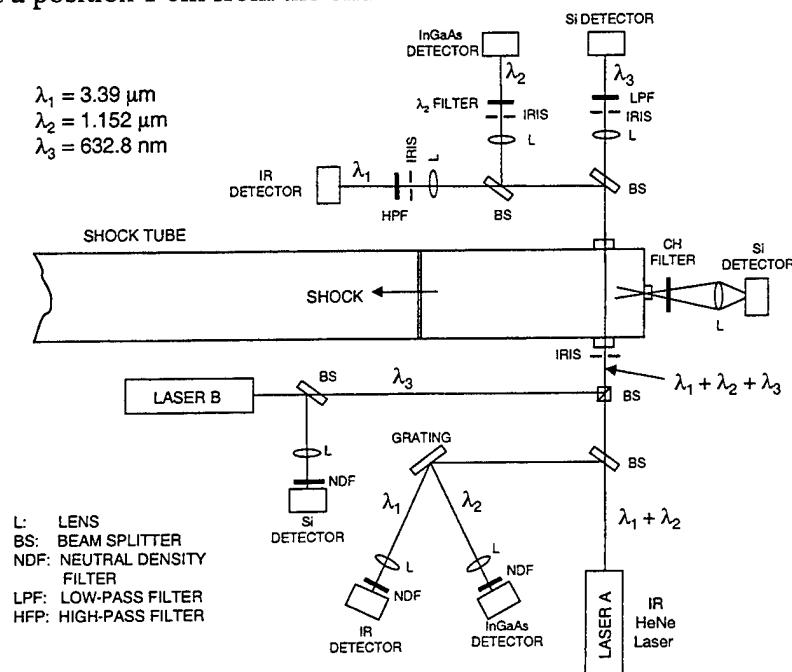


Figure 6. Experimental setup.

4.3 Experimental Results

Toluene and oxygen at an equivalence ratio of $\phi = 5.1$ (0.67% C_7H_8 + 1.18% O_2) highly diluted in argon comprised the baseline mixture. The experiments covered a range of temperatures from approximately 1600 to 2000 K at a total pressure near 1.5 atm. The baseline soot formation measurements compare well with literature data and show a peak yield near 1800 K. Three potential soot-reducing additives were tested: isopropyl nitrate

(i-C₃H₇NO₃), methanol (CH₃OH), and sodium carbonate (Na₂CO₃). Table 2 summarizes the mixtures explored.

Table 2. Mixtures studied (vol %).

Mixture	C ₇ H ₈ (%)	O ₂	Argon	i-C ₃ H ₇ NO ₃	CH ₃ OH	Na ₂ CO ₃	φ
Baseline	0.67	1.18	98.15	-	-	-	5.1
w/ isopropyl nitrate	0.67	1.18	98.115	0.035	-	-	5.1
w/ methanol	0.67	1.18	98.117	-	0.033	-	5.1
w/ sodium carbonate	0.67	1.18	98.15	-	-	*	5.1

* Na₂CO₃ concentration in the gas phase varied. The maximum concentration was 0.035%.

Vapors from the first two additives were mixed with the baseline toluene-oxygen mixtures at a concentration of approximately 5% of the toluene mole fraction. In contrast, the sodium carbonate was in a 99.9% pure crystalline powder form with a particle size range of approximately 10-1000 microns. For most experiments, the powder introduced into the shock tube was sieved to below approximately 100 microns. The technique selected within the Phase I project time constraint utilized the induced gas motion behind the incident shock wave to disperse a collection of powder mounted on a blade protruding 2 cm from the shock tube endwall. Although the powder was dispersed quite well using this technique, most of the particles were recovered after each test (about 80-90%, at least, out of about 100 mg), indicating that only the smallest particles, if any, had time to melt/vaporize and/or oxidize during the shock tube test. First-order calculations indicate that about 1 mg of sodium is needed to get an equivalent additive concentration of 5% of the fuel mole fraction near the shock tube test section. However, if one considers a typical size distribution of particles and assumes only those near 1 micron are actually vaporized in time, we estimate that only a few percent of the additive vaporized during a particular experiment.

