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A Final Report

FUEL PROPERTY EFFECTS ON ENGINE COMBUSTION PROCESSES

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ABSTRACT

One of the major obstacles to improving spark ignition engine efficiency has been the limitations on compression ratio imposed by the tendency of hydrocarbon fuels to "knock" (autoignite). Thus, a research program investigating the knock problem in spark ignition engines was initiated in October, 1987 by the Combustion and Fuels Group at Drexel University under DOE sponsorship (DE-FG04-87AL44658). This program was completed in December 1994 and is documented in this final report.

The objectives of this program were to develop an understanding of the low and intermediate temperature chemistry of combustion processes which are relevant to autoignition and knock and to determine fuel property effects on these processes. To achieve these objectives, we conducted experiments in an optically and physically accessible research engine on loan from Sandia National Laboratories. A static reactor and an atmospheric pressure flow reactor (APFR) were also used to perform more fundamental chemical studies to complement the engine studies. In addition to the experimental approach, we also developed chemical kinetic models for prediction of species evolution and autoignition behavior.

Our work confirmed the importance of and provided insight into low and intermediate temperature chemistry prior to autoignition of typical fuel components such as n-butane, iso-butane, n-pentane, 1-pentene, n-heptane, iso-octane and some binary blends of these fuels. We identified the effects of adding octane enhancing ethers (MTBE, ETBE, TAME and DIPE) and alcohols (methanol and ethanol) on the oxidation and autoignition of primary reference fuel (PRF) blends. Our results showed that all of the ethers and alcohols were effective in reducing preignition reactivity and retarding autoignition, and we proposed mechanistic explanations for the behavior. We also developed a correlation between the maximum low-temperature CO production and octane number in the APFR facility. Finally, we examined the effects of NO addition on the reactivity of PRFs in the engine and of 1-butene and 1-pentene in our pressurized flow reactor. Our work has mapped a complex interaction between NO and the fuel components, which changes as a function of temperature and doping level.

We worked with LLNL to enhance detailed chemical kinetic models related to autoignition and knock, and we extended a reduced kinetic ignition model to improve its prediction of autoignition, heat release and the history of key species.

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I. INTRODUCTION

The United States is trying to decrease energy consumption and to reduce dependence on foreign fuel sources in order to increase industrial competitiveness. It is also faced with continuing concerns about air pollution, global warming and ozone depletion. The solution to these complex problems will require understanding the combustion of present fuels, evaluating the impact on emissions and efficiencies of alternative fuels, and modifying combustion devices based on new technologies. One of the major obstacles to improving spark ignition engine efficiency has been the limitations on engine compression ratio imposed by the tendency of hydrocarbon fuels to "knock" (autoignite). Consequently, a research program examining engine autoignition chemistry was initiated in October, 1987 by the Combustion and Fuels Group at Drexel University under DOE sponsorship (DE-FG04-87AL44658). This program was completed recently in December, 1994, and this final report documents the major results from the study.

The objectives of this program were to understand the oxidation chemistry of combustion processes and to determine fuel property effects on these processes. The scope of the research program has been directed toward the study of the chemistry at low and intermediate temperatures with major emphasis placed on its relationship to autoignition, emissions and engine knock. Efforts were concentrated on the following aspects of the overall problem:

(1) improvement of our understanding of autoignition chemistry and the relevant hydrocarbon oxidation mechanisms;
(2) evaluation of the role and significance of the preignition end-gas reactions and heat release in autoignition and knock;
(3) determination of standard fuel composition effects on autoignition and knock;
(4) development of appropriate models of autoignition and knock.

The approach used to achieve these objectives was to conduct experiments primarily in an optically and physically accessible research engine on loan from Sandia National Laboratories. Bench scale facilities, a static reactor and an atmospheric pressure flow reactor, provide the flexibility to perform more fundamental chemical studies to complement the engine studies. These experimental systems were used to examine chemical processes related to autoignition over a wide range of conditions important in practical combustion systems. The data obtained in these studies were shared with other members of DOE's Fuel Combustion/Emission Interaction Working Group to cooperate in developing and verifying models. The engine system was employed to examine realistic engine effects, such as high pressure combustion and recycled exhaust gases. Studies were conducted using the bench scale systems under controlled conditions to investigate features of the chemistry occurring in the engine. Results from these systems helped determine the role of preignition chemistry and heat release in autoignition and emissions. To study the range of components in gasolines, factors such as chain length, degree of branching, fuel structure, identity of substituents, and fuel type were included. Cooperation with the Working Group allowed the selection of fuels to be adjusted as new technical and regulatory issues arose.

During the initial funding period for this work (10/1/87 - 12/31/90), we installed, validated, and upgraded the single-cylinder research engine facility on loan from Sandia National Laboratories. Initial experiments investigated the autoignition of simple fuels of n-butane, isobutane and mixtures of the two fuels in the knock research engine. Then, studies of n-pentane were initiated in the engine and in the static reactor. In the flow reactor, we developed a correlation between the maximum low-temperature CO production and octane number.

A renewal award was funded (1/1/91 - 12/31/94) with emphasis on extending the engine studies to larger, more fuel-like hydrocarbons and hydrocarbon mixtures. During this period, the research program focused in four main areas: oxidation chemistry of neat hydrocarbons (alkanes and alkenes), fuel component interaction in binary hydrocarbon mixtures, chemical effects of blending oxygenated additives into hydrocarbons, and the interactions between NO and hydrocarbons. In the course of this program, efforts were also made to develop models of autoignition, heat release and emissions. We exercised and enhanced detailed chemical kinetic models in cooperation with Lawrence Livermore National Laboratories (LLNL) and developed a reduced chemical kinetic model to predict the major preignition/autoignition oxidation behavior.

