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MENTATION PAGE

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13. ABSTRACT (Maximum 200 words) Future Air Force aircraft fuels will contain chemical constituents that not only contribute to the propulsion of the aircraft but also to the temperature control of both the combustor walls and the aircraft body. Temperature control may require the use of new, endothermic fuels such as methylcyclohexane (MCH). This cycloalkane in the presence of a catalyst dehydrogenates to toluene. The toluene and hydrogen product, containing a small amount of unreacted MCH, fuel the combustor. The burning characteristics of the mixture as well as its temperature stability as it is transferred to the combustor, most likely as a supercritical fluid, are largely unknown. Clarifying the combustion and thermal stability characteristics of both gaseous and supercritical fluid mixtures of toluene and methylcyclohexane has been the focus of the past year's research. Gas phase flow reactor studies of the pyrolysis and oxidation of pure MCH and of the oxidation of mixtures of MCH and toluene have revealed the chemical means by which MCH affects the oxidation chemistry of toluene. Supercritical fluid flow reactor examinations of the thermolysis of MCH and toluene mixtures have suggested chemical routes to deposit formation in the fluid fuels. These results are described in greater detail in this report.					
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FUELS COMBUSTION RESEARCH



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ANNUAL PROGRESS

A) Pyrolysis Studies of Methylcyclohexane and Oxidation Studies of Methylcyclohexane and Methylcyclohexane/Toluene Blends

Endothermic fuels such as methylcyclohexane (mch) have been proposed to cool high speed Air Force aircraft from the intense heat developed during flight not only by sensible heat uptake, but also through the catalytic, endothermic decomposition of the fuel [1]. Mch, in the presence of a catalyst, is endothermically dehydrogenated to toluene and hydrogen to the extent of approximately 226 kJ per mole of mch converted. The toluene and hydrogen produced by this dehydrogenation process become the fuels consumed in the combustor.

Although the toluene and hydrogen is presumed to enter the combustor in the gas phase, the dehydrogenation of the mch occurs in the liquid phase. Liquid phase dehydrogenation studies reveal that the complete conversion of mch is not always achieved [2]. As a result of this incomplete conversion, the fuel consumed in the combustor will be a mixture of mch, toluene, and hydrogen. In fact, the mch may be a substantial portion of the fuel-oxygen mixture within the combustor. Therefore, knowledge of the vapor phase reactions of pure mch is needed to understand the characteristics of mch decay and oxidation in combustor environments. Studies specifically involving the vapor phase oxidation and pyrolysis of mch exist, but their experimental conditions, low temperature [3,4,5] and very low pressure [6], do not represent typical combustor conditions, nor do they present detailed kinetic mechanisms of mch oxidation and pyrolysis [1,7]. Furthermore, since the concentration of each species in the overall fuel mixture will be a function of the extent of conversion of the mch, knowledge of the vapor phase oxidation of various blends of mch, toluene and hydrogen will be necessary to understand fuel mixture ignition characteristics, reaction times, and pollutant formation, as well as any synergistic or inhibitory effects on the overall combustion scheme that may result from the mixing of these fuels. Unfortunately, data on the vapor phase oxidation of blends of these fuels are not readily available. An experimental program aimed at understanding the gas phase combustion chemistry of endothermic fuels and their reaction products commenced.

EXPERIMENTAL

The pure mch pyrolysis and oxidation studies and the mch/toluene blend oxidation studies were performed in the Princeton Atmospheric Turbulent Flow Reactor, a device that has been thoroughly described elsewhere [8,9]. During the experiments, oxygen concentrations were measured on line with a Leeds and Northrup model 7863 thermomagnetic analyzer. Carbon monoxide concentrations were also measured on line using a Beckman model 864 infrared analyzer. Gas temperatures were obtained from an unshielded type B (platinum-30% rhodium/platinum-6% rhodium) thermocouple. Gas samples from the experiments were collected in a water cooled sampling probe, stored in heated sampling valves, and then analyzed in a Hewlett Packard model 5890 gas chromatograph with FID detection. The gas chromatograph system also included a SGE column switching station. Catalyzed CO and CO₂ and one carbon through three carbon hydrocarbons were eluted from a Plot Q column and four carbon and above hydrocarbons were eluted from a DB5 column. For the blend oxidation experiments, the fuels (mch: Aldrich, 99%; toluene: Baker, 99+%) were blended in the desired concentrations in the liquid phase, and the resulting mixture was vaporized and injected into the flow reactor via the flow reactor evaporator system [8,9]. For the pure mch experiments, only liquid mch

