DOE/AL/43771--T4

A Technical Progress Report to
The United States Department of Energy
Division of Energy Conservation and Utilization Technologies
on
FUNDAMENTAL STUDIES OF FUEL CHEMISTRY AS RELATED TO INTERNAL
COMBUSTION ENGINE PHENOMENA

DOE GRANT NO. DE-FG04-87AL3371

Reporting Period:
July 1, 1988 - June 30, 1989

Principal Investigators

Frederick L. Dryer
Professor
(Correspondent)

Kenneth Brezinsky
Research Scientist

Other Contributors

Dr. R.A. Yetter	Professional Research Staff
Mrs. Y. Stein	Professional Technical Staff
Mr. M. Vermeersch, P.E.	Graduate Student
Mr. T. Held	Graduate Student
Mr. J. Sivo	Technical Associate
Mr. P. Michniewicz	Senior Technical Assistant

Prepared by

Frederick L. Dryer

Department of Mechanical and Aerospace Engineering
School of Engineering and Applied Science
PRINCETON UNIVERSITY
Princeton, New Jersey 08544

July 1989

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT SUMMARY

A better understanding of intermediate and high temperature chemistry and its relative importance in comparison to cool flame chemistry is a necessary pre-requisite to 1) developing appropriate general models for autoignition under engine cycle conditions; 2) improving understanding of the effects of additives which raise octane number (anti-knock compounds); 3) understanding in fundamental terms the effect of blending species of differing autoignition character (blending octane number); and 4) improving lumped parameter (semi-empirical) description of knock chemistry for inclusion in engine design models. This knowledge could significantly aid not only in the development of new fuel compositions to meet future octane requirements with best economy, but to the design and operational optimization of engines which might reduce the octane requirement.

The present twenty four month research effort was initiated in October of 1987 with the intent of providing substantially improved insights (through homogenous gas phase kinetic studies at different constant pressures) to the fuel chemistry issues important to autoignition in engines. The conditions of the proposed experiments were chosen to represent those similar to engine parameters under knocking conditions: temperatures in the range of 700-1100K, pressures from one to approximately 20 atmospheres and stoichiometries around one. However, at the initiation of this work, the existing Princeton flow reactor was capable of operation only at atmospheric pressure and for reaction times too short to study reactions below about 900 K. Thus, a major part of the proposed research has been to design and construct a variable pressure flow reactor facility in which a range of reaction pressures, and in fact, lower reaction temperatures could be accessed. This development has been jointly supported by this research grant and the University.

Unlike the previous flow reactor system, the new flow reactor has a fixed diagnostic sampling location and means to position the point at which reactants are initially mixed relative to it. Crossed beam optical access (to accommodate line resonance absorption and fluorescence diagnostics), as well as continuous on-line gas sampling (to accommodate on-line non-dispersive infrared, oxygen paramagnetic, hydrogen thermo-conductive Fourier Transform Infrared and off-line gas chromatographic, gas chromatographic/mass spectrometric, and wet chemical based analytical techniques), and temperature measurements at the sampling location are available in the new design. Design calculations estimate that chemically reacting systems with characteristic reaction times as long as 15- 20 seconds and as short as 50 - 100 milliseconds can be studied by varying the reactor nitrogen carrier flow rate (0.5 to 2.0 moles per second), temperature (600 - 1300 K), and pressure (1 to 20 atmospheres). The system is also designed to permit changes in the reactor duct diameter from the initial size of 10 centimeters to 5 centimeters to further reduce the characteristic reaction times which can be studied.

The reactor facility design and construction are nearly complete, and initial testing has begun to compare the overall experimental operating characteristics of the reactor with the design parameters. Pressure, temperature, and flow field velocity measurements should be complete and CO/H₂/O₂ chemical kinetic studies (to compare operation with the atmospheric pressure system and with the prediction of a well developed model for higher pressures) should be initiated before the end of the current research period (September 30, 1989). Continuing efforts beyond the present one will focus on studying the chemical

interaction of carefully selected, representative fuels, stable intermediates and anti-knock blending agents.

Experiments on Isobutene/oxygen mixtures have also been conducted in the existing atmospheric pressure flow reactor at about 1150 K and in an equivalence ratio range of pyrolysis with about 100 ppm oxygen background to 0.42. A detailed kinetic model has been developed to interpret the pyrolysis and oxidation characteristics. The mechanism accurately reproduces the fuel consumption and major intermediate species profiles. Closer examination of the model indicates that the observed inhibitory effect of isobutene at high temperatures is due to the depletion of the active radical pool and formation of unreactive stable species and methyl radicals. Because of this, isobutene oxidation and pyrolysis is heavily influenced by the chemistry of methyl radicals. The effects of increased pressure upon the fuel consumption mechanism require further study. In particular, very little data exist regarding the reactions of unsaturated hydrocarbons with the hydroperoxy radical; even the product channels for these reactions have yet to be identified. Even at atmospheric pressure, the reaction of HO_2 with the methyl radical has a profound effect upon the mechanism of isobutene oxidation. These issues will be addressed in future studies in the Princeton variable pressure flow reactor.

TABLE OF CONTENTS

Title Page

Abstract Summary

I. Introduction	1
II. Research Goals	5
III. A Variable Pressure Flow Reactor for High Pressure Kinetic Studies	7
Hydrocarbon Reaction Kinetics as Functions of Temperature and Pressure	8
New Flow Reactor Design Concepts	25
Current Status	30
IV. Experimental and Detailed Kinetic Modeling Studies of the Pyrolysis and Oxidation of Isobutene at Atmospheric Pressure	34
Experimental Methods	35
Experimental Results	36
Computational Model	37
Modeling Results	46
Summary	48
V. Expected Progress within the Existing Research Effort	49
VI. References	50
VII. Figures	57

Appendix A - The Princeton Atmospheric Pressure Flow Reactor Facility

I. Introduction

The rapidly advancing state of understanding in the field of combustion chemistry suggests that significant new insights into autoignition chemistry and its relation to engine knock can be obtained through critical review of existing data and additional experiments which not only accommodate improved instrumental diagnostics (more complete definition of the chemical characteristics), but which can also consider pressure and temperature ranges more similar to those experienced by the charge in engines. Analytical work using existent detailed chemical kinetic mechanisms which have been derived and validated from such experiments can serve as useful tools to interpret the autoignition fuel chemistry under simulated engine pressure/temperature time conditions, and serve as bench marks against which lumped chemical models for autoignition chemistry can be compared.

While considerable modeling efforts have already been performed by Westbrook and a variety of collaborators as well as by Leppard at General Motors Research Laboratories (see references quoted later in this report), a significant difficulty remains in that the mechanisms used in such computations are very limited in terms of their construction and validation. The calculations must extrapolate behavior to considerably different time scales for pressure and temperature time-dependence and substantially beyond the experimental conditions over which even limited validation has been possible. The ability to validate such models is further hampered by the lack of experimental information for the wide range of carbon number and molecular structures (alkane and alkene isomers, cyclo-alkanes, aromatics) which are found in conventional fuels. These molecular structures have different pyrolysis and oxidative behavior than smaller (lower molecular weight) structures, particularly those with less than four carbon atoms. Even formulations of phenomenological models for this chemistry have been limited by the availability of sufficient experi-

mental data on the kinetic behavior of these structures as functions of pressure and temperature. For example, much of the previously available kinetics data have appeared primarily in the form of characteristic times for "ignition", were generated at much lower pressures, or were generated under static reactor conditions where surface effects can substantially complicate observations. Detailed chemical kinetic modeling is further complicated by the lack of required elementary kinetic data or even assessment of which reactions are most important. Finally, a large data base of information on the effects of fuel chemistry in more complex environments such as rapid compression machines, cool flames, and motored engines presently exist. However, with the exception of the recent work of Leppard, experimental diagnostics and knowledge of the controlling chemistry available at the time of these studies were often limiting in defining the appropriate measurements to be made and the interpretation of the results which were obtained.

Princeton atmospheric pressure flow reactor research has been a unique, comprehensive source of pure chemical information for the pyrolytic and oxidative behavior of hydrocarbon structures of molecular complexity commensurate with compounds and additives found in conventional alternate fuels. Recently, we have demonstrated the ability of this facility to provide new insight into the fundamental understanding of autoignition phenomena at atmospheric pressure and temperatures of about 1000K. These experiments and the new ideas derived from them have been reported in a series of articles [1-4] (references appear in brackets in this report) previously.

Atmospheric pressure flow reactor research at Princeton on the oxidation characteristics of normal and iso-octane as well as the inhibition of reactions by intermediates formed in the iso-octane oxidation show that the relative structure and oxidation time (to carbon monoxide and water) for intermediates formed from the initial fuel is a determining factor in the autoigni-

tion behavior of these species. These data as well as detailed kinetic modeling from Lawrence Livermore National Laboratories suggest that, at the very least, chemistry in the temperature range 750K to 1100K must be considered along with cool flame chemistry in understanding autoignition in engines.

Further atmospheric pressure flow reactor studies [3] which have examined autoignition time of various heptane/iso-octane mixtures have also yielded a preliminary correlative index among the octane number, an empirical measure of a fuel's knocking tendency, reaction time to occurrence of significant energy release, and reaction time for maximum yield of CO. For these temperatures, the time of maximum CO also corresponds to the time at which significant energy release from oxidation is initiated. Results for a different pure fuel agreed relatively well on an octane number (defined by engine testing) basis with that predicted from flow reactor results. This is an encouraging development, considering the large disparity in engine methods used to determine octane number and the operation of the flow reactor.

Cernansky and co-workers [5] have extended this correlative method to the study of autoignition behavior of several fuels and n-heptane/iso-octane mixtures at lower temperatures in an atmospheric pressure flow reactor to show that the CO correlation continues to exist with octane number at these conditions. The reaction time for significant energy release is no longer correlated with that for the maximum CO production at these conditions, but it has not been shown that a separate correlation with energy release no longer exists. Indeed, arguments remain [6,7] as to whether the principal effect of cool flame chemistry on engine autoignition is a result of the mechanistic changes resulting from formation of more reactive intermediates with certain fuels or whether the pressure/temperature history imposed by the engine is further amplified by different amounts of energy release associated with cool

flame chemistry for different fuels. Present models do not have any validating data with which to compare their characteristics, and engine pressure/temperature profiles cannot be determined independently (experimentally) or accurately enough to resolve these issues.

Comparative atmospheric pressure flow reactor studies of the pyrolysis and oxidation of normal and iso-octane at Princeton have suggested that some compounds within a fuel mixture may be initially insensitive to the concentration of oxygen present whereas other compounds may react at rates directly correlated with the concentration of oxygen. Therefore, the autoignition characteristics of fuel mixtures may be reflective of the relative degree of pyrolysis and oxidation that each of the constituents initially undergoes. While our previous studies of the oxidation of normal and iso-octane have indicated that the oxidation of intermediates to CO and CO₂ appears to control autoignition, it is nevertheless clear that any process that changes the chemical induction time will also influence, but may not dominate, the autoignition time. Consequently, fuel blends might be attainable which through addition of varying amounts of either easily pyrolyzed or oxidized constituents would permit alteration of the autoignition characteristics of the original fuel.

The phenomenological observations and ideas already derived from the Princeton flow reactor studies and other investigators continue to indicate that better understanding of high pressure, intermediate and high temperature chemistry and its relative importance in comparison to cool flame chemistry is a necessary pre-requisite to 1) developing appropriate general models for autoignition under engine cycle conditions; 2) improving understanding of the effects of additives which raise octane number (anti-knock compounds); 3) understanding (in fundamental terms) the effect of blending species of differing autoignition character (blending octane number); and 4) improving

lumped parameter (semi-empirical) description of knock chemistry for inclusion in engine design models. This knowledge could significantly aid not only in the development of future fuel compositions to meet future octane requirements with best economy, but to the design and operational optimization of engines which might reduce the octane requirement.

II. Research Goals

The present twenty four month research effort was initiated in October of 1987 with the intent of providing substantially improved insights (through homogenous gas phase kinetic studies at different constant pressures) to the fuel chemistry issues important to autoignition in engines. The conditions of the proposed experiments were chosen to represent those similar to engine parameters under knocking conditions: temperatures in the range of 700-1100K, pressures from one to approximately 20 atmospheres and stoichiometries around one. However, at the initiation of this work, the existing Princeton flow reactor was capable of operation only at atmospheric pressure and for reaction times too short to study reactions below about 900 K. Thus, a major part of the proposed research was to design and construct a variable pressure flow reactor facility in which a range of reaction pressures, and in fact, lower reaction temperatures could be accessed. The reactor to be developed was scheduled to begin operation in the beginning of the fourth quarter of the second year of the proposed work.

Research has been focused on studying the chemical interaction of carefully selected, representative fuels, stable intermediates and anti-knock blending agents using flow reactor techniques. The chemistry of single components is also of interest as an adjunct to the understanding of the combustion of fuel blends and for building comprehensive hierarchical mechanisms for computational studies. It was noted in the initiating proposal that the

chemical systems discussed there were far too numerous to be studied in the proposed twenty four month research period, and the initiating summary work statement for concurrent atmospheric pressure experiments was formulated such that the work performed would provide a substantial foundation upon which efforts could be further extended as the new reactor became operational.

Experiments have been concurrently conducted during the variable pressure flow reactor design and construction using the previously developed, atmospheric pressure flow reactor. Deviations from the experimental efforts originally proposed have responded to the continually evolving interests of the field as expressed within the DOE Knock Working Group (organized by Sandia National Laboratories) and the broader community. We have concentrated on attempting to better understand the oxidation chemistry of isobutene, an intermediate prevalent in the oxidation of larger alkane hydrocarbons which are particularly resistant to autoignition. Other atmospheric pressure experiments were also suggested initially. The need for high pressure studies with improved species measurements, and in the lower temperature range of 700 - 1100 K has been further emphasized by the work of others as well as our own [4], and experiments have also shown that the kinetics of isobutene was not fully developed enough in existing kinetics models. These facts have led us to delay other experimental aspects (which were originally contemplated for atmospheric pressure studies) since they can be better addressed in future high pressure experiments and, instead, concentrate on developing sufficient mechanistic understanding of the isobutene oxidation for integration into larger molecule oxidation mechanisms under consideration at Lawrence Livermore National Laboratories.

Progress in the last twelve months on these topics is described in the following sections of the this document.

III. A Variable Pressure Flow Reactor for High Pressure Kinetic Studies

Over the past thirty years, the atmospheric pressure Princeton Flow Reactor (Appendix A describes the details of the present atmospheric pressure Princeton flow reactor facility) has been an evolving, important source of pure chemical kinetic information for the pyrolytic and oxidative behavior of various molecular structures. During the last fifteen years, after chemical sampling and analysis of extracted samples was introduced [8], the ability of this facility to provide new insight into the fundamental kinetics of the carbon monoxide-hydrogen-oxygen system (e.g. [8-11]), of various alkanes (e.g. [12,12-17]), of various olefins (e.g. [2,18-20] al., of various oxygenates (e.g. [21-26]), and aromatics (e.g. [27] has been clearly demonstrated. These flow reactor experiments have provided unique experimental information in the temperature range 950 - 1250 K, with considerable detail of the stable reactants, for characteristic reaction time scales inaccessible to shock tubes or static reactors.