The status and scheduling of the tasks and subtasks for this research program are identified in Table 1. The first grant period (10/87-12/90) is grouped as 'past work', while the grant period of 1/91-12/94 is shown as "recent work".

Brief summaries of our efforts and activities before 1992 were presented in semi-annual progress reports, and our more recent efforts in annual progress reports covering 1992 and 1993. Research progress in 1994 is included in this final report, along with a description of our current and ongoing activities. Specific research efforts are reported in the literature.

TABLE 1. PROGRAM TIME SCHEDULE

	Past Work			Recent Work			
	87-88	89	90	91	92	93	94
1. BENCH SCALE REACTORS							
A. Atmospheric Pressure Flow Reactor							
CO-ON correlation		········	········x				
B. Static Reactor							
1. n-Pentane			········	········	········x		
2. 1-Pentene and n-Pentene/1-Pentene blends					········	········	········x
2. SINGLE CYLINDER ENGINE							
A. Buildup of Facility	····x						
B. n-Butane and iso-Butane	····	········x					
C. n-Pentane			········	x			
D. Primary Reference Fuels				········	········x		·····x
E. Oxygenates/PRFs							
1. PRFs/Ethers					········	········x	
2. PRFs/Alcohols						··	·······x
F. NO/HCs							
1. NO/PRFs						······	········x
2. NO/Alkenes in a Pressurized Flow Reactor							······x
3. MODELING							
A. Detailed Modeling (with LLNL)	········	········	········	········	········	········x	
B. Reduced Model							
1. Initial work					······x		
2. Further development							······

II. RESEARCH PROGRAM

An overview of the research activities carried out as part of this research program is given in Section II A. A discussion of the specific research accomplishments for the program is provided in Section II B. Publications, reports, and presentations currently completed or under preparation are listed in Section II C. These publications and presentations report details of separate research tasks and represent the primary technical documentation of the work.

A. Overview of the Research Program

The primary effort from program inception involved investigating the oxidation chemistry of neat hydrocarbons (alkanes and alkenes) and fuel component interaction in binary hydrocarbon mixtures, with recent emphasis on the chemical effects of blending oxygenated additives into hydrocarbons and the interactions between NO and hydrocarbons. Efforts were also made to develop models of autoignition, heat release and emissions. Experiments were conducted primarily in an optically and physically accessible research engine on loan from Sandia National Laboratories. Bench scale facilities, a static reactor and an atmospheric pressure flow reactor, provided the flexibility to perform more fundamental chemical studies which complemented the engine studies.

The research engine is equipped with a fast-acting gas sampling valve which allows for the acquisition of time-resolved end gas samples prior to autoignition. The samples were analyzed on our GC, GC/MS, GC/FTIR and FTIR instruments, from which concentration histories of the stable species present in the end gas can be constructed. These data were used to examine the preignition chemistry and to interpret the role of fuel oxidation chemistry in engine knock. Two modes of operation were used with the engine: fired and motored. With the former, the progress of the preignition reactions can be followed up to the point of hot ignition. With the latter, species data can be obtained at elevated temperatures and pressures in the absence of a propagating flame.

In addition, the bench scale facilities (static reactor and flow reactor) are used to further examine features of the autoignition chemistry which are observed during the engine studies. The static reactor operates at temperatures below about 750 K and at subatmospheric pressures, while the atmospheric pressure flow reactor operates from about 650 to 1000 K at 1 atm and generally at dilute conditions. Thus, these two systems cover different reaction regimes and together enable studies of fuel oxidation chemistry up to temperatures of 1000 K. As with the engine, the chemical processes leading up to autoignition can be followed in time via gas sampling and chemical analyses by GC, GC/MS, GC/FTIR and FTIR techniques.

Initial experiments with the single-cylinder research engine facility investigated the effects of fuel structure on autoignition. n-Butane, iso-butane and mixtures of the two were used as fuels in a skip-fired strategy (every fired cycle was followed by two non-fired cycles). Products sampled from the end gas during fired cycles confirmed the importance of low and intermediate temperature chemistry prior to autoignition and examined the interaction between n- and iso-butane (SAE paper 890157)*. Chemical pathways were discussed based on the species data (SAE paper 892082). In addition, we worked in cooperation with Drs. Pitz and Westbrook of Livermore National Laboratories and Dr. Green of Sandia National Laboratories to model our experimental data (SAE 900028).

To extend our studies to more complex hydrocarbons, we developed a liquid fuel delivery system for the engine. For initial liquid fuel studies, we measured the critical inlet fuel/air conditions of temperature and pressure which induce autoignition for large hydrocarbons (n-pentane, n-hexane, and the primary reference fuels n-heptane and iso-octane, both neat and in blends) in the engine under motored conditions (Paper No. WSSCI 89-72). A marked difference between the behavior of the neat alkanes and primary reference fuel (PRF) blends was explained in terms of the varying negative temperature coefficient behavior of the fuels.

In the APFR, we developed a correlation between the maximum low-temperature CO production and octane number, using an experimental database from the oxidation of n-heptane and binary mixtures with aromatics, alkenes, isooctane, and MTBE. The correlation accounts for the inhibiting effects measured for all of the additives at low temperature and the accelerating effect of the alkenes at intermediate temperatures. This technique offers a promising method of characterizing autoignition behavior and a possible method for identifying complex behavior in fuel blending.