was vaporized and injected into the reactor. The experimental conditions of these experiments are shown in Table 1.

Temp. (K)	MCH Loading (ppm)	Toluene Loading (ppm)	Trace O ₂ (ppm)	[Phil] _{overall} l
1058	1900	0	240	na
1108	1771	0	185	na
1155	1664	0	180	na
1186	1706	0	170	na
1160	1815	0	na	1.3
1160	1229	1475	na	1.3
1160	598	2154	na	1.4
1160	240	2592	na	1.3

(na = not applicable)

Table 1: Experimental Conditions

RESULTS OF PURE MCH STUDIES

Normalized mch mole fractions (mch mole fraction at a given time divided by initial mch loading) as a function of time for each pure mch pyrolysis experiment is shown in figure 1. These plots give the rate constant for the unimolecular decomposition of the mch at each temperature when first order rate analysis is applied.

Exponential curve fits were calculated for each temperature and are also shown in figure 1. These data can then be used to determine the unimolecular activation energy and pre-exponential factor for mch pyrolysis. An Arrhenius plot of the data is shown in figure 2. From linear regression analysis, the activation energy and pre-exponential factor were determined to be 62.55 kcal/mol (262 kJ/mol) and $2.55 \times 10^{13} \text{ s}^{-1}$, respectively.

The major species profiles as functions of reaction time of a typical mch pyrolysis are shown in figure 3. Identified minor species profiles of the same pyrolysis are shown in figure 4. A few species whose mole fractions may be on the order of 50 ppm (based on chromatograph area counts) have not been conclusively identified. Furthermore, a cyclohexane/benzene peak was observed in each pyrolysis test. Since both compounds have nearly the same retention time on the DB5 column, several gas samples from mch pyrolysis experiments were injected onto a DB1 column for further analysis. These injections revealed that the presumed combined cyclohexane/benzene peak was exclusively benzene. Toluene mole fractions, also observed at each pyrolysis, remained fairly constant as functions of time and never exceeded 20 ppm. (It is interesting to note that while toluene formation is catalytically promoted in the liquid phase conversion reaction mentioned earlier, virtually no toluene is formed in the vapor phase decay of pure mch.) Isoprene (methyl butadiene) mole fraction, also shown in figure 3, never exceeded 100 ppm for any of the pyrolysis studies. Furthermore, isoprene had the highest concentration of any methyl substituted intermediate (e.g. methyl propane, methyl pentene, etc.) produced.

For comparison, mch oxidation experiments were also performed and typical major and minor species profiles versus reaction time are shown in figures 5 and 6 respectively. The oxidation and pyrolysis reactions, carried out at nearly identical temperatures, resulted in the formation of similar intermediate species and species profiles. (This trend ceased when the intermediates were consumed and converted to CO and CO₂ during the oxidations.) However, as can be seen by comparing figures 3 and 5, reaction rates increased during oxidation. Thus, while the oxygen did not introduce new stable

intermediate species into the reaction pool, it did increase the radical pool which led to faster fuel and intermediate species consumption.

The normalized decay profiles of mch and toluene (normalized by initial mch and initial toluene loading, respectively) for the fuel blend oxidation experiments are shown in Figures 7 and 8. Also shown in Figure 7 is a normalized mch decay profile from a pure mch oxidation study at the same experimental conditions.