The data described above, together with shock tube, and static reactor data from the literature have been used to develop and validate comprehensive chemical kinetic mechanisms to describe reacting systems over the parameter ranges commensurate with combustion applications, and engine autoignition in particular. In fact, the atmospheric pressure flow reactor has provided much of the intermediate temperature reaction data used in constructing comprehensive detailed kinetic reaction mechanisms (e.g. [28-34]). It is these mechanisms together with low temperature data (e.g. [35,36] which have provided the base and mechanistic insights from which to extend model development to low temperature chemical mechanisms (e.g. [36-38]) and provide the mechanisms used in modeling autoignition (e.g. [7,39-40]).

Yet all of the measurements in this flow reactor, and most of the other data from shock tubes and static reactors at other temperatures used in

developing such mechanisms have, until very recently [41], been performed at/or near atmospheric pressure. As will be shown in the next section, the extrapolation of this chemistry to pressures which are similar to those found in engines is severely complicated, giving rise to a need for an independent, experimental technique to produce pure chemical kinetic data not only to guide the development of mechanistic insights, but to provide validation for the resulting model construct.

Hydrocarbon Reaction Kinetics as Functions of Pressure and Temperature

In order to understand better the range of experimental parameters which must be studied to accurately extrapolate results and to have some appreciation for the measurements which should be made, we must better understand the transitions which occur in hydrocarbon chemistry as a function of pressure, temperature and chemical structure.

Below about 423 K, the oxidation of organic compounds is immeasurably slow unless either chemical or photochemical initiators are used to promote reaction. Benson [42] terms this temperature regime as one of chemical synthesis reactions; the most important intermediate species produced in terms of reaction mechanism in this regime are hydroperoxides of the type RCH_2OOH or $R'R''CHOOH$, where R, R', etc. denote the remainder of the organic molecule. The reaction is exothermic, and can lead to spontaneous ignition if heat is not removed from the environment. Above 473 K, the hydroperoxides formed undergo homogeneous, autocatalytic, chain decomposition to produce predominantly alcohols ($RC-OH$), ketones ($RC=O$) (or aldehydes, ($R-CHO$)). Further reaction of the aldehydes, which are formed only from primary hydroperoxides (RCH_2OOH), rapidly produce acids ($RC=O-OH$).

As the temperature is raised above about 573 K, the gas phase oxidation of hydrocarbons remains a slow process which increasingly yields olefins ($RC=CH_2$) and hydrogen peroxide (H_2O_2). The olefins formed are more easily

oxidized than the initial hydrocarbon and tend to form epoxides ($\text{RCH-CH}_2\text{O}$) and unsaturated aldehydes (RCH=CH-CHO) along with CO and CO_2 . While the net reaction is nearly thermoneutral (and thus self-heating becomes unimportant), an interesting feature of reaction at these temperatures is the appearance of autocatalysis. The reaction begins at an immeasurably slow rate, eventually accelerates through degenerate branching processes to a maximum rate after which the depletion of reactants causes the rate to decline.

Another interesting characteristic of this reaction regime is the appearance of diffuse luminosity and, further, the production of slowly moving wave(s) of blue light which traverse the reaction volume. Since early observation suggested that the traverse of these waves did not yield an increase in temperature of the overall mixture, they have been historically referred to as "cool" flames. These phenomena apparently do not occur with the simple alkanes, methane, or ethane, the simple olefin ethylene, the simple aromatics, benzene, toluene, ethyl benzene, or p-xylene (exhibits low temperature chemical behavior, but no cool flames) as the initial fuel [42,43], but are observed for all higher carbon number paraffins, other higher carbon number olefins, other xylenes and higher carbon number alkylated aromatics, and all carbon number aldehydes. Careful temperature measurements in low pressure static reactors have now shown that the local temperature rise associated with cool flames may be several hundred degrees Kelvin. Despite this local self-heating, the overall vessel reaction does not accelerate, and, in fact, the appearance of one cool flame may be followed by another, even several more, at short and even long (1 minute) time intervals. The occurrence, number and spacing of the cool flames is sensitive to the choice of initial fuel, vessel size, temperature, pressure, and reaction stoichiometry. While quasi-steady cool flame phenomena have been produced in flow systems [44], early experiments in closed vessels showed that after the passage of one

or more cool flames was often followed by explosion, i.e. very rapid reaction, of the remaining reactive mixture. The oxidation chemistry of hydrocarbons with which such phenomena are associated are generally referred to as "cool flame chemistry". The behavior of this chemistry for the oxidation of propane in low pressure static reactors is shown in Figures 1a [45] and 1b [35]. Note that there is a temperature regime (termed the negative temperature coefficient or "NTC" regime) in which the induction period for reaction and maximum reaction rate observed decreases with increasing temperature. The NTC regime separates the low temperature kinetic regime from the intermediate temperature kinetic regime (In both of these regimes, reaction rate accelerates with increasing temperature).

While Semenov [46] and other workers identified many of the kinetic features of the reaction mechanism in the low and NTC temperature regimes, but according to Benson [43], it was not until about 1965 that the general observed features -- "cool" flames, NTC effect, induction period character -- were fitted into any general oxidation mechanism.

The general mechanism is as follows, with other reactions having to be added as temperature increases (e.g. 12) and as the initial fuel hydrocarbon molecule becomes larger than 3 to 5 carbon atoms (e.g. 13-15).

Some of these reactions are not elementary processes (e.g. 15), but represent the result of several elementary processes.

In the case of alkanes, the initiation reaction at low temperatures is

The reaction is typically slow, reaction-site selective, and quite endothermic (activation energies are the order of 45 to 55 Kcal-mole⁻¹). Despite the production of two radicals, the endothermicity of the reaction does not permit it to play a significant role in the overall destruction of the initial reactant, ie. it is primarily an initiation reaction.

The propagation reactions at low temperature are of two essential types:

Thermal decompositions of radicals, R, are typically highly endothermic processes, becoming important only at higher reaction temperatures (T > 750 K) and therefore play no role in the low temperature regime. Although the formation of peroxy radicals by molecular oxygen attack is always faster than that of olefin formation, the production of peroxy radicals becomes more favored still at lower temperatures. In general, Benson [43] has shown that the formation of peroxy radicals is rapidly reversible above about 473 K, i.e., the reverse reaction to the reformation of the initial radical and molecular oxygen is rapid above these temperatures. Because of these facts, other R + O₂ processes prevail above 500 K such as those resulting in the formation of conjugate olefins. However, experiments by Slagle et al. [47] support the suggestions of Fish [48] that these olefin forming processes are not separate parallel processes but rather the result of a second decomposition channel involving the RO₂^{*} formed in the initial addition step:

Since reaction 3a is highly reversible above 500 K, RO_2^* is constantly formed and decomposed. Rather than decomposing into the initial reactants, some of that formed yields olefins and HO_2 , until there is complete conversion of R to olefin.

The peroxy radical, (RO_2) abstracts an H from any fuel molecule or other hydrogen donor to form a hydroperoxide (ROOH),

The amount of hydroperoxide which will be formed depends upon the competition of reaction 4 with reaction 3 (which forms stable olefin and HO_2). The decomposition of RO_2 formed in reaction 2 can yield molecular products such as aldehydes and ketones (reaction 5),

while the HO_2 formed in reaction 3 leads to the formation of peroxide, H_2O_2 , through,

Destruction of the initial reactant is primarily a result of the attack of RO_2 , HO_2 , and OH formed by the degenerate branching step, reaction 7,

As the temperature is increased, and well into the NTC regime, the dissociation of H_2O_2 formed in reaction 6, becomes a significant source of OH radicals through

However, in the low temperature regime, this dissociation is very slow.

In low temperature, static reactor studies from which much of the understanding of this chemistry has been derived, reaction times (which are the order of many tens of seconds at these low pressures) are such that diffusion to the reactor wall is likely, and the fate of the H_2O_2 is termination (usually heterogeneous) to form water and oxygen,

Thus, a difficult correction must be applied in order to obtain quantitative rate measurements of the gas phase chemistry (which will be governing in high pressure systems).

The build-up of ROOH and R'CHO, the degenerate branching species, is required before chain branching occurs to a sufficient degree to dominate the system, and the required time for this build-up results in the chemical induction times noted in low temperature hydrocarbon combustion experiments.

A recent analysis by Benson [42] sheds further light on the phenomenological result as the relative importance of Reactions 2 and 3 changes. Treating these two reactions as independent processes, Benson performed a steady state analysis of the rates of production of ROOH and the olefin to give the following ratio:

$$\frac{d[\text{olefin}]/dt}{d[\text{ROOH}]/dt} = \frac{d[\text{olefin}]}{d[\text{ROOH}]} = \frac{k_3[\text{R}][\text{O}_2]}{k_4[\text{RO}_2][\text{RH}]} \quad \text{Eq. 1}$$

Under cool flame conditions, it has been shown that $[\text{RO}_2]$ and $[\text{R}]$ are essentially in equilibrium via Reaction 2, so that it is possible to write

$$\frac{[\text{RO}_2]}{[\text{R}]} = K_2 [\text{O}_2] \quad \text{Eq. 2}$$

where K_2 is the equilibrium constant for Reaction 2. Combining these equations,

$$\frac{d[\text{olefin}]}{d[\text{ROOH}]} = \frac{k_3}{k_4 K_2 [\text{RH}]} \quad \text{Eq. 3}$$

which is a somewhat paradoxical result, since O_2 and all radical concentrations have disappeared from the ratio. By assuming that the H was abstracted from a secondary carbon atom and assigning values to the constants in this equation, Benson found that:

$$\frac{d[\text{olefin}]}{d[\text{ROOH}]} = \frac{10^{(5.7 - (8.47/rT))}}{[\text{RH}]} \quad \text{Eq. 4}$$

where r is the universal gas constant ($\text{kcal-mole}^{-1}\text{-K}$), T the temperature (K), 8.47 in units of kcal-mole^{-1} , and (RH) in moles-liter^{-1} .

This last equation predicts that the olefin production becomes more important than the ROOH production as the temperature rises. Thus when a cool flame begins, and the mixture temperature rises as it proceeds, the olefin production becomes prevalent and dominates the step leading to degenerate branching. This results in cessation of chemical reaction on a time scale comparable to that available in the cool flame thermal wave. Indeed, recent experiments and detailed kinetics calculations [49-51] show that it is primarily heat transfer losses and subsequent cooling (causing the local mixture temperature to again decrease) which result in the observation of multiple cool flames in low pressure reactors.

The appropriate analysis will be considerably more complex if reactions 2 and 3 are treated as truly sequential (i.e. as reactions 3a - 3c), but the qualitative result that the competition of the two possible product channels results in the overall reaction rate decreasing with temperature will be similar.

Equation 4 is both temperature and pressure dependent, and thus it appears that the beginning of the NTC region which separates low temperature and intermediate temperature regimes will be at different temperatures as ambient pressure changes. As engines operate at pressures well in excess of ambient, how such transitions vary with pressure is of great importance.

Figure 2, derived in the current work, shows the behavior of the "turn-over" temperature - i.e. that temperature at which the NTC regime begins for a stoichiometric n-butane-air mixture, as a function of pressure. The low temperature, static reactor data of Wilk [35] have been used to define the

magnitude of equation 4 at the turnover condition in his experiments, and the result was then used to extrapolate this condition to other temperatures and pressures.

There are currently no fundamental homogeneous gas phase studies of the kinetics of the negative temperature coefficient regime at high pressure to validate this extrapolation.

However, recent modeling of the autoignition time delay of adiabatically compressed combustible gas mixtures [52,53] qualitatively confirm the pressure dependent character of the turnover temperature represented in Figure 2.

With larger carbon number hydrocarbon molecules, an important internal isomerization reaction to form the hydroperoxy radical ($\dot{\text{R}}\text{OOH}$),

can also occur, and Benson [41,42,54] notes that with six or more carbon atoms, this reaction may compete substantially with reaction 4, yielding the following complex path structure:

More specifically, the overall reaction

typically proceeds through the following general sequence of elementary reaction processes:

Depending on the structure of the radical $\text{OOR}'\text{-R}''\text{OOH}$, internal isomerization may occur (as shown above) or the radical may abstract an H atom from another hydrocarbon to yield ketones, aldehydes, and hydroxyl radicals:

The specific ketones and aldehydes which are produced will depend on which reaction route is followed and the structure produced by the addition of oxygen to the isomerized ROOH radical.

At 600K, Benson [42] suggests that reaction 15 can be some 30 times faster than reaction 4, and therefore, this additional sequence of reactions resulting from oxygen addition to the ROOH radical will contribute substantially to branching. Thus, the competition between olefin production (reaction 3) and chain branching processes resulting from the production of RO_2 becomes more severe at higher temperatures when isomerization of ROOH is significant. It has been suggested that the greater tendency for long chain hydrocarbons to knock as compared to smaller chain and branched chain molecules is a result of this internal, isomerization-branching mechanism [42,43]. Recent modeling of engine processes suggests that this isomerization sequence may be important in autoignition chemistry of paraffin hydrocarbons as small as n-butane [7]. These effects should be partially accounted for in the results presented in Figure 1 since experimental data at low pressure were used generate the figure. However, the fact that oxygen

concentration will be substantially increased at higher pressure may cause the turnover temperature to extend to even higher values as pressure increases. Again, no fundamental homogeneous kinetic data are available to quantify these effects accurately.

The production of CO_2 is strongly associated at the lower temperatures with the reaction:

with some contribution also coming from

Reaction 17 is rather unusual in that it represents a route to carbon dioxide formation which does not require previous formation of CO such as in reaction 18 or 19,

At higher temperatures where the formation of OH becomes prevalent, reaction 19 completely dominates the formation of carbon dioxide.

As temperatures are increased in the intermediate temperature regime, the thermal decomposition,

becomes much faster than reaction 17, preventing direct carbon dioxide formation to occur. Since reaction 18, and reactions 21, 22,

have small rate constants in comparison to reaction 19, and the rate constant for reaction 8,

is typically much greater than that for reaction 19, the presence of hydrocarbon species generally inhibits the formation of CO_2 at higher temperatures.

As temperatures are raised, H_2O_2 production becomes more significant

(reactions 3, 6), and hydrogen peroxide begins to decompose (reaction 12) before it can undergo transport to a heterogeneous destruction site (reaction 11). With the continued increase in the reverse of reaction 2, and the increasing importance of reaction 12, HO_2 and OH become the dominant chain carrying radicals. Functionally, hydroperoxy radicals replace RO_2 , while H_2O_2 replaces ROOH , and the dominant oxidation mechanism at low pressures and higher temperatures becomes:

Termination of the reaction chain is provided by:

It is the increasing dominance of this mechanism over that described earlier which has been suggested to be responsible for the termination of the NTC regime and the beginning of the intermediate temperature oxidation regime. Benson [42,43] has referred to the inception of this regime as the occurrence of "hot ignition". Reaction 12 is bimolecular [55], while the decomposition of ROOH is likely to be in its high pressure limit at these temperatures and pressures. Therefore, the hot ignition condition should occur at lower temperatures as pressure is increased. Thus, based on earlier discussion, it appears that not only does the turnover temperature increase, but the range of temperature over which the NTC regime exists may become smaller as the environmental pressure is increased. Indeed, it is possible that at some higher pressure, the negative temperature coefficient regime may disappear completely. Again, no precise quantitative information is available to confirm this issue.