In following-up the liquid fuels studies in the engine, the autoignition mechanism of n-pentane was further analyzed through gas composition measurements in the engine under conditions where significant pre-ignition reactivity occurred (SAE Paper 932756). This analysis provides additional insight into the chemical pathways leading to the autoignition of n-pentane.

Subsequently, we concentrated on primary reference fuels and conducted in-cylinder sampling studies in our engine. The preignition reactivity and autoignition behavior of several PRF blends with octane ratings from 0 to 100 were investigated under motored conditions. Results showed that all PRF blends with octane rating greater than 55 exhibited Negative Temperature Coefficient (NTC) behavior, with in-cylinder concentrations measurements indicating that a significant amount (up to 40-50%) of both n-heptane and isooctane reacted during the cycle. Also, increasing the amount of n-heptane in a PRF blend increased the level of fuel consumption

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* Refers to the publication documenting and reporting this specific activity; complete bibliographical information is given in Section II C.

for both n-heptane and isooctane as well as the concentrations of stable intermediates (SAE Paper 920807).

In our static reactor facility, we first investigated the oxidation chemistry of n-pentane in the low and intermediate temperature regions. A region of cool flame behavior between 573-648 K and onset of NTC behavior at 673 K were observed. The results indicate that the reaction mechanism is different in these temperature zones; further analysis in conjunction with computer modeling is necessary to explain the transition of the reaction mechanism.

We then looked at the preignition oxidation chemistry of alkenes and their role during the oxidation of alkanes. 1-Pentene and a n-pentane/1-pentene blend were used in our initial studies (submitted to Combustion Science and Technology). Experiments with 1-pentene indicated the presence of an NTC region between 615-665 K with a shift in the mechanism between the low and the intermediate temperature regime, as indicated by the changes in the major species distribution. Results of the blend showed that fuel components interact only via small labile radicals. At low temperatures, the alkene preferentially reacted with the radicals reducing the reactivity of the alkane. In the region of NTC and just beyond, the n-pentane acted as a radical trap, thereby retarding the reactivity of the alkene.

Following the hydrocarbon fuels studies, we began to investigate the effects of oxygenates, proposed as additives to gasoline, on hydrocarbon autoignition. The compression ratio was increased from 5.2 to 8.2 using a new head insert or 'puck' which allowed studies on autoignition of 87 PRF or higher octane fuels. The GC technique was modified for better analysis of intermediate species. Initial experiments investigated the chemical effects of blending octane enhancing ethers (MTBE, ETBE, TAME and DIPE) on the reactivity and autoignition of primary reference fuels blends, primarily 87 PRF (SAE paper 940478). Then, a parallel study of the blending effects of alcohols (methanol and ethanol) followed (SAE paper 950682). The results showed that all of the ethers and alcohols were effective in reducing preignition reactivity and in retarding autoignition, and we proposed mechanistic explanations for the behavior.

In the course of the studies of blending oxygenates, we measured additional reactivity of n-heptane, iso-octane and 87 PRF (SAE paper 942062). Detailed, crank angle resolved species evolution profiles during preignition reactions were generated for the three fuels. The species data revealed a number of features during typical two stage ignition processes which have not been previously observed.

An important component of the program was to develop and/or refine models describing the chemistry of autoignition processes. Numerical modeling of the detailed chemistry of at pressures significant to engine processes has been performed in collaboration with Dr. William Pitz and Dr. Charles Westbrook of Lawrence Livermore National Laboratories and Dr. Joseph Bozzelli of

New Jersey Institute of Technology and Dr. Anthony Dean of Exxon Research and Engineering. The overall modeling efforts have reproduced combustion behavior qualitatively.

In addition to modeling detailed chemistry, we also developed a reduced model to predict major oxidation behavior (ignition delay, heat release, and concentrations of key species) during preignition reaction of end gases. We extended a reduced kinetic model (Hu and Keck, 1987)* to include aldehyde oxidation, CO formation, olefin oxidation and carbonyl oxidation reactions. With reasonable rate parameter adjustment, the predicted heat release, fuel consumption and CO profiles are quite close to the experimental results, although some discrepancies still remain (SAE paper 922328). Using our recent PRF engine data, we have been further refining the model.

We also established a cooperative effort with the University of Texas at Austin. The work involves validating an engine model which will be used to investigate the importance of variability in mixing and turbulence to incipient knock (SAE paper 912345).

In the later stages of the program, we began to examine a broader range of fuel/combustion/emission interaction issues which impact combustion applications. As a transition study, we examined the effects of NO on hydrocarbon (alkanes and alkenes) oxidation in our research engine (SAE paper 932757) and in our pressurized flow reactor (submitted to <u>Combustion and Flame</u>). Our work has mapped a complex interaction between NO and the fuel components, which changes as a function of temperature and doping level.

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* Hu, H. and Keck, J. (1987), "Autoignition of Adiabatically Compressed Combustible Gas Mixtures", SAE Paper No. 872110, <u>SAE Trans.</u>, <u>96</u>.

B. Specific Research Accomplishments

A number of specific research accomplishments for the program are identifiable. The major accomplishments are listed below along with a brief discussion of their significance.

a. Improved our capabilities for gas analysis including detailed species identification and quantification.

We converted several gas chromatographs to multidimensional, capillary operation, developed the GC/FTIR technique, and installed on-line NDIR instruments for CO and CO_2 and an on-line FTIR spectrometer system.

b. Investigated the importance of low and intermediate temperature chemistry in the autoignition of n-butane and iso-butane.