Shown in Figure 9 is the normalized mole fraction of isoprene (methyl butadiene) as a function of fractional conversion of mch for both pure and blended mch oxidation experiments. (Fractional conversion of mch was chosen as the abscissa in an effort to decouple time from the mechanism of mch decay and instead focus on the roles of mch and toluene concentrations on the decay of mch.) As can be seen from Figure 9, the normalized mole fraction of isoprene, a substance not formed during pure toluene oxidation [10], regardless of blend ratio, reaches a maximum value of approximately 0.05 after sixty to eighty percent of the mch has been consumed.

The normalized mole fraction of benzene as a function of fractional conversion of toluene is shown in Figure 10. (Similarly, the fractional conversion of toluene was used to isolate time from the effects of toluene and mch concentrations on the chemistry of toluene decay.) Again, the rate of growth of benzene, a substance not significantly formed during pure mch oxidation (the maximum mole fraction of benzene produced is roughly three percent of the initial mch mole fraction [11]), scales with the fraction of toluene consumed regardless of the blend ratio.

However, intermediates formed from both mch and toluene oxidation (e.g. methane) do not scale with the fractional conversion of either fuel. Intermediates that are not (largely) formed during the oxidation of each fuel but are formed during the oxidation of the fuel blends (i.e. xylene) also exhibit no simple dependence on the fractional conversion of either mch or toluene.

DISCUSSION

Kralikova, Bajus, and Baxa studied the pyrolysis of pure mch in a steel tube reactor at 0.1 MPa and temperatures between 970 and 1095 °K. [7] These investigators deduced an activation energy of 251.2 kJ/mol and a pre-exponential value of $6.31 \times 10^{15} \text{ s}^{-1}$ for the unimolecular decomposition of mch at these conditions, but cited a wide range of values for each Arrhenius parameter: 200 to 340 kJ/mol for the activation energy and 10^{12} to 10^{18} s^{-1} for the pre-exponential factor. The values obtained in the Princeton experiments fall within the ranges established by Kralikova et al. study. Similarly, the Princeton experiments yielded the same intermediates as those of Kralikova et al.: methane, ethene, propene and butadiene. However, the relative proportions were different. In the Princeton flow reactor experiments, ethene was the highest concentration intermediate followed by butadiene, methane, and propene. In the Kralikova et al. steel tube experiments, methane was the highest concentration intermediate followed by ethene, propene, and butadiene.

Of greater importance than the difference in relative proportions of small molecule intermediates was the difference in the amount of toluene observed and the difference in the extents of reactions. Kralikova et al. observed almost seven times as much toluene than was observed in the Princeton flow reactor. Furthermore, at 1073 °K, they achieved a fuel conversion of 93% in 47 milliseconds compared to approximately 50% fuel conversion in 230 milliseconds at 1058 °K in the Princeton flow reactor.

These differences in toluene concentrations and fuel consumption rates may simply be due to differences in experimental conditions. The work of Kralikova et al. was performed in a steel reactor with no dilution, while the Princeton work utilized a quartz reactor and high nitrogen dilution. Kralikova et al. stated that the steel reactor surface catalyzed reactions of the fuel. The dehydrogenation of mch to form toluene and hydrogen is known to be augmented by heterogeneous reaction on catalytic surfaces.[1] The occurrence of catalytic heterogeneous reactions of high concentrations of fuel is consistent with the observations of greater toluene concentrations and faster fuel consumption rate. Catalytic reactions do not occur in the Princeton quartz reactor. The dilute concentrations of fuel in the reactor pyrolyze entirely by homogenous gas phase processes. (The products that result from these homogenous gas phase processes, ethene, butadiene, and methane are more combustible and less prone to soot in jet propulsion devices than a toluene containing mixture formed by catalysis.)