At temperatures above about 800 K (and well within the intermediate

temperature regime), the oxidation chemistry of most hydrocarbons begins to change very significantly. Alkyl radicals formed through abstraction of an H atom by an active center will begin to decompose to yield smaller hydrocarbon radicals and small olefins (primarily with carbon numbers less than 3). Special consideration of methyl, ethyl and propyl radicals formed in this process is warranted as these are the only radicals likely to yield H atoms through further reaction.

In the case of methyl radicals, further decomposition will not occur until temperatures are very high (>1700 K). At low temperatures, the reaction

proceeds as described earlier, i.e.

with the equilibrium for the first reaction largely shifted toward reactants at temperatures above 850 K (i.e. where beta scission, discussed below, becomes prevalent). Methyl radicals therefore tend to react with themselves to form C₂ species (C₂H₆ and C₂H₄), to abstract hydrogen from other molecules to form CH₄, and to react with other radicals. At intermediate temperatures and higher pressures (see later discussion), the prominent radical-radical reaction route is,

followed by,

and at higher temperatures,

Between 850 and 1000 K, there appears to be no significant reaction of methyl radicals and oxygen, while at higher temperatures, the highly endothermic reaction,

occurs [31]. Thus methyl radicals can yield H atoms only through reactions 27 and 29, i.e. through relatively circuitous routes at higher temperatures.

For ethyl radicals, C_2H_5 , which are produced by beta scission of larger hydrocarbon radicals or by H abstraction from ethane formed from methyl radical recombination, thermal decomposition, i.e.

will begin to compete with the overall process,

at higher temperatures. Depending on the oxygen mole fraction, and the total pressure, reaction 31 will be more rapid than 30 up to about 1200 K (for $O_2 = 21\%$). Similar behavior is true for isopropyl radicals and t-butyl radicals. However, even small quantities of H atoms from reactions paths such as 27/29 and 30 may be important.

For alkyl radicals with carbon number greater than 3, uni-molecular loss of an H atom to form an olefin is highly disfavored in comparison to cleavage of a C-C bond because of the relative bond strengths. The higher carbon number conjugate olefins which are formed result primarily from the abstraction of an H atom by molecular oxygen.

For larger carbon number alkyl radicals, cleavage of a C-C bond is favored at a location one C-C bond away from the radical carbon site [16,32]. When more than one C-C bond cleavage site is possible, the scission which leads to the largest alkyl radical will be preferred. The only radicals which will tend to support the loss or abstraction by oxygen of another H atom will be those for which no such scission site exists, e.g. ethyl, isopropyl, and t-butyl radicals as mentioned above. This type of C-C bond scission process has been referred to in the literature as "beta" scission or "alpha" cleavage and has already been successfully incorporated in combustion modeling

of larger hydrocarbons [32,40].

For example, for n-butyl radicals one would expect

and

to be the important reactions which compete with

and

One must also take into account the possibility of internal isomerization reactions after the initial addition process in reactions 34 and 35.

Figure 3 displays the ratio of the rate of reaction 34 to the rate of 35 as a function of pressure (M = air). It can be seen that conjugate olefin formation can be prevented by beta scission processes in the intermediate temperature range, at temperatures only about 100 K higher than the turnover temperature. Beta scission processes may therefore compete with internal isomerization of RO_2 to the ROOH radical in the negative temperature regime at high pressures.

Above about 500 K, any alkyl radical, $\text{C}_n\text{H}_{2n+1}\cdot$, with carbon number greater than 4 may undergo rapid reversible isomerization (H atom migration) across 5 carbon atoms and more slowly across 4 and 6 carbon atoms [1]. Benson [53] suggests that this is the most rapid of any alkyl radical reactions at this temperature. Under this assumption, all positional isomers for the radical would be essentially in equilibrium with one another. This fact implies that even if product distributions generated by the fission of each alkyl radical differ, the total product distribution formed from the decomposition of all

alkyl radicals will be independent of the initial abstraction site. Furthermore, the rate of formation of products will depend only on the total rate of alkyl radical production, independent of which species was originally responsible for the abstraction of an H atom, and the site at which the abstraction occurred. Whether isomerization is indeed as rapid relative to scission reactions at higher temperatures and pressures remains in question, again from the lack of adequate experimental information.

At intermediate temperatures, the yield of hydrogen atoms from reactions such as 27/29 and 30 yield HO_2 through

Not until conditions are such that the reaction rate of

becomes comparable with that of the major competing H atom loss processes, i.e. reaction 36 and 38,

are O atoms available in significant quantities to react with the hydrocarbon species or their fragments. Figure 4 displays the ratio of the rate for reaction 38 divided by the sum of the rates for reactions 36 and 37 for a stoichiometric butane-air mixture at different pressures and temperatures. It is interesting to note the large range of temperatures over which reaction 38 dominates, particularly for the pressures (< 1 atmosphere) which have been more commonly studied experimentally.

The transition between "intermediate" and "high temperature" kinetic regimes is generally defined by the conditions under which reaction 36 dominates over reaction 37. This transition is not only a function of pressure but of the third body efficiencies of molecules present in the reaction system. Figure 5 displays the ratio of the rates of reactions 36 and 37 as a function of pressure for nitrogen as the third body. It is

seen that the transition to the high temperature kinetic regime is in the temperature range of the atmospheric pressure flow reactor experiments described earlier, but will occur at temperatures well above 1100 K at high pressures.

As peroxide decomposition to form OH radicals is fast above 800 K, OH and HO₂ remain as the principal abstracting radicals until this transition condition is reached. In the high temperature regime, however, the reactions,

control the relative concentrations of O, OH, and H available to react with hydrocarbons through

Additional complexities may exist depending on the species RH and the temperature, as reactions with OH and O may be both abstractions as noted above as well as additions:

Such radical addition reactions occur with small olefins such as ethene and propene as well as with acetylene. Considerable experimental work and discussion continues on the possible transition of some radical-hydrocarbon reactions from addition to abstraction as temperature increases, and the possibility of the adducts themselves to further react if they are stabilized by increased collisions at high pressure is completely unknown.

Figure 6 simultaneously plots all of the transitional kinetic behavior discussed in the last section, along with the conditions at which engine knock typically occurs, a pressure and temperature envelope which encloses those temperatures and pressures which fuel/air charges see in engines. The

data line labeled FR refers to the range of conditions typically available in the Princeton atmospheric pressure flow reactor, While the data line SR refers to those conditions typically available in static reactor studies. Shock tube derived kinetic information typically falls above 1200 K and in the 1 to 10 atmosphere pressure range. Considerable extrapolation of available data are required to address chemistry issues in engines. Thus the actual locations of the transitions between the various chemical regimes are not well defined both because of extrapolation and limited experimental information even at the atmospheric pressure conditions themselves. More importantly, it is also clear that the separations of the various regimes of chemistry are crossed during the compression stroke of a premixed, spark ignition engine, and that it is therefore difficult to unravel the effects resulting from the actual rate of these crossings (related to engine parameters such as rpm, etc.) and the rate of chemistry which is occurring in the unburned gas. If the characteristic chemical times for a certain regime are large in comparison to characteristic time the charge sees in that regime, then even though a system passes through conditions which would yield certain chemical behavior for homogeneous isothermal, isobaric reaction, there is not time for that chemistry to substantially contribute to the observed phenomena. On the other hand, if chemical and residence times are of the same order, substantial chemistry may occur and result in some conversion of initial reactants. Intermediates and products produced, together with the remaining reactants compose a dynamically changing "initial mixture" for the next chemical regime. As the system moves to a new set of environmental conditions which define a different reaction regime, the result is to modify initial conditions for that chemical regime in comparison to those which would be present if no reaction had occurred previously. Finally transport of species and energy can cause drastic changes in the chemical initiation, rates of oxidation, and chemical

behavior from that which might be expected under isothermal, homogeneous conditions. It is for these reasons that construction of comprehensive chemical kinetic mechanisms is important, and that experimental validation data are available to develop and validate such mechanisms.

New Flow Reactor Design

Mr. M. Vermeersch, a third year graduate student, has been collaborating with Prof. Dryer for the past three years in formulating the variable pressure design concepts described below. As he is a licensed professional mechanical engineer with considerable previous experience in high pressure equipment design for the petroleum industry, Mr. Vermeersch has performed all of the detailed mechanical, and control design work in the laboratory. With the exception of the high pressure shell itself, much of the apparatus has been fabricated at Princeton with the aid of the laboratory technical staff.

The design of the new variable pressure was conceived not only to meet the needs of providing the necessary data for the task mentioned above, but, through modifications in its construction concept, to improve the control and diagnostic abilities substantially over those available in the present atmospheric pressure flow reactor. Some of the limitations of the existing flow reactor (in addition to the pressure range at which it operates) which have been reduced are itemized below:

1. Operation, precise control, and experimental reproducibility, since all functions (carrier, fuel and oxidizer flows, operating temperature, sampling operations, data acquisition, etc.) are difficult and time consuming, since almost all functions are manually controlled. Although some control technology is used for setting heater temperatures, etc., control technology advances since 1972 have not been retrofitted to the original construction.
2. Gas sampling and later analyses of some of the species (e.g. oxygenates) expected to be present as intermediates in high pressure chemistry is difficult in that the species must be kept from further reactions until analyses can be performed. Although some methods are available to do this (see, for example, the DNPH method described later in this report), operations are unreliable as well as tedious.

3. Optical access for the use of optical diagnostics is very limited and difficult to achieve. Efforts [56] have recently shown the feasibility of measuring OH concentrations using laser resonance absorption and fluorescence methods. However, the difficulty of such measurements is substantially increased by the fact that the optical sampling position must be moved relative to the fuel/oxidizer mixing location, but the reactor itself must be enclosed in heaters and insulation to approximate adiabatic conditions.

The new reactor design is schematically shown in Figure 7a. The design concept is based on fixing the location of the diagnostic sampling position, and moving the point of fuel air mixing relative to it to vary the relative reaction time one wishes to observe. The approach is very similar to that which is normally performed in the study of pre-mixed laminar one dimensional flames where the burner rather than the diagnostic sampling position is moved. Crossed-beam optical access ports (normal to the flow direction) are positioned at the same location at which a hot water cooled, wall convection quenched, gas sampling probe and silica coated thermocouple probes are to be axially located.

Figure 7b shows a design drawing of the reactor system including, the pressure shell itself. The shell is made of carbon steel and is ASME stamped for operation from full vacuum to 30 atm and 245 K to 533 K. The external surfaces of the shell are only natural convective cooled and remain warm enough to prevent water vapor condensation inside the reactor shell. The exhaust flow temperature is partially reduced to below 700 K by a water cooled heat exchanger, and is directed through a sealed carbon steel section to the induced draft laboratory exhaust system.

Figure 8 schematically shows the control approach used in the new reactor facility design. All flows are monitored by electronic mass flow meters and positioning of motor driven metering valves are controlled by Proportional - Integral - Derivative (PID) Controllers which sense the mass flow meter output. Similar closed loop controllers are used to con-

trol all heater temperatures and the flow reactor operating pressure. Operating pressure of the reactor is controlled by closed loop control of a high temperature back pressure valve in the exhaust flow section.

The PID controllers may be manually operated. Each controller is also linked to a IBM/PC/AT microprocessor via a RS-485 port connection so that all control parameters may be read or altered by the PC

The pressure shell is designed to enclose not only the reactor section, the reactor duct heaters and insulation, but also the positioning mechanism and fuel vapor injection probe which axially position the fuel/carrier mixing section relative to the sampling position. With this design there is no pressure thrust and the dynamic seal is not critical. The fuel vapor injection probe is partially insulated from the carrier flow to prevent premature pyrolysis reactions of the nitrogen diluted fuel vapor inside the probe from occurring. All fuels will be prevaporized into varying amounts of added nitrogen diluent to reduce residence time within the fuel injection probe and to accommodate vaporization at pressure and at temperatures low enough to prevent pyrolysis.

The mixer section itself is approximately 47 cm long and is machined from a low porosity, silica foam block to an outside diameter about 0.1 mm less than the nominal 10.16 cm inside diameter of cylindrical reactor duct. Either stainless steel screen or ceramic honeycomb will be placed at the entrance to the mixer section as a means of uniformizing the flow. The interior contour of the mixer section is shaped as a converging/diverging nozzle with a throat diameter of 2.5 cm and an expansion half angle of 7 degrees. Flow resistance through the long annular space between the mixer section and reactor duct wall is very large in comparison to that through the central venturi and more than 97% of the carrier flow therefore passes through the center venturi. The fuel vapor injection probe is

connected to the mixer section such that the outwardly radial injection holes are concentrically located within the nozzle venturi. A thermocouple is also positioned at its tip to control the desired inlet temperature.

The reactor duct itself is a 173 cm long, 2mm wall thickness, fused silica tube which extends from a inconel mating flange at the fuel injection probe entrance to a similar mating flange located at the entrance to the exhaust port of the reactor shell (see Figure 7b). A maximum of about 100 cm and a minimum of 1 cm of axial distance from the exit of the mixing section to the sampling position are possible. The reactor duct is surrounded by a 0.5 cm annular air gap and five independently closed loop controlled Kanthal resistance heaters mounted in pre-formed cylindrical ceramic fiber insulation sections. Reactor duct heaters maintain the wall temperatures very near the carrier gas temperature to approximate adiabatic flow conditions throughout the reaction section of the duct. In principle, reactor duct diameter should be able to be reduced to as small as 5 cm inside diameter by replacing the inconel mating flanges, the reactor duct itself, and installing a smaller diameter mixing section. The carbon steel shell is manufactured in two separate parts in order to accommodate such changes.

An arc plasma torch heater similar to that described in Appendix A is used to supply hot nitrogen carrier gas to the reactor (see Figure 7b). The desired carrier flow temperature is monitored at the fuel/carrier mixer location (thus radiation losses to the fuel injection probe from the carrier gas do not affect the inlet carrier temperature). The plasma heater is mounted vertically above the main reactor shell at approximately the location of the fuel vapor probe flange.

The upper residence time limit criteria for flow reactors is the maintenance of convective residence times which are short in comparison to diffusion times to the reactor wall surface. This limiting criteria is

strongly influenced by the selection of the flow reactor diameter. Estimating the order of the diffusion time to the wall as

$$\tau_d = d^2 / 4 D$$

where d is the diameter of the reactor tube and D is the mass diffusion coefficient, and the convective residence time as

$$\tau_c = L/u$$

where L is the length of the reactor duct and u is the mean flow velocity,

$\tau_d \gg \tau_c$ when

$$(Re)(Sc) \gg 4L/d$$

where Re designates the flow Reynolds number based on the reactor duct diameter and Sc designates the Schmidt number of the carrier gas. For the present parameter conditions, this translates to

$$(Re)(Sc) \gg 40$$

As the Schmidt number is the order of one, this means the flow Reynolds number should be much larger than 40 to meet this condition. The reactor is intended to be run only at Reynolds numbers greater than about 1000. As the duct L/d downstream of the mixer section will always be less than 10, the flow is not fully developed. As the boundary layer develops at the duct surface, radially uniform conditions continue to exist near the flow centerline. As the flow field further develops, axial velocity will change as a function of distance from the mixer section. Axial velocity profiles must therefore be defined in order to determine the relative reaction time as a function of distance from the mixer to the sampling position. These design issues have already been studied for the atmospheric pressure reactor [57] and will be further verified by actual velocity measurements under cold flow operating conditions in the new facility.