Experiments sampling products from the end gas during the oxidation of n-butane/isobutane mixtures in a knock research engine confirmed the presence and importance of low and intermediate temperature chemistry prior to autoignition. Products indicative of low temperature processes, such as formaldehyde, methanol, acetaldehyde and propene oxide were measured.

Following these experiments, we continued study of n-butane and iso-butane with emphasis on the effects of fuel mixing on heat release using a skip-fire strategy. Pressure profiles showed that there is a decrease in the heat release occurring during the second skip cycle when the percentage of iso-butane in the mixture increases. Analysis of the chemical species indicate that there are two competing chemical pathways occurring during the heat release. We worked in cooperation with Drs. Pitz and Westbrook of Livermore National Laboratories and Dr. Green of Sandia National Laboratories to model these data. The chemical kinetics predicted the formation of all the intermediate species measured in the experiments. The quantitative agreement between the measured and predicted values was mixed. Areas for improving the model were discussed.

c. Developed a correlation between the maximum low-temperature CO production and octane number.

Using an experimental database from the oxidation of n-heptane and binary mixtures with aromatics, alkenes, isooctane, and MTBE, a correlation between low-temperature CO production and octane number was developed. The correlation accounts for the inhibiting effects measured for all of the additives at low temperature and the accelerating effect of the alkenes at intermediate temperatures. This technique offers a promising method of characterizing autoignition behavior and a possible method for identifying complex behavior in fuel blending.

d. Evaluated the oxidation mechanism of olefins using data from experimental studies of ethene and propene.

Olefins are found to be major intermediates in the preignition chemistry of paraffinic hydrocarbons as well as a significant component of unleaded gasoline. Mechanistic analysis of our experimental data indicate comparative dependence of the effects olefins have on the overall rate of oxidation. The observed effects can be explained by the interaction of the olefin and the dominant chain propagating radical species. At low temperatures, the olefin scavenges the RO_2 and interferes with OH production resulting in inhibition of the reaction. At intermediate temperatures, the olefin scavenges HO_2 which promotes the formation of OH, resulting in enhancement of the oxidation rate.

e. Conducted liquid fuels studies in determining critical inlet fuel/air conditions of temperature and pressure which induce knock.

We compared the critical inlet fuel/air conditions of temperature and pressure which induce knock for large hydrocarbons (n-pentane, n-hexane, and primary reference fuels neat and in blends). The behavior of the neat alkanes and primary reference blends was considerably different with respect to both critical manifold temperature and the formation of carbon monoxide. This was explained in terms of the enhanced negative temperature coefficient behavior of the branched alkane iso-octane.

f. Investigated the detailed reaction chemistry controlling the autoignition of n-pentane in the engine system.

The autoignition behavior of n-pentane was further analyzed through gas composition measurements in a motored engine under conditions of significant pre-ignition reactivity. This analysis indicated that acetone is not produced in the gas phase during n-pentane oxidation and that the initial n-pentane decomposition proceeds through 2-pentyldihydroperoxide. Overall the study provides additional insight into the chemical pathways leading to the autoignition of n-pentane.

g. Validated a fractal engine model code for autoignition.

We established a cooperative effort with the University of Texas at Austin. They use a fractal engine model code (UT-FEM) to predict engine conditions for knocking and non-knocking cycles. The work involves validating the code with experimental data and using the code for parametric studies to investigate the importance of variability in physical processes such as mixing and turbulence on the onset of knock.

h. Extended the liquid fuels studies in our research engine to primary reference fuels.

This study consists of two sets of experiments using the motored engine technique. The first concentrated on measuring preignition reactivity and autoignition behavior of primary reference fuel (n-heptane/isooctane) blends (PRF) with octane ratings of 0, 25, 55, 63, 75, 87, and 100. Reactivity was quantified by measuring exhaust manifold carbon monoxide concentration [CO], cylinder pressure histories, and in-cylinder gas composition. All PRF blends greater than 55 PRF exhibited significant heat release and Negative Temperature Coefficient (NTC) behavior. Heat release calculations indicated that the energy release for the 63 PRF blend was 6.9% of the total energy available when 48% of the fuel had reacted. n-Heptane initiates reactivity in the Primary Reference Fuel blends in which it is initially converted into intermediate species which react with isooctane. This investigation successfully quantified heat release trends, intermediate and product species ($<C_4$) magnitudes, and individual fuel component consumption levels.

The second set of experiments were conducted at an upgraded compression ratio of 8.2 which allows studies on autoignition behaviors of 87 PRF and higher octane fuels. The GC technique was modified for better analysis of intermediate species. Detailed, crank angle resolved species evolution profiles during preignition reactions were generated for n-heptane, iso-octane and an 87 octane blend, 87 PRF. An oxidation mechanism has been assembled to describe the chemical processes responsible for the measured species and ignition behavior. Some reactions have been examined and discussed in detail based on the experimental data. The results of 87 PRF oxidation show that the oxidation paths for each fuel component are essentially the same as in the case of neat fuel, with the interaction between the two components primarily via the reactive radical pool.

i. Improved the kinetic mechanism for numerical modeling of the detailed chemistry of NTC behavior.

The numerical modeling of the detailed chemistry of NTC behavior has been carried out both in house and in collaboration with Dr. William Pitz and Dr. Charles Westbrook of Lawrence Livermore National Laboratories. We have modeled the oxidation chemistry of small hydrocarbons using data from our engine and other facilities. These efforts included modeling the autoignition of n-butane, iso-butane and their blends in our single cylinder engine and oxidation of ethene and propene in our static reactor. These studies were among the first to incorporate low and intermediate temperature chemistry in detailed kinetic models of combustion.