Figure 7 presents typical soot-yield results as a function of time. The yield is defined herein as the concentration of soot relative to the total available carbon in the mixture at the test temperature and pressure. Each experiment lasted about 2.5 ms (limited by the arrival of expansion waves at the test section). The time to soot formation, or soot delay time, is defined as shown in Fig. 7 by taking the intercept of the steepest formation rate with the zero line. The results in Fig. 7 compare a baseline experiment with an experiment wherein sodium carbonate was present, both at a temperature near 1890 K. The presence of the Na₂CO₃ clearly has an effect on the soot-yield time history at times greater than about 1 ms.

A summary of the data is presented in Fig. 8 in the form of the soot yield at $t = 2.5$ ms. The soot yield is defined as the soot concentration relative to the total possible carbon concentration at the test temperature and pressure. The 2-ms observation time was selected because it corresponded to the maximum residence time for the conditions of the tests. Since soot yield does not reach plateau values by the end of 2 ms, it can be expected

that extrapolation of experimental data to longer observation times will result in higher levels of soot suppression. Longer test times can be achieved by tailoring the composition of the shock-tube driver gas in future experiments.

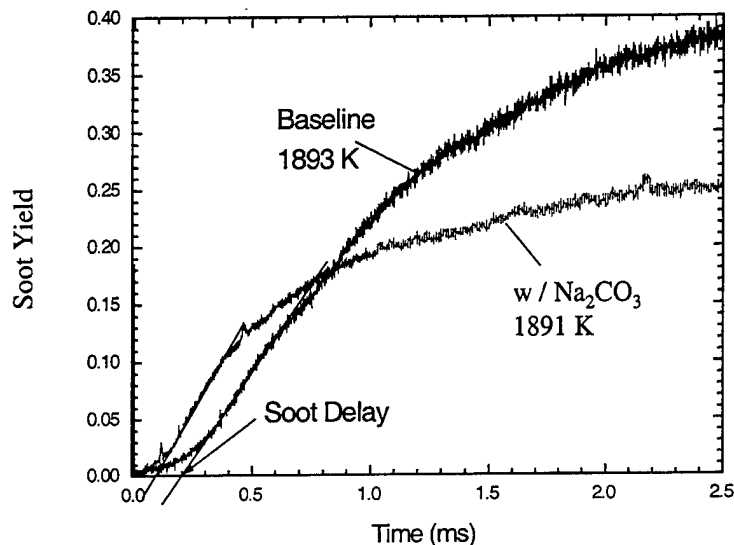


Figure 7. Representative soot (carbon) yield time histories.

The baseline points and all three additives are represented in Fig. 8. The isopropyl nitrate and methanol additives did not decrease the soot yield by a noticeable level. However, the presence of sodium carbonate had an impact on the soot yield, decreasing the peak values between 20 and 55%. Although the present powder tests lack consistency because of difficulties in maintaining the desired gas-phase metal concentration, the results are nonetheless encouraging and clearly demonstrate a high efficiency for the mechanism of homogeneous catalysis in the reduction of soot yield.

A qualitative comparison of the modeling prediction with the experimental data is difficult for two reasons. First, different fuels were used in the modeling than in the tests. As mentioned earlier, the $C_8H_{18} + C_6H_6$ mixture better represents the chemical composition of aviation fuels and was chosen in the modeling effort to identify the most promising soot-suppression mechanisms. Toluene was used in the experiments because soot formation during the oxidation of toluene is well characterized in shock tubes, and experimental data for comparison with the present study were readily available. Second, the concentration of sodium in the gas phase during the shock tube tests was difficult to control due to limitations of the induced-gas-motion technique used to evaporate Na_2CO_3 . Nonetheless, the effects observed in the experiments (20-55% reduction) qualitatively support the modeling predictions (60% reduction).