However, very important implications result from these observations,

particularly at increased operating pressures. Figures 9 and 10 show Reynolds number of the flow for a 10 cm diameter reactor duct as a function of available reaction time for various operating pressures and temperatures. Note that at higher pressures and lower reaction temperatures, the reaction test times at Reynolds numbers exceeding 1000 cover a range from 10 milliseconds to more than 20,000 milliseconds. Figure 11 shows the reaction times for a butane/oxygen mixture typical of flow reactor conditions as predicted using the numerical codes and kinetic mechanisms of Pitz et al. [35]. It is clear that for simple $C_3 - C_{10}$ alkanes as well as for many other hydrocarbons, this new facility presents the possibility of studying the NTC, intermediate and high temperature kinetic regimes using the same technique and in the same apparatus (without surface effects). This approach has another distinct advantage over the static reactor, shock tube, compression ignition, and motored engine approaches in that pressure and temperature are independently and experimentally defined. Furthermore, continuous acquisition of reaction-quenched sample flow from a specific extent of reaction (i.e. reaction time) permits adaptation of on-line continuous analysis methods such as FTIR for determination of species which can not be stored for later gas chromatographic analyses.

Current Status

At a cost of about \$150,000, the University completed the construction of new room and mechanical /electrical facilities for the reactor, reactor controls and diagnostics in March 1989.

The room is equipped with ventilation to create a slightly negative air pressure (in the room section housing the reactor) relative to the control room area. The reactor room is equipped with a 2 ton movable ceiling crane assembly for relocating the pressure shell sections and flanges of the

reactor. A ceramic lined, induced fan exhaust facility is available in the room floor trenches to remove the reactor exhaust to exit at the fourth story level of the building through an exhaust ventilation stack.

Major equipment for the construction of the reactor facility was purchased on a 1 to 2 cost sharing basis with the University. Estimated total costs of the construction (including CO, CO₂ nondispersive infrared, electrochemical based O₂, and H₂ thermoconductive on line analytical equipment and gas chromatographic sample storage valve interfacing, but excluding additional new diagnostic equipment for FTIR and in situ optical measurements) was \$120,000, and as of this date, we expect to complete the fully operational facility slightly over this budget (less than \$5000). All major pieces of hardware for the pressure shell assembly, exhaust system connections and pressure controls, arc plasma heating facility, reactor duct and heating systems, have been ordered, received, assembled and functionally tested as of June 30, 1989. Automating controls have been fully assembled, wired to the control console which incorporates an IBM PC/AT, and are fully operational for all pressure, plasma heater control, duct heater temperature, fuel injection probe positioning and flow control functions. Initial software for instrument control has been written and is also fully operational, although additional modifications are to be expected as operational testing begins.

The arc plasma heating system utilizes direct current rectifier systems shared with and an arc plasma torch design similar to that used in the previous atmospheric pressure facility described in Appendix A, but with an entirely new microprocessor based flow and arc power control system. Test firing of the new arc plasma heating facility began in early July. As of July 7, the arc plasma torch has been successfully started and fired, using the new PC-based control system and fully integrated flow control systems. Additional software and hardware modifications to improve initial start-up of the torch

and automatic control to the desired operational set-point are presently being completed. and the operating stability achieved thus far suggests that closed loop control of the nitrogen carrier temperature should be able to be accomplished through standard control methods and the hardware already in place. Additional testing to map plasma torch operating conditions will be completed in July, and complete operational mapping of the pressure, temperature and flow characteristics of the assembled flow reactor facility are expected to be complete by late August.

With regard to diagnostics, we expect to bring various diagnostic functions on-line in stages. Initially, the flow reactor will be operated with window port locations in the reactor shell sealed with solid carbon steel plugs. It should be noted, however, that the new facility is located immediately adjacent to the laser diagnostic facility (purchased under a DOE University Research Initiative grant in 1986) which has already been used to make laser resonance absorption and fluorescence measurements of OH in the atmospheric pressure reactor [56]. Adaptation of this facility to the new reactor involves primarily optics for transferring the laser beam to the facility and mating window designs for the reactor shell.

A hot water cooled sampling probe will be mounted in the reactor end-flange such that the sampling position can be adjusted axially (+/- 1.0 cm). Future designs will also accommodate radial adjustments (centerline to 5cm). Initially, the extracted flow will be analyzed continuously for CO, CO₂, O₂, and H₂. Non-dispersive infrared CO and CO₂, electro chemical O₂, and H₂ analyzers have been purchased and cabinet mounted. Data acquired by these instruments will be forwarded to an a/d board interface and recorded on a hard disk based microprocessor system. This continuous sampling and analysis system is expected to be fully operational in early August and will also accommodate

intermittent sample trapping for gas chromatographic analysis.

An on-line Fourier Transform Infrared Analyzer (FTIR, Nicolet Model 730) is to be added to this system some time late in the fourth quarter of this effort and should permit on-line measurement of most hydrocarbon species with carbon number less than four to levels of about 0.1 ppm. This instrument is being acquired with \$50,000 of funds advanced by the University (to the principal investigators), contingent on their return as one-time contract equipment costs or as capital equipment use-charges (over several years) to those contracts which employ this FTIR instrumentation in the future.

IV. Experimental and Detailed Kinetic Results on the Oxidation of Isobutene at Atmospheric Pressure

Isobutene has been identified as an important intermediate in the high temperature oxidation of several hydrocarbons, and as the primary intermediate formed during low temperature pre-knock reactions in an engine study of isobutane. In an earlier work at Princeton, the oxidation of two octane isomers, n-octane and 2,2,4-trimethyl pentane (iso-octane) was examined in the atmospheric pressure flow reactor [1]. These two fuels, which exhibit markedly different propensity to knock, were also shown to have very different high temperature reaction characteristics.

Each fuel was found to first react to produce an intermediate pool of hydrocarbon species and some water, then CO, with additional evolution of water, and finally carbon dioxide. Very little energy release, i.e. any indication of "ignition", occurred before the oxidation of CO to CO₂ was initiated. However, at these conditions, energy release occurred in much shorter reaction times for n-octane than for iso-octane. While both fuels produced intermediates at about the same rate, n-octane produced primarily simple olefins (ethene, propene) while isobutene was the principal intermediate formed in the oxidation of iso octane. The oxidation of isobutene was much slower than that of the mixture of simple olefins produced in n-octane oxidation, thus prolonging the time necessary for energy release to become significant. A subsequent investigation indicated that when isobutene was used as an additive to n-octane, the overall oxidation rate (primarily of the simple olefinic intermediates) was significantly reduced [2]. Other experimental studies of isobutene have also shown has an inhibitory effect on oxidation and pyrolysis of hydrocarbon fuels [58,59]. Other work at Princeton has also been shown that two of the most commonly used anti- knock fuel additives, tertiary butyl alcohol and methyl tertiary butyl

ether, both form isobutene as the primary intermediate under oxidative conditions [60].

In spite of the practical interest in understanding the oxidation of isobutene, few experimental results have been published. Two early papers examining isobutene oxidation in static reactors were published, and mechanisms for the low temperature ($< 480\text{C}$) oxidation were postulated [58,61]. A mechanism for the pyrolysis of isobutene has been proposed based on the results of a single-pulse shock tube study [62]. No studies have yet addressed the oxidation of isobutene at high pressures.

To prepare for future studies in the Princeton variable pressure flow reactor, we have studied the oxidation and pyrolysis of isobutene in the temperature range 1100K to 1150K in the existing, atmospheric pressure flow reactor. A detailed chemical kinetic reaction mechanism has been developed, refined and verified on the basis of comparison with these experimental results. The mechanism provides insight into the inhibitory nature of isobutene, and also reveals the relative importance of methyl radical chemistry in this system.

Experimental Methods

The atmospheric pressure turbulent flow reactor is described in Appendix A, and only issues specific to the present experiments are described here. Fifteen gas samples were collected along the duct centerline, quenched by a water-cooled sampling probe, and stored in 12 cm^3 stainless steel loops. In order to prevent condensation of any low vapor pressure species, the loops were maintained at a constant temperature of 70-80C prior to their analysis.

On-line continuous analyzers were used to measure O_2 , CO and CO_2 . The stored gas samples were analyzed by gas chromatography and mass spectroscopy. The gas chromatograph was a Hewlett Packard 5890A with flame ionization detector and nickel catalyst for conversion of CO and CO_2 to methane. Two

different columns were used for the analysis, a 60m DB-1 and a 25m PlotQ. The DB-1 column gave superior resolution of the many C_5 and C_6 species that were detected in less than 10 part per million levels, but could not resolve allene and propyne, which are present in significant concentrations. For this reason, the PlotQ column was used for later experiments.

As part of the present effort, for use in one of the of the later experiments, the DNPH method of Lipari and Swarin [63] was adapted to measure aldehyde concentrations. To collect the samples, the sampled gas stream was diverted from the on-line analyzers to a 30 ml impinger containing the 2,4 dinitrophenylhydrazine (DNPH) reagent solution. At each of eight sampling positions, one liter of sample gas was collected in a 20 ml aliquot of 3.1 micro-mol/ml DNPH solution. The reagent solutions were then analyzed by HPLC with a 25cm x 4.6mm DuPont Zorbax ODS column, using a 65:35 acetonitrile:water solvent ratio at 1 ml/min, and a 365nm UV absorption detector.

Consistent with the practice recently adapted by this research group, the axial sampling position is converted to time after injection by integration of the axial, centerline velocity profile within the duct. Additional measurements of the velocity profile were made as part of this contract research using a hot wire anemometer probe at ambient temperature and several Reynolds numbers. To within the error limits of the less precise pitot static probe, these measurements were in agreement with pitot static probe velocity measurements made previously at typical flow reactor operating temperatures

Experimental Results

The experimental species concentration profiles (symbols) versus time, obtained at several different stoichiometries are shown in Figures 12 through 19. The principal intermediates observed are the two C_3H_4 isomers (allene and propyne), methane, propene and carbon monoxide. Other species present in lower concentrations are ethane, ethene, acetylene, 1,3 butadiene and benzene.

Around fifteen to twenty C_5 and C_6 species were detected as trace species in all the experiments. Analysis by GC/MS indicated that these were mainly pentene, pentadiene and hexadiene isomers.

The DNPH analysis provided an accurate determination of the formaldehyde concentration, a very important intermediate specie which is difficult to analyze by gas chromatography. In addition, two oxygenated compounds were identified in significant concentrations, acetone and methacrolein (both at about 30ppm maximum). Acetaldehyde and isobutyraldehyde were also identified as trace species.

The effect of oxygen concentration on the net rates of formation of the intermediate species can be observed more clearly by replacing the time axis by the percent of fuel reacted. In this way the variation in the overall reaction rate is normalized for the different stoichiometries. As can be seen in Figures 20-23, the change in stoichiometric ratio has little effect on the net rates of production of propene and C_3H_4 , although it appears that later in the reaction the C_3H_4 consumption rate appears to be sensitive to the oxygen concentration. Methane follows a significantly different trend; the net production rate as a function of fuel consumption is strongly affected by oxygen concentration throughout the reaction.

Presenting the data in this manner also provides some inference of the main source of a particular intermediate. The species profiles which are linear in these coordinates are likely to be the result of reactions involving the fuel, while those such as ethene and acetylene which are upwardly curving indicates that the predominant formation pathways of those intermediates are due to reactions involving the primary intermediates.

Computational Model

Over the past year, computational modeling of these experimental results has been performed to develop further insights to the mechanism of pyrolysis

and oxidation and to provide some indication as to why isobutene might inhibit the oxidation of other hydrocarbon species. Mr. Tim Held visited Drs. Westbrook and Pitz at Lawrence Livermore National Laboratories for six weeks during the summer of 1988 to develop expertise in the use of the numerical modeling tool, HCT [64], and to collaborate on the development of a detailed kinetic model for the pyrolysis and oxidation of isobutene. Initial efforts in modeling began, and shortly thereafter, the Fuels Research Group at Princeton obtained through a separate research award a SUN 4 microcomputer. Mr. Held returned to Princeton in August 1988 bringing with him a modified, UNIX, version of the HCT code which LLNL recently developed. Much of the work reported below has been conducted by Mr. Held at Princeton over the past year.

The mechanism currently in use consists of 250 reactions involving 55 species. As the mechanism is not yet in final form, a full listing is not provided here, but will be published later this fall. The reaction numbers listed in this section of the text correspond the numbers internal to this particular mechanism. The species profiles have been computed using the HCT code under the assumptions of constant pressure, adiabatic reaction. Since the initial time of injection is not well defined in the flow reactor experiment, the computed species profiles were matched to the experimental profiles at the point where 50% of the fuel had been consumed.

The H_2 , O_2 , CO submechanism was taken from Yetter et al. [11], the C_1 - C_2 submechanism from Norton et al. [24,25], and the propene submechanism from Westbrook and Pitz [33]. The rates from these submechanisms have not been modified from those presented in the original publications.

Because of the large concentrations of the C_3H_4 isomers measured in the experiments, the submechanism involving these species and the propargyl, methyl vinyl and allyl radicals was expanded from that published in the Westbrook and Pitz [33] propene mechanism. Rate constants for the reactions

involving these species, as well as isobutene and the methyl allyl and butyl radicals have been taken from the literature where available. Two initiation reactions involving isobutene were considered:

The rate of reactions (1) and (2) were both initially taken from Bradley and West [62]. Both reactions are assumed to be in their high pressure limits. However, the proposed activation energy for reaction (2) of 60.7 kcal/mol is significantly below the bond dissociation energy of 85.6 kcal/mol given by Trentwith and Wrigley [65], and thus the rate for reaction (2) is estimated based on an activation energy of 85.6 kcal/mol, and using the same absolute rate at 1150 K.

Hydrogen atom abstraction from isobutene is expected to occur almost exclusively at the allylic sites, with very little abstraction of the vinylic hydrogen atoms [66,67]. Normally, the dominant abstracting radicals in alkane oxidation are H, OH and O, with HO₂ and CH₃ being of secondary importance. However, in olefin oxidation the possibility of radical addition to the unsaturated carbon sites exists as well, and must be considered.

Three possible reactions of isobutene with hydrogen radicals are considered:

The rate constant proposed by Tsang and Walker [66] for reactions (3) and (5) are used without modification. The rate constant for reaction (4) was initially set to Tsang and Walker's value [66], but was adjusted to give agreement with the experimental propene profiles.

At the elevated temperatures of this study, OH is expected to act primarily as an abstractor, and again, the dominant abstraction site is

expected to be the allylic hydrogen atoms.

The low temperature rate constant proposed by Atkinson and Pitts [69] is a factor of 8 lower than that measured at 1259 K by Smith [67]. The rate expression used here was assigned an activation energy of 1.5 kcal/mol and fitted to the high temperature constant of Smith [67].

The acetone detected in the experiments can be accounted for by the Waddington mechanism of OH addition to one of the unsaturated carbon sites [69],

followed by O₂ addition to the resulting radical site,

This complex radical then breaks down to form OH, formaldehyde and acetone.

However, at the temperatures in this study, the lifetime of the $iC_4H_8 + OH$ adduct is expected to be so short that the Waddington mechanism does not adequately explain the quantities of acetone observed experimentally.