Our recent efforts have focused on the propane oxidation data at 10 and 15 atm from the Drexel PFR in order to include pressures significant to engine processes. In this particular activity, the collaboration was expanded to include QRRK calculations of unimolecular rate constants of the $R^\bullet + O_2$ reactions of C_2 and C_3 hydrocarbons by Dr. Joseph Bozzelli of New Jersey Institute of Technology and Dr. Anthony Dean of Exxon Research and Engineering. Overall this effort has been able to roughly reproduce the qualitative behavior of fuel consumption and some major reaction products.

j. Developed a reduced chemical kinetic model to predict major preignition reactivity.

We investigated the ability of a reduced chemical kinetic model of 18 reactions and 13 active species to predict the heat release for a blend of primary reference fuels with octane rating 63 in a motored research engine. The induction time of apparent heat release predicted by the chemical kinetic model could be matched to the experimental data. However, the overall experimental heat release profile could not be matched because the mechanism could not provide the specific heat release observed in our experiment. The original kinetic model was extended to include aldehyde oxidation, CO formation, olefin oxidation and carbonyl oxidation reactions, ending up with 5 new active species and

11 additional reactions. With some rate parameter adjustment, the predicted heat release, fuel consumption and CO profiles are quite close to the experimental results, although some discrepancies still remain. This indicates that the reduced kinetic model has good potential to be a useful tool in this area.

Recently, we continued the development of the reduced chemical kinetic model. The model was further refined and tested against our recent results with n-heptane and iso-octane. The experimental results were obtained at 600 rpm engine speed, 8.17 compression ratio, 108.2 kPa inlet pressure, and 376 K inlet temperature. With some rate parameter adjustment, the ignition delay could be matched. The preignition heat release, fuel consumption and CO formation could be reproduced with an error less than 20 %. In addition, the distribution of other species, aldehydes, cyclic ethers, other oxygenates, conjugate alkenes, and lower molecular weight alkenes is in agreement with experimental results. Current efforts are testing the performance of the model at other engine operating conditions. Experiments showed that the preignition reactivity can first increase and then decrease with temperature, exhibiting the so-called NTC behavior, and showed increased reactivity as pressure increases. These issues are not sufficiently addressed by existing models like the Shell model and the Hu and Keck model. Our analysis has shown that these models overpredict the NTC behavior and are insufficiently sensitive to pressures. We are testing and refining the current model to correct these deficiencies.

k. Investigated the effect of nitric oxide (NO) on the oxidation of hydrocarbon in the research engine

The effects of adding small amounts (25 - 400 ppm) of NO on the reactivity and autoignition of n-heptane, 87 PRF and 92 PRF were investigated under motored engine conditions. The results show that, at low inlet manifold temperatures, low concentrations of nitric oxide promoted reactivity and high concentrations caused a significant decrease in reactivity. With an increase in manifold temperature, the promoting effect extended to higher NO concentrations. We observed that 400 ppm NO caused autoignition of 87 PRF at a manifold temperature of 477 K whereas baseline fuel (0 ppm) did not autoignite even at 500 K. In-cylinder sampling was conducted for 92 PRF with and without addition of NO. Exhaust NO and NO_2 concentrations were also recorded. Preliminary analysis of the results indicate that NO has a significant effect on the oxidation chemistry. The in-cylinder sampling data and the exhaust NOx data are presently being examined to identify key reaction pathways involved in this interaction.

Given the fact that residual fractions and recycled exhaust gases in spark ignited engines typically result in about 200-600 ppm of NO in the unburned charge, our results highlighted the need to include NO/hydrocarbon interaction chemistry in detailed models being developed to predict autoignition in engines and in the analysis of engine control techniques such as exhaust gas recirculation.

l. Fundamental studies of NO/alkene interaction chemistry in a pressurized flow reactor

The effect of adding 0-500 ppm NO on the oxidation of 1-pentene was examined in a pressurized flow reactor facility. The experiments were conducted at 6 atmospheres over the temperature range of 600-800 K. 1-Pentene showed alkane type behavior exhibiting low temperature reactivity and strong NTC behavior. Addition of a low concentration of NO (200 ppm) enhanced reactivity at all temperatures, while addition of higher concentration of NO (400 ppm) inhibits reactivity at low temperatures but enhances reactivity in the NTC region. The effect of NO is attributed to a result of the competition between its promoting effect through reaction with $HO_2\bullet$ radicals and its retarding effect through reaction with $OH\bullet$ radicals.

This study also provides additional information on alkene oxidation chemistry. The results revealed that for alkenes of this size, hydrogen abstraction reactions leading to allyl radicals are more important than radical addition to the double bond. We believe that, as carbon number of the terminal olefin increases, alkane type reaction behavior occurs at the other end of the molecule and this is the reactivity observed in our experiments.

m. Investigated reaction chemistry significant to autoignition and engine knock in a study of n-pentane oxidation in the Drexel static reactor facility.