The shock tube tests also indicate that the Na_2CO_3 additive decreases the time to soot formation, or soot delay time. Thus, it is possible that the same additives that are effective in soot suppression could be effective in the reduction of ignition delay.

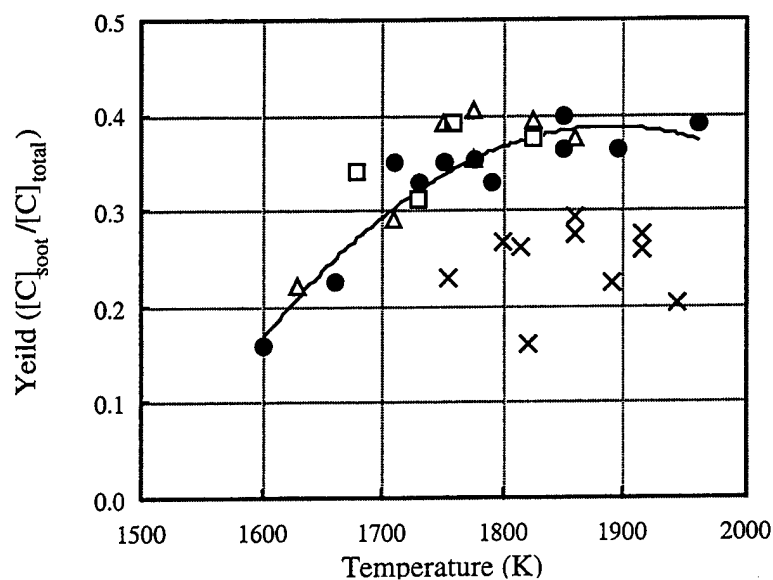


Figure 8. Soot yield at $t = 2.5$ ms. Filled circles represent the soot yield in the unpromoted mixture, squares with $i\text{-C}_3\text{H}_7\text{NO}_3$ added, triangles with CH_3OH added, and crosses with Na_2CO_3 added.

Table 3 shows the effect of Na_2CO_3 additives on the time to soot formation, or soot delay time. Soot delay time is defined as time required for a noticeable amount of soot to be formed and is an indication of the fuel chemical reactivity: the shorter the soot delay time, the more reactive the fuel is. For comparison, Table 3 also shows the reduction in soot yields determined in the same tests.

Table 3. Effect of Na_2CO_3 additives on soot delay time.

Temperature (K)	Soot Reduction (%)	Soot Delay Reduction (%)
1750	29	30
1840	55	40
1870	40	27

Experiments demonstrate that Na_2CO_3 additives increase fuel reactivity by up to 40%. As in tests on soot suppression, data scatter is significant.

5.0 PHASE I CONCLUSIONS

The following conclusions can be drawn from modeling and experimental work:

1. The Phase I program has demonstrated the feasibility of a modeling based search for soot suppressing additives. The suggested approach allows to develop multiple-action additives, which will not only reduce soot formation during the combustion of aviation fuels, but increase their reactivity as well.

2. Several mechanisms of soot reduction in the presence of additives were considered by kinetic modeling, and homogeneous catalysis was identified as the most effective mechanism of soot suppression out of those considered. The modeling predicts that under optimum conditions, soot can be reduced by 95+% when the amount of additive is 5% of the fuel.
3. A shock tube technique for studying the effects of soot-reducing additives was demonstrated. The effects of several additives on soot formation during the oxidation of C_7H_8 were determined. Experimental data confirmed the modeling predictions that additives acting through the mechanism of homogeneous catalysis are effective in reducing soot yield, where additives of sodium carbonate decreased the peak values of the soot yield by 20 – 55%. Sodium carbonate also enhanced fuel reactivity up to 40%. The significant data scatter for sodium carbonate is due to the difficulties in maintaining the desired concentration of the metal in the gas phase during the shock tube tests.

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