Instead, it is proposed that the hydroxyl adduct can undergo a hydrogen atom shift from the hydroxyl group to the radical carbon site, followed by decomposition of the adduct to form either propyl radical and formaldehyde or methyl radical and acetone.

The rate constants used for these reactions are estimates, and assigned a low value due to the apparently small fraction of the fuel which is consumed via this pathway.

The reactions of O atoms with olefins are still a matter of some uncertainty. The only fundamental studies involving these reactions were conducted at low temperatures, and indicated that a complex pathway involving

addition followed by an H atom migration was dominant [70,71], while abstraction played a relatively minor role. Again, both abstraction and addition pathways are included.

The rate constant for reaction (11) is estimated to be 0.1 times the H atom abstraction rate, while that used for reaction (12) is based on the analogous reaction with C_3H_6 and O atoms [33].

The reactions of isobutene with methyl radical are of significance despite their low rate constants (relative to abstraction by hydrogen radicals). The rate constant for abstraction by methyl radicals,

was taken from Bradley and West [62], and is in reasonably good agreement with the values suggested by Pacey and Wimalasena [72] and Leathard and Purnell [66]. Although the addition reactions of methyl radical to isobutene were considered, they were not included as the resulting adduct would decompose rapidly back to the initial reactants by beta scission.

Very little information is available in the literature involving the reactions of the hydroperoxy radical with olefins. For the purposes of this work, a rate constant was estimated for the abstraction of a hydrogen atom from isobutene by HO_2 ,

but it is as yet unclear whether this is the dominant product channel. Since HO_2 is expected to become much more important at higher pressures, this type of reaction requires further study.

Because abstraction of allylic hydrogen atoms is the dominant mechanism of isobutene consumption, a large amount of the methyl allyl radical (iC_4H_7) is produced. The methyl allyl radical is resonantly stabilized, and thus its

unimolecular decomposition has a very high activation energy of 50.07 kcal/mol (cp. 30 kcal/mol for iC_4H_9 decomposition). The rate constant measured by Tsang [73] was used. The products of this reaction, following a beta scission path, are allene and methyl radical.

Initially, the experimental results and a literature survey indicated that this was the only reaction involving the methyl allyl radical. Slagle and Gutman [74] attempted to measure a rate for the reaction of the allyl radical (C_3H_5), which is structurally similar to methyl allyl, with molecular oxygen, but were not able to observe any reaction. Abstraction of a hydrogen atom from the remaining methyl group can likewise be ruled out, as no stable branched C_4H_6 specie exists. However, the presence of methacrolein as an intermediate indicates the possibility of an addition reaction involving methyl allyl and either O or HO_2 radical.

A similar reaction has been postulated for allyl radical and O or HO_2 by Brezinsky et al. [75] and Wilk et al. [76].

The tertiary and iso butyl radicals formed by reactions (4) and (5) primarily decompose unimolecularly via beta scission paths.

The sequence of reactions (4) followed by (18) constitutes the second most important consumption mechanism for isobutene, and is responsible for the majority of the propene production.

As was stated earlier, the submechanism of the C_3H_4 isomers and the radicals associated with them is of much greater importance in the isobutene mechanism than it is in the propene mechanisms. In particular, the propene mechanism of Westbrook and Pitz [33] made no distinction between isomers of

C_3H_4 and the three C_3H_5 isomers although there are significant differences in terms of their thermochemical properties.

The isomerization of allene and propyne has received much attention over the past twelve years, primarily by Lifshitz et al. [77], Hidaka et al. [78], Kakumoto et al. [79], Wu and Kern [80] and Karni et al. [81]. Karni et al. [81] have proposed that the isomerization proceeds via a cyclopropene intermediate, but since the fate of the cyclopropene seems to be almost entirely isomerization to either allene or propyne, it does not appear to be mechanistically significant and is not included here. The forward and reverse rates for

are taken from Hidaka et al. [78], as they are in generally good agreement with the other authors' values.

The reactions of the C_3H_4 isomers with H, OH and O radicals have been studied by several groups, notably Wagner and Zellner [82,83], and Liu et al. [84]. In general, the submechanisms of Wu and Kern [85] and Dagaut et al. [86] have been incorporated into this mechanism, with the following significant modifications. The rate constants for allene + OH recently determined by Liu et al. [84] have been incorporated. The rate constant for the reaction of allyl with molecular oxygen has been set to the lower limit proposed by Slagle et al. [44]. The rate constant of Westbrook and Pitz [33] for the unimolecular decomposition of allyl is used.

The reactions of the various C_3H_5 radicals are critical to the consumption of allene and propyne. Although, as will be discussed shortly, abstraction does occur with the C_3H_4 species, the model predicts that they are primarily consumed by hydrogen radical addition with either subsequent consumption of the C_3H_5 radical or its decomposition back to C_3H_4 and hydrogen radical.

Hydrogen addition to allene occurs at two possible sites:

Analogously for propyne:

Unimolecular decomposition of the allyl radical is expected to be relatively slow due to its resonantly stabilized nature, and would form allene and hydrogen radical. The methyl vinyl isomers are unstable, and rapidly decompose to form

A particularly significant change in this mechanism is that only the 2 methyl vinyl radical is allowed to decompose to form acetylene and methyl radical, while Wu and Kern [85] assert that 1 methyl vinyl will also form those products. Since the beta scission rule for 1 methyl vinyl favors the formation of allene and hydrogen radical, it is unlikely that acetylene and methyl radical will be formed at an appreciable rate. Under pyrolytic conditions then, the dominant method of consumption of the allene formed by the decomposition of the methyl allyl radical must proceed first through the isomerization to propyne.

In an oxidative environment, reactions of the methyl vinyl radicals with molecular oxygen can also occur, following the mechanism proposed by Slagle et al. [86] for 1 methyl vinyl and an assumed analogous mechanism for 2 methyl vinyl.

Abstraction reactions involving allene and propyne have been considered in other work, notably Kiefer et al. [87] and Kanofsky et al. [88]. The experimental data in this study supports the existence of an abstraction

route, due to the presence of both 1,3 butadiene and benzene in the intermediates. Abstraction of a hydrogen atom from either allene or propyne results in the propargyl radical (C_3H_3) and molecular hydrogen. Wu and Kern [80] have proposed the overall reaction

The benzene is assumed to be unreactive, and only the reverse of reaction (28) has been included for its consumption. Wu and Kern's rate constant was used initially and adjusted downward to obtain agreement with the measured benzene levels. The propargyl radical can also recombine with a methyl radical to form 1,2 butadiene or 1 butyne:

Small concentrations of both 1,2 butadiene and 1 butyne were measured in these experiments. However, it has been shown recently [89] that in order to accurately model the pyrolysis of 1,2 butadiene, an isomerization reaction to 1,3 butadiene must be included. Thus it is believed that the significant concentration of 1,3 butadiene measured in the isobutene experiments is in fact due to formation of 1,2 butadiene, followed by the rapid isomerization reaction. For the purposes of the model, all C_4H_6 isomers are assumed to be 1,3 butadiene.

Propargyl can also react with molecular oxygen,

using the rate and mechanism proposed by Slagle and Gutman [44]. However, this reaction does not consume a significant fraction of the propargyl radicals under these conditions.

Because of the relative abundance of the resonantly stable, and therefore long lived allylic radicals, recombination processes can become important. This was evidenced in the experiments by the numerous C_5 and C_6 species

detected. In particular, recombination of methyl allyl and allyl radicals with methyl radicals are modeled as

with the rate constant of Westbrook and Pitz [33] for reaction (33). The rate constant for reaction (32) was chosen to produce a level of 2 methyl 1 butene roughly equivalent to the concentrations of all the C_5 and C_6 combined, and thus simulate the depletion of all the resonantly stable radicals by recombination processes.

Modeling Results

The computed species profiles are shown as the solid curves in Figures 12-19. Because allene and propyne could not be distinguished in the experiments which were analyzed with the DB-1 column, the calculated mole fractions of the two species were summed for comparison to the experiments. The agreement with the experimental data for the fuel consumption and the major intermediates is good over the range of stoichiometries tested. It can be seen, however, that the consumption of allene and propyne late in the reaction is not modeled particularly well. This is not surprising, considering the lack of experimental studies of the oxidation of these species.

The inhibitory effect of isobutene on high temperature oxidation and pyrolysis can be explained on the basis of the reaction mechanism described above. The primary consumption route of the fuel is abstraction of the allylic hydrogen atoms (reactions 3 and 6), which consumes an active radical. In other words, hydrogen and hydroxyl radicals are converted to molecular hydrogen and water respectively, and methyl allyl radical is produced. At high temperatures, the resulting methyl allyl radical then will decompose to form allene and methyl radical. Allene and its isomer propyne are both fairly

unreactive, and when consumed, either form acetylene (and methyl radical), benzene or butadiene, all of which are very unreactive. The methyl radical formed by reaction (15) is also unreactive, when compared to the H or OH radical that was consumed by the initial abstraction reaction. Thus the net effect of the overall sequence is the consumption of one or more active H and OH radicals and the formation of relatively unreactive stable species and methyl radicals. In fact, because of the low C-H bond energy of the allylic sites, the radical pool is expected to abstract preferentially from isobutene when it is present in a mixture of two or more hydrocarbons. Thus by depleting the active radical pool, isobutene will inhibit the overall oxidation process.

It can also be postulated that, due to the resonantly stable character of the methyl allyl radical, the inhibitory effect will become even more prominent as the temperature decreases. The activation energy of reaction (15) is very high (50.07 kcal/mol), and thus its rate will drop far more rapidly than the abstraction reactions' rates as the temperature decreases. Unlike alkyl radicals which will react with molecular oxygen to form peroxy radicals or olefins and HO_2 , the methyl allyl radical appears to be virtually non-reactive with O_2 . Unless another mechanism for the consumption of methyl allyl becomes important, it will not react further except for recombination processes. In this case then, the overall process is simply one of consumption of an active radical through abstraction from isobutene, and the formation of an extremely stable radical which mainly undergoes termination reactions.

Because the two main fuel consumption reactions, abstraction and hydrogen addition, both produce methyl radicals, and the OH and H concentrations are depressed due to the previously discussed mechanisms, isobutene oxidation is heavily dependent on the methyl radical chemistry. At pyrolysis and rich

oxidation conditions, the primary fate of methyl radical is abstraction of a hydrogen to form methane:

As the oxygen concentration is increased, the following reaction sequence begins to compete with the abstraction process:

This is of significance for two reasons. First, the increasing competition of this pathway with oxygen level is responsible for the decrease in methane production rate as seen in Figure 20. And secondly, although strictly speaking this sequence is only chain propagating, the exchange of the methyl and hydroperoxy radicals for hydrogen and hydroxyl radicals is certainly accelerating overall. In fact, the model indicates that reactions (35) and (36) are responsible for the majority of H and OH production in stoichiometric and lean mixtures. This reaction sequence is likely to become even more important in the high pressure oxidation of hydrocarbons, where HO₂ becomes more prevalent. It also is worth noting here that contrary to common belief, the main source of hydroperoxy radical at atmospheric pressure is not from the three body recombination of hydrogen radicals and molecular oxygen,

but rather the abstraction of hydrogen from radical specie by O₂. In particular, the reaction

is the primary source of HO₂ in high temperature, atmospheric pressure isobutene oxidation.

Summary

The detailed kinetic model of isobutene pyrolysis and oxidation accurately reproduces the fuel consumption and major intermediate species profiles.

Closer examination of the model indicates that the observed inhibitory effect of isobutene at high temperatures is due to the depletion of the active radical pool and formation of unreactive stable species and methyl radicals. Because of this, isobutene oxidation and pyrolysis is heavily influenced by the chemistry of methyl radicals.

At this point there are still some unanswered questions relating to isobutene and other hydrocarbon oxidation chemistry. Certainly, the effects of increased pressure upon the fuel consumption mechanism require further study. In particular, very little data exist regarding the reactions of unsaturated hydrocarbons with the hydroperoxy radical; even the product channels for these reactions have yet to be identified. Also, it has been shown that even at atmospheric pressure, the reaction of HO_2 with the methyl radical has a profound effect upon the mechanism of isobutene oxidation.

IV. Expected Progress within the Existing Research Period

The efforts on further development of the variable pressure flow reactor to be completed by the end of the present 24 month effort have been described earlier. As for further experimental in the atmospheric pressure facility and modeling work, we intend to further develop the isobutene model described here and publish the work later this fall. Unfortunately further effort on these aspects of the work will not be possible before middle October, as Mr. Held, the graduate student involved in this work, will be preparing for the general examination from late July through September.

V. References

1. F.L. Dryer and K. Brezinsky, "A Flow Reactor Study of N-Octane and Iso-Octane", Comb. Sci. and Tech. 45,199 (1986).
2. K. Brezinsky and F.L. Dryer, "A Flow Reactor Study of the Oxidation of Iso-Butylene and an Iso-Butylene/N-Octane Mixture", Comb. Sci. and Tech. 45,225, (1986).
3. S.P. Kennedy, K. Brezinsky and F.L. Dryer, "Flow Reactor Oxidation Studies of the Extent of Reaction in Heptane/Iso-Octane Mixtures as a Function of Octane Number", Eastern States Section/The Combustion Institute paper #69, November, 1985. Also see, "Molecular Structure and Component Effects on Knock Related Chemistry", Society of Automotive Engineers International Fuels and Lubricants Meeting and Exposition, Toronto, Ont., Nov. 2 -5, 1987. SAE Paper No. 872109.
4. K. Brezinsky and F.L. Dryer, "The High Temperature Pyrolysis of N-Octane and Iso-Octane", Western States Section/The Combustion Institute paper # 3-5A, April, 1985.
5. R.D. Wilk, D.N. Koert, N.P. Cernansky, "Fuel Structure and Blending Effects on Autoignition", Knock Working Group Meeting Drexel University, Philadelphia, PA, May 5,6, 1987. Also Western States Sectional Meeting of the Combustion Institute, Salt Lake City, UT, March 21,22, 1988. Paper No WSSCI 88-52.
6. J.R. Smith, R.M. Green, C.K. Westbrook and W.J. Pitz, "An Experimental and Modeling Study of Engine Knock", Twentieth First International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1985. p 91.
7. R.M. Green, N. Cernansky, W.J. Pitz, and C.K. Westbrook, "The Role of Low Temperature Chemistry in the Autoignition of n-Butane" Society of Automotive Engineers International Fuels and Lubricants Meeting and Exposition, Toronto, Ont., Nov. 2 -5, 1987. SAE Paper No. 872108.
8. F.L. Dryer, "High Temperature Oxidation of CO and CH₄ in a Turbulent Flow Reactor", PhD Thesis, Aerospace and Mechanical Sciences Department, Princeton University, Princeton, NJ, 1972. Report AMS 1034-T.
9. R.A. Yetter, "An Experimental/Numerical Study of Carbon Monoxide - Hydrogen - Oxygen Kinetics with Applications of Gradient Sensitivity Analysis", PhD Thesis, Mechanical and Aerospace Engineering Department, Princeton University, Princeton, NJ, 1985. Report No. MAE 1720-T.
10. R.A. Yetter and F.L. Dryer, "An Experimental Study of the CO-H₂-2O-O₂-N₂ System in a Flow Reactor", Combust. Sci. and Tech., Submitted for Publication, 1989.
11. R.A. Yetter and F.L. Dryer, , "A Comprehensive Kinetic Mechanism for the CO-H₂-2O-O₂-N₂ System", Combust. Sci. and Tech., Submitted for Publication, 1989.