Experiments have been conducted in the static reactor to study n-pentane oxidation at equivalence ratios of 0.36 and 0.8. These experiments were conducted over the temperature range 548 to 742 K and at pressures from 200 to 400 torr. Profiles of temperature, pressure and concentration of product species with respect to time were obtained. The experimental results showed a region of cool flame behavior between 573 -648 K, and onset of negative temperature coefficient behavior at 673 K. Although the results indicate that the reaction mechanism is different in these temperature zones, further analysis of the results is necessary to explain the precise cause of the transition.

n. The oxidation of 1-pentene and a n-pentane /1-pentene blend in the low and intermediate temperature regions

Experiments were carried out in a static reactor at initial temperatures between 548 and 773 K. Gas chromatographic analysis was used for the identification and quantification of the stable species. Experiments with 1-pentene at an equivalence ratio of 0.8 and 1.3 indicated the presence of a Negative Temperature Coefficient (NTC) region between 615 and 665K. Changes in the major species distribution indicated a shift in the mechanism between the low and the intermediate temperature regime. Experiments at higher equivalence ratio showed weakened NTC behavior. Based on data obtained, a modified mechanism of 1-pentene was proposed. A blend of 1-pentene and n-pentane (20% 1-pentene in the mixture by moles) with an overall equivalence ratio of 0.8 was compared to neat n-pentane and 1-pentene experiments at the same conditions to determine the effect of the alkene on the alkane. As expected, no intermolecular interaction between the fuels was observed, with the only interaction being through small labile radicals. At low temperatures, the alkene preferentially reacted with the radicals and increased its reactivity significantly while reducing that of the alkane. At higher temperatures, specifically in the NTC region and in the beginning of the intermediate temperature regime, the alkane reacted preferentially with the radicals reducing the alkene reactivity.

o. The effects of blending octane enhancing ethers on reactivity and autoignition of primary reference fuels blends in a motored engine

The octane enhancing ethers, MTBE, ETBE, TAME, and DIPE, were blended into 63 PRF and 87 PRF at a constant O atom fraction of 1.94% in the fuel mixtures and tested under motored engine conditions. The results showed that all ethers were effective in eliminating autoignition. The inhibition effects preignition reactivity were also observed, as indicated by i) requiring higher inlet temperature for initial reactivity, and ii) producing lower maximum CO concentration, which was found to be the result of both dilution effects and the chemical effect from the ether addition. The magnitude of effects varied with the ether used. ETBE and MTBE were found to be the most effective ethers in inhibiting autoignition, followed by TAME, and finally DIPE. In-cylinder gas analyses were conducted using 87 PRF and its mixture with MTBE and DIPE, providing concentration profiles as a function of crank angle degree. The results showed that i) the oxygenates interact with 87 PRF principally via the small labile radical pool; ii) the ethers were effective in inhibiting autoignition because they consume the active radical pool generated by 87 PRF, substituting a relative stable pool of radical and intermediate species which reduces the overall reactivity; and iii) the effects on reactivity and autoignition were determined both by the ability of the ether to consume OH· radicals and to regenerate active radicals.

p. The effects of blending alcohols on reactivity and autoignition of primary reference fuels blends in a motored engine

As a parallel study to the blending effects of the octane enhancing ethers, the effects of blending methanol and ethanol on the oxidation and autoignition of 87 PRF were studied under motored engine conditions. Each alcohol was blended on a 1.94% oxygen gravimetric basis with 87 PRF. Oxidation of neat methanol and ethanol were also examined. Results showed that the reactivity of 87 PRF/alcohol mixtures were significantly reduced, as indicated by the higher inlet temperature required to initiate reactivity, the lower CO production, and the higher inlet temperature required to generate autoignition. Ethanol showed a larger effect than methanol. Fuel concentration measurements showed that ethanol reacts with active radicals at a faster rate than methanol, with the radical attack on ethanol essentially occurring at the C-H bond. The three observations describing the effect of ethers also describe the effect of alcohols in this study.

In addition to the DOE supported research activities described above, there are other relevant research programs in our laboratory sponsored by ARO and NSF which are providing useful information for addressing the issue of fuel property effects on engine combustion processes. These programs are designed to develop the kinetic and mechanistic information on fuel oxidation in the low and intermediate temperature regimes (650-1000 K) and at elevated pressure (up to 20 atm). The fuels being studied include C2-C5 alkanes and alkenes, neat and in binary mixtures. The basic approach is to generate and analyze detailed, time resolved species evolution data while reacting the fuels in our pressurized flow reactor (PFR) and static reactor facilities. In addition to the analytical capabilities mentioned earlier in this report, we also have developed an in-situ laser system using degenerate four wave mixing (DFWM) for species measurements. Our work has identified the effects of fuel structure and pressure on oxidation behavior in the low temperature and in the NTC regions, and has provided detailed species measurements for use in the development and validation of autoignition models incorporating low temperature and NTC chemistry.

C. Reports, Publications and Presentations

1.* Cernansky, N.P., Green, R.M., Pitz, W.J., and Westbrook, C.K. (1986), "Chemistry of Fuel Oxidation Preceding End Gas Autoignition", Combust. Sci. Technol., 50, 1, 3-25.

2. Henig, Y., Addagarla, S., Miller, D.L., Wilk, R.D., and Cernansky, N.P. (1988), "Investigation of Fuel Structure and Blending Effects on Autoignition Using a Knock Research Engine", Paper No. WSS/CI 88-100, presented at the Fall Meeting of the Western States Section/The Combustion Institute, Dana Point, CA.

3. Henig, Y., Addagarla, S., Miller, D.L., Wilk, R.D., and Cernansky, N.P. (1989), "Autoignition of n-Butane/Isobutane Blends in a Knock Research Engine", SAE Paper No. 890157; SAE Transactions, 98.

4.* Green, R.M., Cernansky, N.P., Westbrook, C.K., and Pitz, W.J., (1987), "The Role of Low-Temperature Chemistry in the Autoignition of n-Butane", SAE Paper No. 872108, SAE Trans., Section 7, 96.