If the difference in products observed between the two studies is due to the difference between a catalytically assisted decomposition and a homogenous gas phase pyrolysis, then a mechanism for the homogenous route would probably involve the cleavage of the C-C bond between the methyl group and the C₆ ring because this is the weakest bond in the molecule. The C-CH₃ bond has a bond energy between 327 and 336 kJ/mol and is approximately 20 kJ/mol lower than the C-C bonds contained in the ring.[7] This cleavage of the C-CH₃ bond is consistent with the low concentrations of methyl containing intermediates observed in the flow reactor studies; the most prevalent methyl containing species, isoprene, never exceeded 100 ppm in any pure mch pyrolysis experiment.

As can be seen from Figure 7, the rate of mch consumption was a function of the initial concentration of both mch and toluene. Mch decay was fastest in the pure mch system and the lower mch concentration blends decayed at correspondingly slower rates. If the mch decay rate were first order in mch concentration, the normalized decay rate would be independent of both initial mch and toluene concentration, contrary to what has been observed in these fuel blend flow reactor studies. One explanation of this observation is that the mch decay rate is a nonlinear function only of the initial mch concentration. To address the role of initial mch mole fraction on mch oxidation, a pure, diluted (i.e. 900 ppm fuel loading) mch oxidation at the same experimental conditions as above is planned. Indeed, in order to explain the observed experimental trends one must keep in mind both the initial fuel concentrations and the blend ratio.

The importance of the blend ratio suggest that the difference in mch decay rates may be due to the mechanism of toluene oxidation. Toluene oxidation proceeds by radical attack [10], and toluene may therefore inhibit mch oxidation by effectively competing with the mch for radicals present in the system. The fact that the initial toluene mole fraction is greatest when mch decay is slowest and that the initial toluene mole fraction is lowest when mch decay is fastest is consistent with this explanation. (To further elucidate the effects of initial mch loading and initial toluene loading on mch decay, a series of blend oxidations in which the initial mch loading is held constant while the initial toluene loading is progressively increased is planned. Any differences in mch decay rates obtained from this series of experiments will then be solely attributable to toluene.)

The toluene consumption rates are readily explained in terms of system radical population. Of the three blend experiments, the 50% mch/50% toluene experiment had the highest initial mch concentration. Thus, this system had the greatest amount of radicals produced from the mch decay, and therefore should have resulted in the fastest toluene consumption rate. (From the point of view of toluene oxidation, higher mch concentrations

produce higher radical populations available for toluene attack. However, from the point of view of mch oxidation, higher toluene concentrations produce lower radical populations available for mch attack.) Similarly, the 10% mch/90% toluene experiment had the lowest amount of mch, and mch related radicals, and thus should have yielded the slowest toluene consumption rate. The experimental results, as seen in Figure 8, are consistent with this explanation of toluene consumption during blend oxidation.

Intermediates that are predominantly formed from mch decay appear to form via the same mechanisms, regardless of the blend ratio. Again, the normalized mole fraction of isoprene, a substance not produced from toluene oxidation, scales with the fractional conversion of mch and is independent of the initial toluene mole fraction. Fuel blending changes the rate at which mch is consumed, and thus the rate at which the intermediates are formed, rather than changing the chemical reactions responsible for the production of the given intermediates. The same reasoning seems to apply to the products of toluene decay. (Recall the growth rate of benzene as a function of fractional conversion of toluene is independent of the initial mch mole fraction.)

If this hypothesis that both fuels are decaying independently of each other is correct, then common intermediates of both fuels' decay should have a simple dependence on the blend ratio. For instance, methane and cyclopentadiene are intermediates that are produced from both toluene and mch decay. Therefore, the total amount of either intermediate produced in the blend should simply be equal to the amount produced by the mch decay plus the amount produced by the toluene decay. Shown in figure 11 is a plot of methane mole fraction as a function of time for the 10% mch/90% toluene blend. The projected amount of methane produced by each fuel is also shown in this figure. (These projected amounts of methane were extrapolated from pure mch and toluene oxidations at the same experimental conditions as the blend run. Further, these projected values are based on the fractional conversion of each fuel and are not based simply on reaction time.) As can be seen from the figure, there is good agreement between the experimentally obtained methane mole fraction values and the sum of the two projected methane mole fraction values. A similar plot of cyclopentadiene mole fraction as a function of time for the 50% mch/50% toluene blend is shown in figure 12. Again, there is good agreement between the experimentally obtained mole fraction values and the sum of the projected amounts of cyclopentadiene independently produced by the mch and the toluene. The agreement between the projected and the experimentally obtained methane and cyclopentadiene mole fractions is consistent with the hypothesis that while the rate of decay of toluene and mch is dependent on the fuel blend ratio, the subsequent oxidation mechanism of each fuel is not dependent on this ratio. Rather, these subsequent oxidation mechanisms occur independently of each other.