12. F.L. Dryer and I. Glassman, "High Temperature Oxidation of CO and CH₄", Fourteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1973. p. 987.
13. R.S. Cohen, "The High Temperature Oxidation of Ethane", PhD Thesis, Aerospace and Mechanical Sciences, Princeton University, Princeton, NJ. Report No. AMS 1338-T.
14. D.J. Hautman, "Pyrolysis and Oxidation Mechanisms of Propane", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 1979. MAE Report No. 1471-T.
15. D.J. Hautman, F.L. Dryer, K.P. Shug, and I. Glassman, "A Multiple Step Overall Kinetics Mechanism for the Oxidation of Hydrocarbons, Comb. Sci. and Tech., 25, 219 (1981).
16. F.L. Dryer, and I. Glassman, "Combustion Chemistry of Chain Hydrocarbons", Progress in Astronautics and Aeronautics, American Institute of Aeronautics and Astronautics, New York, 62, 55 (1979).
17. W.M. Proscia, "High Temperature Flow Experiments and Multi-Step Overall Kinetics for the Oxidation of High Carbon Number Paraffin Hydrocarbons", M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 1983. MAE Report No. 1625-T.
18. C.K. Westbrook, F.L. Dryer, and K.P. Shug, "A Comprehensive Mechanism for the Pyrolysis and Oxidation of Ethylene, Nineteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1983. p. 153.
19. E.J. Burke, "A Study of the High Temperature Oxidation of 1,3 Butadiene", MSE Thesis, Mechanical and Aerospace Engineering Department, Princeton University, Princeton, NJ. MAE report No. 1664-MAE.
20. T.J. Held, F.L. Dryer, and K. Brezinsky, "High Temperature Oxidation of Isobutene", Eastern States Sectional Meeting of the Combustion Institute, Clearwater Beach, FL, Dec. 5-7, 1988. Updates presented at the Knock Working Group Meeting, Princeton University, Princeton, NJ, May 11, 12, 1989.
21. M.B. Colket III, "The Pyrolysis and Oxidation of Acetaldehyde", PhD Thesis, Aerospace and Mechanical Sciences Department, Princeton University, Princeton, NJ, 1974.
22. D. Aronowitz, "The Pyrolysis and Oxidation of Methanol", PhD Thesis, Department of Chemistry, Princeton University, Princeton, NJ, 1979.
23. D. Aronowitz, R.J. Santoro, F.L. Dryer, and I. Glassman, "Kinetics of the Oxidation of Methanol: Experimental Results, Mechanistic Concepts, and Global Modeling", Nineteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1979. p. 633.
24. T.S. Norton and F.L. Dryer, "Some New Observations on Methanol Oxidation Chemistry", Comb. Sci. and Tech., 63, 107 (1989).
25. T.S. Norton and F.L. Dryer, "A Comprehensive Kinetic Mechanism for the Pyrolysis of Methanol", Int. J. Chem. Kin., 1989. Accepted for Publication.

26. S. Hochgreb and F.L. Dryer, "Preliminary Results on the Pyrolysis and Oxidation of Formaldehyde in a Flow Reactor", Eastern States Sectional Meeting of the Combustion Institute, Clearwater Beach, FL, Dec. 5-7, 1988.
27. K. Brezinsky, "The High Temperature Oxidation of Aromatic Hydrocarbons", Prog. Energy Combust. Sci., 12, 1 (1985).
28. C.K. Westbrook, J. Creighton, J. Lund, and F.L. Dryer, "A Numerical Model of Chemical Kinetics of Combustion in a Turbulent Flow Reactor", J. Phys. Chem., 81, 2542 (1977).
29. C.K. Westbrook and F.L. Dryer, "A Comprehensive Mechanism for Methanol Oxidation", Comb. Sci. and Tech., 20, 125 (1979).
30. C.K. Westbrook and F.L. Dryer, "Chemical Kinetics and Modeling of Combustion Processes", Eighteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1981. p. 749.
31. C.K. Westbrook, and F.L. Dryer, "Chemical Kinetic Modeling of Hydrocarbon Combustion", Prog. Energy Combust. Sci, 10,1 (1984).
32. E.I. Axelsson, K. Brezinsky, F.L. Dryer, W.J. Pitz, and C.K. Westbrook, "Chemical Kinetic Modeling of the Oxidation of Large Alkane Fuels: n-Octane and Iso-Octane", Twenty-First International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1988. p. 783. Also see "A Detailed Kinetic Mechanism for Oxidation of n-Octane and Iso-Octane, Lawrence Livermore National Laboratory Report UCRL-94449 (1986).
33. C.K. Westbrook and W.J. Pitz, "A Comprehensive Chemical Kinetic Reaction Mechanism for Oxidation and Pyrolysis of Propane and Propene", Comb. Sci and Tech., 37, 117 (1984).
34. W.J. Pitz, C.K. Westbrook, W.M. Proscia, and F.L. Dryer, "A Comprehensive Chemical Kinetic Reaction Mechanism for the Oxidation of n-Butane, Twentieth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1984. p. 831.
35. R.D. Wilk, "Preignition Oxidation Characteristics of Hydrocarbon Fuels", PhD Thesis, Department of Mechanical Engineering and Mechanics, Drexel University, Philadelphia, PA, June, 1986.
36. E.W. Kaiser, C.K. Westbrook, and W.J. Pitz, "Acetaldehyde Oxidation in the Negative Temperature Coefficient Regime: Experimental and Modeling Results", Int. J. Chem. Kinet., 18, 655 (1986).
37. R.D. Wilk, N.P. Cernansky, W.J. Pitz, and C.K. Westbrook, "Propene Oxidation at Low and Intermediate Temperatures: A Detailed Chemical Kinetic Study, Comb. and Flame. In Press, 1988.
38. W.J. Pitz, R.D. Wilk, C.K. Westbrook, and N.P. Cernansky, "The Oxidation of n-Butane at Low and Intermediate Temperatures: an Experimental and Modeling Study", Western States Section/The Combustion Insititute, Salt Lake City Utah, Mar. 21-22, 1988. Also available as Lawrence Livermore National Laboratories Report UCRL 98402 (1988).

39. W.R. Leppard, "A Detailed Kinetics Simulation of Engine Knock", Comb. Sci. and Tech., 43, 1 (1985).
40. C.K. Westbrook, J. Warnatz, and W.J. Pitz, "A Detailed Chemical Kinetic Reaction Mechanism for the Oxidation of Iso-Octane and n-Heptane over an Extended Temperature Range and Its Application to Analysis of Engine Knock", Twenty Second International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. 1989. p. 893
41. W.J. Pitz, Presentation and Discussion at the Knock Working Group Meeting, Drexel University, Philadelphia, November 7,8 1988, and Princeton University, Princeton, NJ, May 11,12, 1989.
42. S.W. Benson, "The Kinetics and Thermochemistry of Chemical Oxidation with Application to Combustion and Flames", Prog. Energy Combust. Sci., 7, 125 (1981).
43. S.W. Benson, "Cool Flames and Oxidation: Mechanism, Thermochemistry, and Kinetics", Oxidation Comm., 2, 169 (1982).
44. F.W. Williams, and R.S. Sheinson, "Manipulation of Cool and Blue Flames in the Winged Vertical Flow Tube", Comb. Sci. Tech., 7, 85 (1973).
45. D.M. Newitt, and L.S. Thornes, J. Chem. Soc., 1656 (1937). See also Reference 41.
46. N.N. Semenov, Some Problems in Chemical Kinetics and Reactivity, Princeton University Press, Princeton, NJ, 1958, Chapter VII.
47. I.R. Slagle, J-Y Park, and D. Gutman, "Experimental Investigation of the Kinetics and Mechanism of the Reaction of n-Propyl Radicals with Molecular Oxygen From 297 K to 635 K", Twentieth International Symposium on Combustion, The Combustion Institute, Pittsburgh, 1985. pp.733.
48. A. Fish, In Organic Peroxides; Swern, D. Ed.; Wiley-Interscience, New York, 1970; Vol.1, pp 141-198.
49. P.G. Lignola and E. Reverchon, "Dynamics of n-Heptane and Iso-Octane Combustion Processes in a Jet Stirred Flow Reactor Operated under Pressure", Comb. and Flame, 62, 1772 (1986).
50. K. Chinnick, C. Gibson, and J.F. Griffiths, "Isothermal Interpretations of Oscillatory Ignition during Hydrogen Oxidation in an Open System I. Analytical Predictions and Experimental Measurements of Periodicity, Proc. R. Soc. Lond., A405, 117 (1986).
51. K. Chinnick, C. Gibson, and J.F. Griffiths, "Isothermal Interpretations of Oscillatory Ignition during Hydrogen Oxidation in an Open System II. Numerical Analysis, Proc. R. Soc. Lond., A405, 129 (1986).
52. H. Hu and J. Keck, "Autoignition of Adiabatically Compressed Combustible Gas Mixture", Society of Automotive Engineers International Fuels and Lubricants Meeting and Exposition, Toronto Ont., Nov. 2-5, 1987. SAE Paper No. 872110.

53. W.R. Leppard, Presentation and Personal Communication, Knock Working Group Meeting, Princeton University, Princeton, NJ, May 11, 12, 1989.
54. S.W. Benson, "Combustion, A Chemical and Kinetic View", Twenty-First International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1986. p.703
55. E. Meyer, H.A. Olschewski, J. Troe, and H.Gg. Wagner, "Investigation of N_2H_4 and H_2O_2 Decomposition in Low and High Pressure Shock Waves", Twelfth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1969. pp. 345.
56. G. Linteris, R.A. Yetter, K. Brezinsky, F.L. Dryer, and I. Glassman, "Preliminary Hydroxyl Radical Concentration Measurements in Moist Carbon Monoxide Oxidation in the Princeton Flow Reactor", Eastern States Sectional Meeting of the Combustion Institute, Clearwater Beach, FL, Dec. 4-7, 1988.
57. E. Chang, "A Study of the Axial Flow Velocity Characteristics in a Flow Reactor using Hot Wire Techniques", Undergraduate Independent Work Report, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton NJ, May 1989.
58. G.Skirrow and A.Williams, "The Gas Phase Oxidation of Isobutene", Proc. Roy. Soc. 1962, 268A, 537.
59. F.Barronet, G.M. Come, and M. Niclaus, "Inhibition et Auto-Inhibition de la Pyrolyse du Neopentane par L'Isobutene", J. Chem. Physique 1974, 71, 1214.
60. T.S.Norton, and F.L. Dryer, "Some Preliminary Observations on the High-Temperature Oxidation of Tert-butyl Alcohol and Methyl Tert-butyl Ether", Proceedings of the Eastern Section of The Combustion Institute, Fall Technical Meeting, 1985, 70-1.
61. R.R. Baker, R.R. Baldwin and R.W. Walker, "Addition of i-Butane to Slowly Reacting Mixtures of Hydrogen and Oxygen at 480 C", J. Chem. Soc., Faraday I, 1978, 74, 2229.
62. J.N. Bradley and K.O. West, "Single-Pulse Shock Tube Studies of Hydrocarbon Pyrolysis, Part 6 - Pyrolysis of Isobutene", J. Chem. Soc., Faraday I 1976, 72, 558.
63. F. Lipari and S.J. Swarin, "Determination of Formaldehyde and Other Aldehydes in Automobile Exhaust with an Improved 2,4-Dinitrophenylhydrazine Method", J. Chromatog. 1982, 247, 297.
64. C.M. Lund, "HCT - A General Computer Program for Calculating Time Dependent Phenomena Involving One-Dimensional Hydrodynamics, Transport, and Detailed Chemical Kinetics", University of California, Lawrence Livermore National Laboratory Report UCRL-52504, August 1978.
65. A.B. Trentwith and S.P. Wrigley, "Dissociation of 2-Methylbut-1-ene and the Resonance Energy of the 2-Methyl allyl Radical", J. Chem. Soc., Faraday I 1977, 73, 817.

66. W. Tsang and J.A. Walker, "Mechanism and Rate Constants for the Reactions of Hydrogen Atoms with Isobutene at High Temperatures", Twenty Second International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. 1989.
67. C.P. Smith, "Laser Pyrolysis Studies of OH Reaction Rates with Several Butenes at 1200K", Int. J. Chem. Kin. 1987, 19, 269.
68. R. Atkinson and J.N. Pitts, "Rate Constants for the Reaction of OH Radicals with Propylene and the Butenes over the Temperature Range 297-425K", J. Chem Phys. 1975, 63, 3591.
69. D.J.M. Ray, R.R. Diaz, and D.J. Waddington, "Gas Phase Oxidation of Butene-2: The Role of Acetaldehyde in the Reaction", Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1973, p.259.
70. J.R. Kanofsky, D. Lucas, and D. Gutman, "Direct Identification of Free-Radical Products of O-Atom Reactions with Olefins, Using High-Intensity Molecular Beams", Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1973, p.285.
71. R.J. Cventanovic, Can. J. Chem. 1955, 23, 1375.
72. P.D. Pacey and J.H. Wimalasena, "Kinetic Study of Neopentane during its Induction Period", J. Phys. Chem. 1980, 84, 2221.
73. W. Tsang, "Pyrolysis of 2,4-Dimethylhexene-1 and the Stability of Isobutenyl Radicals", Int. J. Chem. Kin. 1973, 5, 929.
74. I.R. Slagle, J.Y. Park, M.C. Heaven, and D. Gutman, "Kinetics of Polyatomic Free Radicals Produced by Laser Phtolysis. 3. Reaction of Vinyl Radicals with Molecular Oxygen", J. Amer. Chem. Soc. 1984, 106, 4356.
75. K. Brzinsky, E.J. Burke, and I. Glassman, "The High Temperature Oxidation of Butadiene", Twentieth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1984. p.613.
76. R.D. Wilk, N. Cernansky, and R.S. Cohen, "An Experimental Study of Propene Oxidation at Low and Intermediate Temperatures", Combust. Sci. and Tech. 1987, 52, 39.
77. A. Lifshitz, M. Frenklach and A. Burcat, "Pyrolysis of Allene and Propyne behind Reflected Shocks", J. Phys. Chem. 1976, 80, 2437.
78. Y. Hidaka, T. Chimora, and M. Suga, "Isomerization of Propyne to Allene in Shock Waves", Chem. Phys. Lett. 1985, 119, 435.
79. T. Kakumoto, T. Ushirogouchi, K. Saito, and A. Imamura, "Isomerization of Allene and Propyne in Shock Waves and ab Initio Calculations", J. Phys. Chem. 1987, 91, 183.
80. C.H. Wu and R.D. Kern, "Shock-Tube Study of Allene Pyrolysis", J. Phys. Chem. 1987, 91, 6291.