5. Wilk, R.D., Pitz, W.J., Westbrook, C.K., and Cernansky, N.P. (1989), "Chemical Kinetic Modeling of Ethene Oxidation at Low and Intermediate Temperatures", Paper No. WSSCI 89-31, presented at the Spring Meeting of the Western States Section/The Combustion Institute, Pullman, WA.

6. Wilk, R.D., Koert, D.N., and Cernansky, N.P., (1988), "Fuel Structure and Blending Effects on Autoignition", Paper No. WSSCI 88-52, presented at the Spring 1988 Western States Section/Combustion Institute Meeting, Salt Lake City, UT.

7. Wilk, R.D., Koert, D.N., and Cernansky, N.P. (1989), "Low-Temperature Carbon Monoxide Formation as a Means of Assessing the Autoignition Tendency of Hydrocarbons and Hydrocarbon Blends", Energy & Fuels 3: 292.

8. Henig, Y. (1989), "Examination of The Autoignition Behavior of n-Butane and Isobutane Mixtures Using a Knock Research Engine", M. S. Thesis, Drexel University, Philadelphia, PA.

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* Reports work carried out while NPC was a visiting scientist at Sandia

9. Addagarla, S., Henig, Y., Miller, D.L., Wilk, R.D., and Cernansky, N.P. (1989), "Effect of Fuel-Air Mixture Stressing on Preignition Heat Release in a Knock Research Engine", SAE Paper No. 892082; SAE Transactions, 98.

10. Wilk, R.D., Addagarla, S., Miller, D.L., Cernansky, N.P., Pitz, W.J., Westbrook, C.K., and Green, R.M. (1989), "An Experimental and Kinetic Modeling Study of the Combustion of n-Butane and Isobutane in an Internal Combustion Engine", Paper No. WSSCI 89-70, presented at the Fall Meeting of the Western States Section/The Combustion Institute, Livermore, CA.

11. Addagarla, S., Miller, D.L., Cernansky, N.P., and Green, R.M. (1989), "Investigation of the Effects of Manifold Conditions on Autoignition in a Knock Research Engine", Paper No. WSSCI 89-72, presented at the Fall Meeting of the Western States Section/The Combustion Institute, Livermore, CA.

12. Wilk, R.D. and Cernansky, N.P. (1989), "The Role of Olefins in the Autoignition Chemistry of Paraffinic Hydrocarbons", Paper No. ESSCI 89-14, presented in Session A-3 of the 1989 Technical Meeting of the Eastern States Section of the Combustion Institute, Albany, NY.

13. Wilk, R.D., Green, R.M., Pitz, W.J., Westbrook, C.K., Addagarla, S., Miller, D.L., and Cernansky, N.P. (1990), "An Experimental and Kinetic Modeling Study of the Combustion of n-Butane and Isobutane in an Internal Combustion Engine", SAE Paper No. 900028.

14. Gupta, A.V., Koert, D.N., and Miller, D.L. (1990), "Investigation of the Relationship Between Octane Number and Low Temperature Reactivity for Primary Reference Fuel Blends", Paper No. CSSCI 90-34, presented at the Central States Section of the Combustion Institute Spring Meeting, Cincinnati, OH.

15. Wilk, R.D., Pitz, W.J., Westbrook, C.K., Addagarla, S., Miller, D.L., Cernansky, N.P., and Green, R.M. (1990), "Combustion of n-Butane and Isobutane in an Internal Combustion Engine: A Comparison of Experimental and Modeling Results", Twenty-third Symposium (International) on Combustion, p. 203, The Combustion Institute, Pittsburgh.

16. Wilk, R.D., Pitz, W.J., Westbrook, C.K., and Cernansky, N.P. (1990), "Chemical Kinetic Modeling of Ethene Oxidation at Low and Intermediate Temperatures", Twenty-third Symposium (International) on Combustion, p. 1047, The Combustion Institute, Pittsburgh.

17. Addagarla, S. (1991), "Preignition Chemical Reactions Leading to Autoignition and Knock in Spark-Ignition Engines", Ph.D. Thesis, Drexel University, Philadelphia, PA,.

18. Matthews, R.D., Sarwar, M.G., Hall, M.J., Filipe, D.J., Li, H., Miller, D.L., and Cernansky, N.P. (1991), "Predictions of Cyclic Variability in an SI Engine and Comparisons with Experimental Data", SAE Paper No. 912345, SAE Trans., Section 3.

19. Filipe, D.J., Li, H., Miller, D.L., and Cernansky, N.P. (1992), "The Reactivity Behavior of n-Heptane and Isooctane Blends in a Motored Knock Research Engine", SAE Paper No. 920807.

20. Filipe, D.J. (1992), "Reactivity Studies of Primary Reference Fuel Blends in a Motored Engine", M.S. Thesis, Drexel University, Philadelphia, PA.

21. Li, H., Miller, D.L., and Cernansky, N.P., (1992), "A Study on the Application of a Reduced Chemical Reaction Model to Motored Engines for Heat Release Prediction", SAE Paper No. 922328, SAE Trans., Section 5.

22. Cernansky, N.P., Miller, D.L., and Addagarla, S. (1993), "The Autoignition of n-Pentane in a Non-Fired Single Cylinder Engine", SAE Paper No. 932756.

23. Prabhu, S.K., Li, H., Miller, D.L., and Cernansky, N.P. (1993), "The Effect of Nitric Oxide on Autoignition of a Primary Reference Fuel Blend in a Motored Engine", SAE Paper No. 932757.