B) Fuel Line Deposit Formation

A high temperature liquid/ supercritical fluid study of toluene/methyl cyclohexane that complements the gas phase examination described above was begun in the recently constructed fluid phase reactor apparatus, figure 13. The reactor was designed and constructed with AFOSR support in order to better understand the chemistry responsible for fuel line fouling in aircraft engines.

The fuels initially chosen for the prototypical fouling studies were toluene (C_7H_8) and methylcyclohexane (MCH, C_7H_{14}) and their blends for the same reasons that these species were selected for the gas phase tests.

The experimental procedure, which is described in the following paragraphs, is best appreciated when figure 13 is kept readily available for reference. The reactant is first sparged of dissolved air with nitrogen gas while in the pump cylinder. Sparging removes atmospheric oxygen and precludes any oxidative chemistry from taking place. Oxidative chemistry has been shown to form deposits in heated tubes and alters the composition of the reactant. Since the chemistry of interest is high temperature liquid/supercritical fluid pyrolysis, it is desirable to eliminate extraneous reactions promoted by oxygen. The tubular reactor itself is also purged with nitrogen to remove the previous experiment's residue and air bubbles. Following the nitrogen purge, the deoxygenated fuel is pumped through the reactor with the high pressure piston pump.

After passing through a filter, the reactant enters a heated coil, that has a length and cross sectional area chosen to ensure "plug flow". Thus every element of fluid experiences the same pressure and temperature history (a constant residence time). The reactor coil is nickel capillary tubing with an inside diameter of 0.43mm (0.017in); the typical length of a heated coil is 20m (66ft). The coil is immersed in a Techne™ sand bath which maintains the coil at a constant heated temperature within $\pm 1^\circ\text{C}$. Temperature is measured with nine Type K thermocouples at various points on the coil and in the bath.

Pressure is measured upstream of the heated coil with a pressure gauge and transducer, and downstream with another transducer. As deposits are formed, the effective tube radius decreases, increasing the pressure drop across the coil, which can be monitored to determine the onset of deposit formation. Flow rates are set such that the pressure drop is less than 1% of the pressure in the reactor. Residence times in the heated coil can be varied from seconds to tens of minutes by changing the pump's volumetric flow rate.

Upon leaving the heated coil, the products are reduced to atmospheric pressure with a back pressure device and two needle valves, which also serve as pressure regulators. The fluid then passes through a phase separator which splits the products into their gaseous and liquid components. When present, solid particles are suspended in the liquid samples. The liquid samples have been analyzed with a Hewlett-Packard™/Nicolet™ Gas Chromatograph-Fourier Transform InfraRed spectrometer (GC-FTIR). Solid particle samples have been observed under optical microscope, and will be analyzed by electron microscopy at the Princeton Materials Institute.

Toluene was found to be fairly stable at the supercritical conditions tested: temperatures were as high as 701°K (802°F) and pressures as high as 5.02MPa (728psia) for residence times on the order of minutes. MCH, on the other hand, created deposits which quickly plugged the capillary tube on two occasions. Liquid samples taken immediately before the plugging showed the formation of pentanes, hexenes, heptanes, octanes, and naphthalenes. A blend of [0.9] toluene and [0.1] MCH at $T=797^\circ\text{K}$ (975°F) also showed a tendency to plug; pentanes and benzenes were found in the liquid sample. Gas samples were not taken at the time these tests were run; they are expected to contain hydrogen, methane, ethane, ethene, and acetylene.