81. M. Karni, I. Oref, S. Barzilai-Gilboa, and A. Lifshitz, "Isomerization of Cyclopropene to Allene and Propyne at Elevated Temperatures. Experimental, ab Initio, and Model Calculations", J. Phys. Chem. 1988, 92, 6924.
82. H.Gg. Wagner and R. Zellner, "Reaktionen von Wasserstoffatomen mit ungesättigten C₃-Kohlenwasserstoffen. II. Die Reaktion von H-Atomen mit Methylacetylen", Ber. Bunsen-Ges. Phys. Chem. 1972a, 76, 518.
83. H.Gg. Wagner and R. Zellner, "Reaktionen von Wasserstoffatomen mit ungesättigten C₃-Kohlenwasserstoffen. III. Die Reaktion von H-Atomen mit Allen", Ber. Bunsen-Ges. Phys. Chem. 1972b, 76, 667.
84. A. Liu, W.A. Mulac, and C.D. Jonah, "Rate Constants for the Gas-Phase Reactions of OH Radicals with 1,3-Butadiene and Allene at 1 atm in Ar and over the Temperature Range 305-1173 K", J. Phys. Chem. 1988, 92, 131.
85. P. Dagaut, M. Cathonnet, and J.C. Boettner, "Experimental Study and Kinetic Modeling of Propene Oxidation in a Jet Stirred Flow Reactor", J. Phys. Chem. 1988, 92, 3.
86. I.R. Slagle, J.R. Bernhardt, and D. Gutman, "Kinetics of the Reactions of Unsaturated Free Radicals (Methylvinyl and i-C₄H₃) with Molecular Oxygen, Twenty Second International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. 1989. p. 893
87. J.H. Kiefer, M.Z. Al-Alami, and K.A. Burdach, "A Shock Tube, Laser-Schlieren Study of Propene Pyrolysis at High Temperatures", J. Phys. Chem. 1982, 86, 808.
88. J.R. Kanofsky, D. Lucas, F. Pruss and D. Gutman, "Direct Identification of the Reactive Channels in the Reactions of Oxygen Atoms and Hydroxyl Radicals with Acetylene and Methylacetylene", J. Phys. Chem. 1974, 78, 311.
89. R.D. Kern, H.J. Singh, and C.H. Wu, "Thermal Decomposition of 1,2 Butadiene", Int. J. Chem. Kin. 1988, 20, 731.

VI. Figures

- 1a Kinetic Features of the Propane - Oxygen System in the Cool Flame Regions. To the left of the cool flame region are regions of slow reaction. Regions to the Right of the cool flame region are where "hot" ignition occurs. Data are for a 500 cm³ quartz vessel and equi-molar mixtures of propane and oxygen. Figure taken from Ref. 44.
- 1b Effect of initial Temperature and Equivalence Ratio on the Chemical Induction Period. Data are for a 1395 cm³ quartz vessel and mixtures of propane and air at the initial pressure of 600 torr. Figure taken from Reference 35.
- 2 "Turnover" Temperature as a Function of Reaction Pressure for a Stoichiometric mixture of Butane and Air. Data are obtained from Eq. 1.4 fitted to replicate the measured value reported in Ref. 35 at 600 Torr. Developed in this Research Effort.
- 3 Temperature for a Constant Ratio of the Rate of H Atom Abstraction by Molecular Oxygen and the Rate of Radical Beta Scission for n-Butyl Radicals as a Function of Reaction Pressure. Results are for a Stoichiometric mixture of butane - air. Developed in this Research Effort.
- 4 Temperature for a Constant Ratio of H atom addition to Oxygen and the H atom - Oxygen Metathesis Reaction as a Function of Pressure. Developed in this Research Effort.
- 5 Temperature for a Constant Ratio of the Rate of H Atom Abstraction from n-Butane and the Total Rate of Reaction of H atoms with Molecular Oxygen as a Function of Reaction Pressure. Data are for a stoichiometric mixture of butane and air. Developed in this Research Effort.
- 6 Comparison of regions defined by kinetic constraints shown in Figures 2,3,and 5 with the Pressure-Temperature Regime Experienced by the Fuel air Charge in Spark Ignition Engines and the Estimated Pressure-Temperature Conditions When Engine Knock is Experienced. Engine charge regime is shown in dashed lines. Experimental conditions in engines at which knock typically occurs are shown as data points. A conservative operational window for the new variable pressure reactor is also shown in dotted lines. (The reactor facility is designed for operating pressures as high as 30 atms, but the existing liquid nitrogen vaporization system can not deliver gaseous nitrogen carrier at pressures greater than about 20 atm.)
- 7a Conceptual Design Schematic of the New Variable Pressure Flow Reactor.
- 7b Crosssectional Line Drawing of the Variable Pressure Reactor Pressure Shell and Interior.
- 8a Block Diagram of the Control System for the New Variable Pressure Flow Reactor.
- 8b Gas Flow Control Schematic for the New Variable Pressure Flow Reactor
- 9 Operational Reaction Test Time as Function of Flow Reynolds Number and

Operating Pressure for a 10 cm Diameter Reactor Duct.

- 10 Operational Reaction Test Time as a Function of Flow Reynolds Number and Flow Temperatures and 15 Atmospheres Operating Pressure for a 10 Centimeter Diameter Reactor Tube.
- 11 Predicted Reaction Times for a 1% O_2 , Stoichiometric Mixture of Oxygen and n-Butane in Nitrogen at 10 atmospheres Pressure. Predictions were performed by W. Pitz of LLNL using an updated mechanism of that published in Reference 33.
- 12 Concentrations of Fuel and Major Intermediates for Isobutene Oxidation. $T_0 = 1140$ K, $\Phi = 0.91$. Curves represent computed results, and symbols represent experimental results.
- 13 Concentrations of Minor Intermediates for Isobutene Oxidation. $T_0 = 1140$ K, $\Phi = 0.91$.
- 14 Concentrations of Fuel and Major Intermediates for Isobutene Oxidation $T_0 = 1142$ K, $\Phi = 1.29$.
- 15 Concentrations of Minor Intermediates for Isobutene Oxidation $T_0 = 1142$ K, $\Phi = 1.29$.
- 16 Concentrations of Fuel and Major Intermediates for Isobutene Oxidation. $T_0 = 1139$ K, $\Phi = 0.42$.
- 17 Concentrations of Minor Intermediates for Isobutene Oxidation. $T_0 = 1139$ K, $\Phi = 0.42$.
- 18 Concentrations of Fuel and Major Intermediates for Isobutene Pyrolysis, $T_0 = 1150$ K.
- 19 Concentrations of Minor Intermediates for Isobutene Pyrolysis. $T_0 = 1150$ K.
- 20 Concentration of CH_4 Versus the Percentage of Fuel Reacted for Three Stoichiometries.
- 21 Concentration of C_4 Versus the Percentage of Fuel Reacted for Three Stoichiometries.
- 22 Concentration of C_3H_6 Versus the Percentage of Fuel Reacted for Three Stoichiometries.
- 23 Concentration of CO Versus the Percentage of Fuel Reacted for Three Stoichiometries.

FIGURE 1A

FIGURE 1B

Turnover Temperature (Butane)

(per Benson)

Fitted Through Data of Wilk et al

FIGURE 2

n-Butyl, Intermediate Temperature

FIGURE 3

FIGURE 4

H + RH vs H + O2

Ratio of Rates

FIGURE 5

FIGURE 6

Test Section

FIGURE 7A

Sliding Fuel Injection
and mixing section

FIGURE 7B

**FUELS
COMBUSTION
LABORATORY**
Department of Mechanical
& Aerospace Engineering
PRINCETON UNIVERSITY

SCALE : 1"=1'
DATE : 05/01/88
DESIGNED : M. VERONISSE
DRAWN : M. VERONISSE
CHECKED :
NO. REV'D :
MATERIAL :

TOLERANCES UNLESS SPECIFIED
XX = 1.02 IN. ± 0.02 (INCHES)
FRACTIONS = 1/32 IN. ± 0.001 (INCHES)
FINISH UNLESS SPECIFIED

TITLE :
HP Flow Reactor Layout

PART NO. :
Dwg. NO. : 1-1

FIGURE 8A

FIGURE 8B

FUELS COMBUSTION LABORATORY Department of Mechanical & Aerospace Engineering POWERSON UNIVERSITY		SCALE : _____ DATE : _____ DESIGNED : M. Verma DRAWN : M. Verma CHECKED : _____ NO. REV : _____ MATERIAL : _____	TOLERANCES UNLESS SPECIFIED XX = ±.02 XX = ±.002 (HIPS) FRACTIONS = 1/32 ANGLES = 1° FINISH UNLESS SPECIFIED ✓
TITLE : Process Flow Diagram		PART NO. : _____ DWG. NO. : _____	

Pressurized Flow Reactor

800 K, 10 cm ID, 1 M Long

FIGURE 9

Pressurized Flow Reactor

15 atm, 10 cm ID, 1 m Long

FIGURE 10

HCT Predicted Butane Reaction Times

1% O₂, stoich., 10 atm

FIGURE 11

FIGURE 12

FIGURE 13

FIGURE 14

FIGURE 15

FIGURE 16

FIGURE 17

FIGURE 18

FIGURE 19

FIGURE 20

FIGURE 21

FIGURE 22

FIGURE 23

APPENDIX A

The Flow Reactor Experiment

A flow reactor will be used to obtain the intermediate temperature, atmospheric pressure kinetic data required to complete this proposed effort. The reactor is designed to approximate a steady, one-dimensional and adiabatic reacting flow with negligible radial gradients of species and energy. Gaseous samples are withdrawn from the reactor at up to fifteen discrete locations along its longitudinal axis with a variable temperature, convection quenched, isothermal sample acquisition and storage system. The sampling system can operate at temperatures between 25°C and 80°C, but the studies presented here were conducted at about 70°C. The elevated storage temperature prevents the condensation of high boiling point intermediate species and prevents polymerization reactions. The storage system interfaces with a microprocessor controlled gas chromatograph for fully automatic analysis of the stored samples. In addition, a continuous analysis train has been developed for determining CO, CO₂, O₂, and H₂ concentrations in the sample stream from which the discrete samples are obtained. The flow reactor, its sampling system, and the analytical instrumentation are discussed in detail below.

The Princeton Flow Reactor

The Princeton flow reactor, developed in this laboratory and extensively documented elsewhere [A-1 - A-3] is shown schematically in Figure A-1. Fundamentally, it consists of a cylindrical quartz duct through which hot inert carrier gas (nitrogen) flows at high velocities. A small fraction of the carrier (5-10%) is diverted through an arc plasma discharge, which heats and partially ionizes it. The hot, partially ionized gas is remixed with the bulk of the nitrogen in a plenum chamber, where recombination results in metastable nitrogen molecules (N₂*). Collisional de-excitation of the meta-stable N₂ is necessary to prevent its further reaction with O₂:

and to promote this de-excitation the carrier flow continues through a high surface area, ceramic honeycomb section, and emerges as inert N₂. Because the ceramic section has a large thermal capacity, the temperature of the nitrogen leaving the section is constant, ($\pm 1\text{K}$, relative) even though fluctuations in the power output from the plasma torch itself ($\pm 2\%$) results in temperature fluctuations in the nitrogen entering the section. Desired reaction temperatures (800-1300 K) are achieved by variation of the split ratio of the nitrogen flow and of the power to the plasma torch.

Oxygen is injected into the carrier gas upstream of a converging/diverging inlet section and is well mixed with the carrier gas before it reaches the throat of the section. At that point, gaseous fuel is injected through four radially opposed quartz injector tubes. The technique used to pre-vaporize liquid fuel species is described later.

The high velocity radial injection of gaseous fuel into the flowing carrier provides for rapid mixing of the fuel with the oxygen/carrier gas stream. In

Figure A-1

CHEMICAL KINETIC FLOW REACTOR

the original design of this flow reactor [A-1], the carrier flow velocity are restricted to a range of values for which turbulent flow conditions would exist within the flow reactor section. By the time the gases have traversed the diverging section of the inlet nozzle, well-mixed, fully-developed, small scale, high intensity turbulent flow has been established: simple one-dimensional plug flow relations therefore provide a good approximation to the fluid mechanics in the main reactor duct. Through proper control of carrier gas temperature, mixture ratio, and total gas flow rate, a steady reaction zone extending over approximately a meter in length can be established which represents total chemical reaction times between 10 and 150 msec. Simple conversion of relative distance to time is easily made by using perfect gas laws at atmospheric pressure (average molecular weight is very near that of nitrogen) and experimentally measured carrier mass flow, duct crosssection area and local gas temperature. More recently, mean velocity along the axis of the reactor duct has been experimentally determined using static pilot probes [A-4]. The use of small initial concentrations of both fuel and oxidizer and the spreading of the reaction zone over a meter gives rise to longitudinal gradients small enough for diffusion of mass and energy along the length of the duct to be neglected with respect to convection [A-5]. Furthermore, the dilute nature of the reaction and in particular, the limitations therefore imposed on the turbulent fluctuations of temperature from the mean ($\pm 1\%$) limits any turbulent fluctuation coupling [A-6] with chemical kinetics to be negligible. Measured kinetics have been found to be independent of Flow Reynolds number within the limits of experimental accuracy ($\pm 10\%$).

The relatively large duct diameter (10.16 cm) results in a small surface to volume ratio and minimizes wall effects. In fact the dilute nature of the flow and the large reactor diameter have permitted the requirement for turbulence to produce "plug" flow characteristics to be relaxed. Experiments at low flow velocities (normally laminar mean Reynold's number range) have shown data along the axis of the flow reactor are not modified by radial diffusion or wall effects. Chemical residence times have been extended from the turbulent operating restriction (< 150 msec) to over 600 msec.

Adiabaticity is approximated by heating and insulating the inlet section and main reactor duct, so that the walls are quickly equilibrated to the inlet temperature of the carrier gas. The wall temperature is monitored at four locations along the length of the duct by Pt/Pt 13% Rh thermocouples placed in an air gap between the heaters and the duct.

The flow reactor experiment requires that fuels be in a gaseous state, and thus any liquid material is pre-vaporized using an evaporator. The evaporator is shown schematically in Figure A-2. Nitrogen pressure on the fuel in the storage tank forces metered amounts of liquid fuel through an orifice onto a heated finger, which is at a temperature above the boiling point of the fuel. The finger vaporizes the fuel, and a pressure builds up in the heated, insulated evaporator chamber. This pressure forces a flow of fuel vapor through a critical orifice (330 micrometer diameter) into a manifold which, in turn, feeds the radical injector tubes. Eventually, a steady state is established in which the liquid fuel flow into the evaporator is equal to the gaseous fuel flow out. In order to prevent condensation in the transfer lines leading into the reactor, the flow lines from the evaporator are heated and insulated and a small amount of heated nitrogen is mixed with the gaseous fuel flow at the evaporator exit.

EVAPORATOR SCHEMATIC

FIGURE A-2

Adjustment of the evaporator pressure, and hence fuel flow to the reactor, is obtained by control of the liquid fuel flow to the evaporator and of the evaporator temperature. The pressure of the evaporator tank, the pressure of the manifold and various evaporator temperatures are monitored to aid in this control.

In summary, the flow reactor provides a well-defined and well-monitored reaction zone which can be accurately represented as:

1. constant pressure (small energy release, low Mach number flow system)
2. one-dimensional (fully-developed turbulent flow)
3. quasi-steady
4. homogeneous (wall effects negligible)
5. adiabatic
6. with negligible longitudinal diffusion of mass and energy

A photograph of the reactor system appears in Figure A-3. These operation characteristics and the reproducibility of the experimental data will be discussed later in this appendix.