24. Li, H., Prabhu, S.K., Miller, D.L., and Cernansky, N.P. (1994), "The Effect of Octane Enhancing Ethers on the Reactivity of a Primary Reference Fuel Blend in a Motored Engine", SAE Paper No. 940478.

25. Li, H., Prabhu, S.K., Miller, D.L., and Cernansky, N.P. (1994), "Autoignition Chemistry Studies on Primary Reference Fuels in a Motored Engine", SAE Paper No. 942062.

26.[+] Prabhu, S.K. (1994), "The Oxidation of n-Pentane in the Low Temperature and the Negative Temperature Coefficient Regions", M.S. Thesis, Drexel University, Philadelphia, PA.

27.[+] Kumar, A. (1994), "The Oxidation of 1-Pentene and a 1-Pentene - n-Pentane Blend in the Low and Intermediate Temperature Regions", M.S. Thesis, Drexel University, Philadelphia, PA.

28. Kumar, A., Bhat, R.K., Cernansky, N.P, and Miller, D.L. (1995), "An Experimental Investigation of the Oxidation of 1-Pentene and a n-Pentane - 1-Pentene Blend In the Low and Intermediate Temperature Regions", Combustion Science and Technology (accepted).

29. Li, H., Prabhu, S.K., Miller, D.L., and Cernansky, N.P. (1995), "The Effects of Methanol and Ethanol on the Oxidation of a Primary Reference Fuel Blend in a Motored Engine", SAE Paper No. 950682.

30. Prabhu, S.K., Bhat, R.K., Miller, D.L., and Cernansky, N.P. (1995), "1-Pentene Oxidation and its Interaction with Nitric Oxide in the Low and Negative Temperature Coefficient Regions", Combust. and Flame (submitted).

31. Prabhu, S.K., Wood, C.H., Miller, D.L., and Cernansky, N.P. (1995), "Effect of Nitric Oxide on 1-Pentene Oxidation at Low Temperature and Negative Temperature Coefficient Regimes (600-800 K)", Paper No. 95S-5, to be presented at the combined meeting of the Central States/Western States/Mexican National Sections of the Combustion Institute and American Flame Research Committee, San Antonio, TX.

32. Koert, D.N., Miller, D.L., and Cernansky, N.P., (1994), "Experimental Studies of Propane Oxidation through the Negative Temperature Coefficient Region at 10 and 15 Atmospheres", Comb. Flame, 96:34-49.

33. Li, H. (1995), "Autoignition Chemistry Studies of Primary Reference Fuels and Their Mixtures with Oxygenates in a Research Engine", Ph.D. Thesis (in preparation), Drexel University, Philadelphia, PA.

[+] Primary funding for this work was from ARO and NSF

III. RESEARCH STAFF AND ACTIVITIES

The project was coordinated under the overall direction and supervision of Professor Nicholas P. Cernansky and Professor David L. Miller as co-principal investigators. However the responsibility for conducting, directing, and reporting the various phases of the research program was shared by the research staff which included both post-doctoral research associates and graduate students. The group of graduate students associated with this work represented a major component of the research staff. Key research personnel, dates of involvement, degrees awarded, and present positions are summarized in Table 2. Individuals with only a brief or temporary association with the program are not listed.

In addition to direct involvement in the research, the research personnel have participated in the regular DOE working group meetings and in a number of scientific meetings, site visits, and seminars. These activities were undertaken with the overall objectives of exchanging scientific information and establishing the basis for future and continuing dissemination of the results of the work.

TABLE 2. RESEARCH PERSONNEL

Faculty Investigators	**Dates**	**Degrees**	**Present Position**
N.P. Cernansky	10/87-12/94	-	Co-Principal Investigator
D.L. Miller	10/87-12/94	-	Co-Principal Investigator
Research Staff			
R.D. Wilk	1987-1989	-	Assoc. Prof., Union College
D.N. Koert	1991-1993	-	Assist. Prof., The Wichita State University
Support Staff			
R. Tidona	-	-	Research Engineer
P. Partridge	-	-	Laboratory Technician
L. Haas	-	-	Electronics Technician
R. Miller	-	-	Machinist
G. Mora	-	-	Secretary
Graduate Students			
Y. Henig	9/86-6/89	M.S. 1989	Research Staff, Ford Motor Co.
S. Addagarla	10/87-6/91	Ph.D. 1991	Research Engineer, Chevron R&T Co.
A. Gupta	10/89-6/91	M.S. 1991	Post Master's Work, West Chester Univ.
K. Jaouabi	1/90-12/91	M.S. 1991	Staff, University Mission of Tunisia
D. Filipe	6/90-3/92	M.S. 1992	Research Staff, Ford Motor Co.
A. Kumar	10/91-6/94	M.S. 1994	Ph.D. Candidate, Univ. of Wisconsin
H. Li	2/91-present	Ph.D. 1995	Ph.D. Candidate
S. Prabhu	7/91-present	M.S. 1994	Dual M.S. (Mech/Envr)
		Ph.D. 1996	Ph.D. Candidate
A. Tipnis	9/94-present	M.S. 1996	M.S. Candidate
Undergraduate Students			
D. Filipe	9/89-6/90	B.S. 1990	Continued in Graduate School
W. Kuhn	9/90-6/91	B.S. 1991	Engineer, General Dynamics
D. Hurst	9/91-6/92	B.S. 1992	Engineer, Mobil Oil Co.
M. Zipeto	6/94-present	B.S. 1996	B.S. Candidate