Data Acquisition

Extractive and Immersion Measurements

Mean temperature, and species profiles are measured along the length of the reactor duct. The temperature is measured, with a silica coated Pt 30% Rh/Pt 6% Rh alloy thermocouple with a bead diameter of 38 micrometers and a spatial resolution of about twenty bead diameters. Dryer [A-2] has discussed this technique at length in his Ph.D. thesis.

The gas sampling techniques, in principle, are also those used in earlier flow reactor studies: combustion gases are withdrawn continuously from the reactor with a hot water cooled, water convection quenched probe. The sample stream can be analyzed continuously and discrete volumes can also be extracted from the sample stream and stored for later analysis by a gas chromatograph.

The gas sample probe itself appears in section A of Figure A-1 and is constructed of three concentric type 316 stainless steel tubes. The two outer tubes provide passages for the hot water (60-90°C) used to convection cool the flowing gas sample and maintain the mechanical integrity of the probe. The gas sample quench is accomplished purely by convection heat transfer at a rate greater than 10⁴ K/sec (estimated; see [A-2]). The sample is transferred from the probe to the sampling assembly through heated (thermostated) teflon lines by a heated stainless steel bellows pump. The flow exiting the pump is at approximately 2 atmospheres pressure supplying sample flow to one or several multiloop sampling valves (described later) and the continuous analysis train.

PRINCETON TURBULENT FLOW REACTOR

Figure A-3

The continuous analysis system (Figure A-4) provides two principle advantages in conducting flow reactor research:

1. it permits accurate placement of the reaction zone within the reactor and thus optimizes the experiment for the ranges of extent of reaction to be studied.
2. it relieves several complications imposed when simultaneous gas chromatographic analysis of light permanent gases H_2 , CO, CO_2 and higher molecular weight hydrocarbons is required.

Carbon monoxide and carbon dioxide are determined using non-dispersive infrared analysis (Beckman, Inc.). Oxygen is determined using a thermomagnetic technique (Leeds and Northrup). A measurement of hydrogen is obtained by catalytic conversion of the dried sample stream and determination of the resulting water vapor by a Dupont Acoustic water vapor analyzer.

What has recently advanced the analytical technology to deal with the oxidation of higher carbon number paraffins and aromatics is the development of a system which would simultaneously acquire and store up to two discrete, heated samples at each longitudinal position sampled in the flow reactor. This technique permits simultaneous use of a Hewlett Packard HP5840 gas chromatograph (GC) for quantitative analysis of the sample for hydrocarbons and of a HP 5895 gas chromatography/mass spectrometer (GC/MS) for the respective specie identifications (both by column retention time and mass fractionation patterns).

Successful discrete chemical sampling involves satisfactory accomplishment of each of the following goals:

1. isolation of a flow of reactive media from a specific point in the reaction environment.
2. prevention of further chemical or thermodynamic alteration of the contained species.
3. introduction of a defined quantity of this sample, intact, to an analytical instrument.

The heated sampling system [A-3] which is now commonly used has several distinct advantages. It interfaces with all analytical equipment in a manner completely analagous to its GC interface, and allows ready identification of species which are impractical to identify with a GC alone and which would be lost to condensation at room temperature.

A heated storage temperature of $70^\circ C$ has a second advantage related to the integrity of the stored sample: by preventing polymerization reactions associated with the storage of formaldehyde at room temperature, it should allow accurate formaldehyde analysis. Condensation of other, low vapor pressure species is also prevented by heated storage.

Furthermore, the heated sampling system has the advantages of preventing exposure of stored samples to light and to adsorptive surfaces (e.g. mercury, synthetic rubber), both of which occurred in the older system. All surfaces

Figure A-4

which contact sample gases in the heated sampling system are stainless steel, so the exposure to light that resulted from storage in glass bottles on an exposed sampling rack is circumvented. Furthermore, gases are pressurized for injection with a stainless steel welded bellows pump and not with the mercury system previously in use.

Operation of the heated sampling storage and chromatographic injection facilities are as follows (Figure A-5). Combustion gases are withdrawn from the reactor through the probe and a length of heated line by a heated stainless steel welded bellows pump. The bellows pump raises the pressure of the sampled gases to approximately two atmospheres pressure, and the flow proceeds through a heated 7 micro filter and temperature equilibrium coils to two sample storage valves. The temperature equilibration coil and the storage valves are contained in separate, portable, thermostatted oven assemblies.

Each storage valve itself (Figure A-6) is a Valco 32 port, 16 position pneumatically actuated valve fitted with sixteen stainless steel sample storage loops. Each of the valve loops has a pre-determined volume of 12 cc. When the valve is actuated, the flow is switched from one loop to the next, a defined quantity of sample is trapped in the sealed loop (P, V and T are all defined), and the next sample loop is purged. Up to fifteen discrete samples can be stored in this manner, with the remaining loop open to the flow path. Once filled, the multiposition valve system is carried (in its oven) to a gas chromatograph, where the loops are flushed, one by one, into a chromatographic gas sample injection system (Figure A-7) and injected onto the GC columns for analysis.

A heated 1 cc. single loop sample injection valve is used to determine the sample size for actual analysis. This sample injection valve is connected on the inlet side to the multiposition valve (i.e. to the stored samples) through a length of heated line, and on the outlet side to a manostat/vacuum system. When the multiposition valve is actuated and a new storage loop is exposed to the sample injection system, the gases in the 12 cc. loop, at 2 atmospheres, flow through the 1 cc. secondary sample injection loop until the pressure in the system is equilibrated to .5 atmospheres (controlled by a cartesian manostat). Sufficient excess sample is stored in the multiposition valve loops to assure complete displacement of any residual gases in the secondary sample valve and transfer lines. The .5 cc atm. sample in the secondary sample valve is then injected onto the gas chromatograph columns for analysis. Actuation of both the multiposition valve and the secondary sample valve is controlled by a microprocessor indigenous to the gas chromatograph, so fully automatic analysis of successive samples is possible. This procedure not only assures a constant systematic error, but minimizes sample storage times and reduces dramatically the manpower which must be devoted to the analysis of samples. Previous (manual) injection techniques required operator attention throughout the 25+ hour analysis time required for a complete flow reactor analysis. With the present system interfaced to the gas chromatograph and the GC microprocessor pre-programmed, no additional operator attention is required for complete analysis.

Because the sample injected onto the GC columns is set in the same loop each time, the effects of loop volume variability are eliminated. Sample storage valve leakage problems are also circumvented: since samples are stored at a positive pressure, gases leak out, not in. Any loss of sample at the small

SAMPLE ACQUISITION SYSTEM SCHEMATIC

Figure A-5

INSULATION

MULTIPOSITION VALVE AND OVEN

Figure A-6

SAMPLE ANALYSIS SYSTEM SCHEMATIC

Figure A-7

rates resulting from loop to atmosphere and loop to loop diffusion is not reflected in the sample delivered to the sampling injection valve, since a large volume of sample gas is initially stored. Cross leak distortion of the stored sample has been shown to be less than 1%, even for the lightest gas expected in hydrocarbon oxidation studies (CH_4). Note that since diffusion rates are inversely proportional to the square root of the molecular weight of the diffusing species, errors for most species will be significantly smaller.

In summary, the advantages of this unique sampling storage and chromatographic injection system are:

1. control of the sample acquisition and storage temperatures (up to about 80°C).
2. sample isolation from adsorptive surfaces.
3. sample isolation from light surfaces.
4. automation.

Additional details appear in the recent thesis of Euchner [A-3], and will appear in publication in the near future.

Optical Measurements

The flow reactor has been modified to provide optical access at three axial positions. A schematic of the modified flow reactor is given in Figure A-1. The initial intent of the modification was to permit measurement of hydroxyl radical concentration through absorption of ultra violet radiation. Now that optical access is available, however, other measurements besides OH concentration can conceivably be performed as part of our ongoing progress to detect and measure highly reactive or unstable intermediates. In particular, visible and ultra violet chemiluminescence generally associated with cool and blue flames could in principle be detected in the flow reactor if such phenomena are indeed occurring.

Reproducibility of Experimental Data

We have recently performed two research studies [A-4, A-7] which adequately demonstrate the nature and quality of the experimental data obtained from the flow reactor.

In a study on the elementary combustion chemistry of the $\text{CO}/\text{H}_2/\text{O}_2$ system [A-4], we have performed extensive experiments which involve the turbulent flow reactor and the continuous sampling system. In the performance of some of these experiments we investigated the ability to reproduce the same experimental initial conditions and chemical analysis data by attempting to repeat the same experiment on six occasions over a period of 6 months. The experimental conditions and results are shown in Figure A-8. The precision of these data is clearly evident and indicates of both the ability to reproduce experimental variables and also the continuous sampling instrumentation calibration effects.

Figure A-8

Experimental Profiles of Carbon Monoxide Disappearance for Six Different Flow Reactor Experiments Performed Over a Six Month Period

Initial Temperature 1038 K

X_{CO} .96%

X_{O_2} 1.02%

X_{H_2O} 0.56%

Balance N_2

Pressure 1 atmosphere

Figure A-9 presents the comparison of elementary kinetics calculations performed using accepted literature rate constants and mechanism with experimental measurements on the $\text{CO}/\text{H}_2/\text{O}_2$ system [A-4] (Table A-I). In the four flow reactor experiments (point data), only the initial reaction temperature was changed. The three calculations (line data) performed show very good agreement with the experimental data, even for reaction times approaching 0.6 seconds! It should be emphasized that there was no performance of "empirical fitting" of the model to the data, and no effects of diffusive and turbulent transport or coupling with chemistry were considered in the model. These comparisons therefore support the "pure chemistry" interpretation of flow reactor data. Finally it should be emphasized that the experimental and calculated results are for condition crossing the explosion limit regime for $\text{CO}/\text{H}_2/\text{O}_2$ chemistry at one atmosphere.

A second set of data which demonstrate the precision of the discrete chemical sampling and gas chromatographic analytical results are presented in Figure A-10. These data were performed as part of a recent thesis [A-7] and were obtained from the analysis of samples (16 samples by each valve, one sample in each valve at each sampling position) taken by two sample storage valves in parallel in the flow reactor sampling systems. The 16 loops of each sample valve were then analyzed sequentially, with the analysis of the second valve samples following the first. The chemical analysis thus spanned a period of some 72 hours after the flow reactor experiment had been concluded. The reproducibility of this data is again excellent.

Figure A-9

Comparison of Flow Reactor Experiments (data points) and Elementary Kinetic Calculations (lines) of the Carbon Monoxide Disappearance for the $\text{CO}/\text{H}_2\text{O}/\text{O}_2$ Reaction System:

Pressure 1 atmosphere

X_{CO} 0.93%

Equivalence Ratio 1.0

$X_{\text{H}_2\text{O}}$ ~ 1.4%

Balance Nitrogen

Initial Temperature

diamonds 920K

squares 935K

triangles 950K

circles 960K

Table A-1

CO/H₂/O₂ MECHANISM

	Reaction	A	n	E	B	m	F
1,2	HCO+H=CO+H ₂	2.0E14	0.0	0.0	1.53E-1	0.0	-90.0
3,4	HCO+OH=CO+H ₂ O	1.0E14	0.0	0.0	3.57E-2	0.0	-105.15
5,6	O+HCO=CO+OH	1.0E14	0.0	0.0	3.47E-1	0.0	-87.9
7,8	HCO+O ₂ =CO+HO ₂	3.3E12	0.0	7.0	4.46E-1	0.0	-32.29
9,10	CO+HO ₂ =CO ₂ +OH	1.5E14	0.0	23.65	8.82E-2	0.0	-61.85
11,12	CO+OH=H+CO ₂	1.5E07	1.3	-0.77	8.93E-3	0.0	-22.34
13,14	CO ₂ +O=CO+O ₂	2.78E12	0.0	43.83	8.85	0.0	6.23
15,16	H+O ₂ =O+OH	2.2E14	0.0	16.79	1.26E01	0.0	16.11
17,18	H ₂ +O=H+OH	1.8E10	1.0	8.9	2.17	0.0	1.95
19,20	O+H ₂ O=OH+OH	6.8E13	0.0	18.35	1.08E01	0.0	17.25
21,22	H+H ₂ O=OH+H ₂	9.5E13	0.0	20.3	4.32	0.0	15.15
23,24	H ₂ O ₂ +OH=H ₂ O+HO ₂	1.0E13	0.0	1.8	3.57E-1	0.0	-30.99
25,26	HO ₂ +O=O ₂ +OH	5.0E13	0.0	1.0	7.79E-1	0.0	-55.61
27,28	H+HO ₂ =OH+OH	2.5E14	0.0	1.9	2.08E01	0.0	-38.20
29,30	H+HO ₂ =H ₂ +O ₂	2.5E13	0.0	0.7	4.55E-1	0.0	-57.1
31,32	OH+HO ₂ =H ₂ O+O ₂	5.0E13	0.0	1.0	7.9E-2	0.0	-72.86
33,34	H ₂ O ₂ +O ₂ =HO ₂ +HO ₂	4.0E13	0.0	46.64	4.0	0.0	41.64
35,36	HO ₂ +H ₂ =H ₂ O ₂ +H	7.3E11	0.0	18.7	4.29E-1	0.0	14.95
37,38	O ₂ +M=O+O+M	5.1E15	0.0	115.0	1.09	0.3	115.0
39,40	H ₂ +M=H+H+M	2.2E14	0.0	96.0	7.32E-2	0.0	96.0
41,42	OH+M=O+H+M	8.0E19	-1.0	103.72	8.0E03	-1.0	103.72
43,44	H ₂ O ₂ +M=OH+OH+M	1.2E17	0.0	45.5	1.32E02	0.0	50.57
45,46	H ₂ O+M=H+OH+M	2.2E18	0.0	105.0	1.57E-7	2.0	105.0
47,48	HO ₂ +M=H+O ₂ +M	2.31E15	0.0	45.9	1.4	0.0	46.9
49,50	CO ₂ +M=CO+O+M	5.5E21	-1.0	131.78	9.32E05	-1.0	127.68
51,52	HCO+M=H+CO+M	1.45E14	0.0	19.0	2.87E02	-1.0	17.45

Forward rate coefficients are expressed as $k=AT \exp(-E/RT)$ and equilibrium constants as $K=BT \exp(-F/RT)=k(\text{forward})/k(\text{reverse})$; both in cm³-mole⁻¹-sec-kcal units.

N-BUTANE OXIDATION

Figure A-10

Appendix References

- A-1. Crocco, L., Glassman, I. and Smith, I.E., Jet Propulsion, 1266 (1957).
- A-2. Dryer, F.L., Ph.D. Thesis, Department of Aerospace and Mechanical Sciences, Princeton University, Princeton, NJ (1972).
- A-3. Euchner, J.A., M.S.E. Thesis, Mechanical and Aerospace Engineering Department, Princeton University, Princeton, NJ (1980).
- A-4. Work in Progress under DOE Contract No. DE-AC02-83ER13045 A002 (1983).
- A-5. Westbrook, C.K., Creighton, J., Lund, C. and Dryer, F.L., J. Phys. Chem., 81, 2542 (1977).
- A-6. Gouldin, F.C., Comb. Sci. Tech., 9, 17 (1974).
- A-7. Proscia, W.M., M.S.E. Thesis, Mechanical and Aerospace Engineering Department, Princeton University, Princeton, NJ (1983).