Preliminary observation of the solid particles collected prior to plugging indicates that they are small, black, and are insoluble in common solvents. When left standing, they will settle to the bottom of the liquid. Under the optical microscope, the particles look almost like gas phase soot particulates, but lack the "pearl necklace" structure found in soot. Instead, they look like agglomerations of smaller, self-similar particles, all having rough edges and no apparent orderly structure. Electron microscopy should be able to deduce the composition and structure of the particles. The expected result is an isotropic form of graphite lattice structure connected by polyaromatic hydrocarbons.

Summary

The experimental apparatus for the examination of chemical reactions in supercritical and high temperature hydrocarbon liquids has been built, and is being continually used, upgraded and refined. Toluene, MCH, and mixtures of the two have been reacted under supercritical conditions. Liquid products have been analyzed, and the gaseous phase products are now being sampled for GC-FTIR as well. The solid carbonaceous deposits were found to resemble soot particles in some ways; they will be examined using electron microscopy. Further work will encompass mixing reactants together in the heated zone, performing high temperature / short residence time tests, and including other fuel components such as decalin and JP-10.

C. Current Work

Current research is focused on clarifying further the implications of the studies of methylcyclohexane/toluene blends. The blends are being examined with additional control over initial fuel concentrations so that parametric studies can be conducted of the effect of varying toluene concentration on the oxidation of a constant concentration of MCH and the effect of varying MCH concentration on the oxidation of a constant concentration of toluene.

Current research on deposit formation is focused on characterization of the carbon based material that plugs the reactor tubes. Further investigation of chemical changes in the bulk fluid that may precede the formation of the carbon particles is also underway.

D. Articles/Presentations/Personnel

Articles

"Pyrolysis and Oxidation Studies of Methylcyclohexane", S. Zeppieri, K. Brezinsky and I. Glassman, Eastern States Section/Combustion Institute Meeting, Extended Abstract, #83, 1993.

"The High Temperature Oxidation of Naphthalene: A Benzene Analog? C.R. Shaddix, K. Brezinsky and I. Glassman, Eastern States Section/ Combustion Institute Meeting, Extended Abstract, #88, 1993.

"Oxidation Studies of Methylcyclohexane/Toluene Blends", S. Zeppieri, K. Brezinsky and I. Glassman, Eastern States Section/Combustion Institute Meeting, Extended Abstract, #16, 1993

Presentations

"Pyrolysis and Oxidation Studies of Methylcyclohexane", S. Zeppieri, Eastern States Section/Combustion Institute Meeting, New Orleans, LA, March, 1993.

"The High Temperature Oxidation of Naphthalene: A Benzene Analog? C.R. Shaddix, Eastern States Section/ Combustion Institute Meeting, New Orleans, LA, March, 1993.

"Oxidation Studies of Methylcyclohexane/Toluene Blends", S. Zeppieri, Eastern States Section/Combustion Institute Meeting, Princeton, N.J., October, 1993.

"Chemical Reaction Studies in a High Pressure Reactor", K. Brezinsky, University of Dayton, Dayton, OH, August, 1993.

Participating Professionals

S. Zeppieri; Graduate student. Mr. Zeppieri is in the later stages of completing his Masters degree. His thesis topic will be the chemical interaction of toluene/cyclohexane blends. It is expected that Mr. Zeppieri will remain at Princeton in order to pursue a Ph.D.

G. Davis; Graduate student. Mr. Davis is in his second year of the Masters degree program. His thesis topic is deposit formation in jet engine fuels. Mr. Davis intends to seek employment on receipt of his degree.

J. Sivo; Senior technician. Mr. Sivo has been associated with our laboratory for more than 30 years. In addition to his responsibilities for flow reactor experiments, he has participated in the design and construction of the high temperature liquid/supercritical fluid reactor.

I. Glassman; Professor. Principal Investigator

K. Brezinsky; Senior Research Scientist. Co-principal Investigator.

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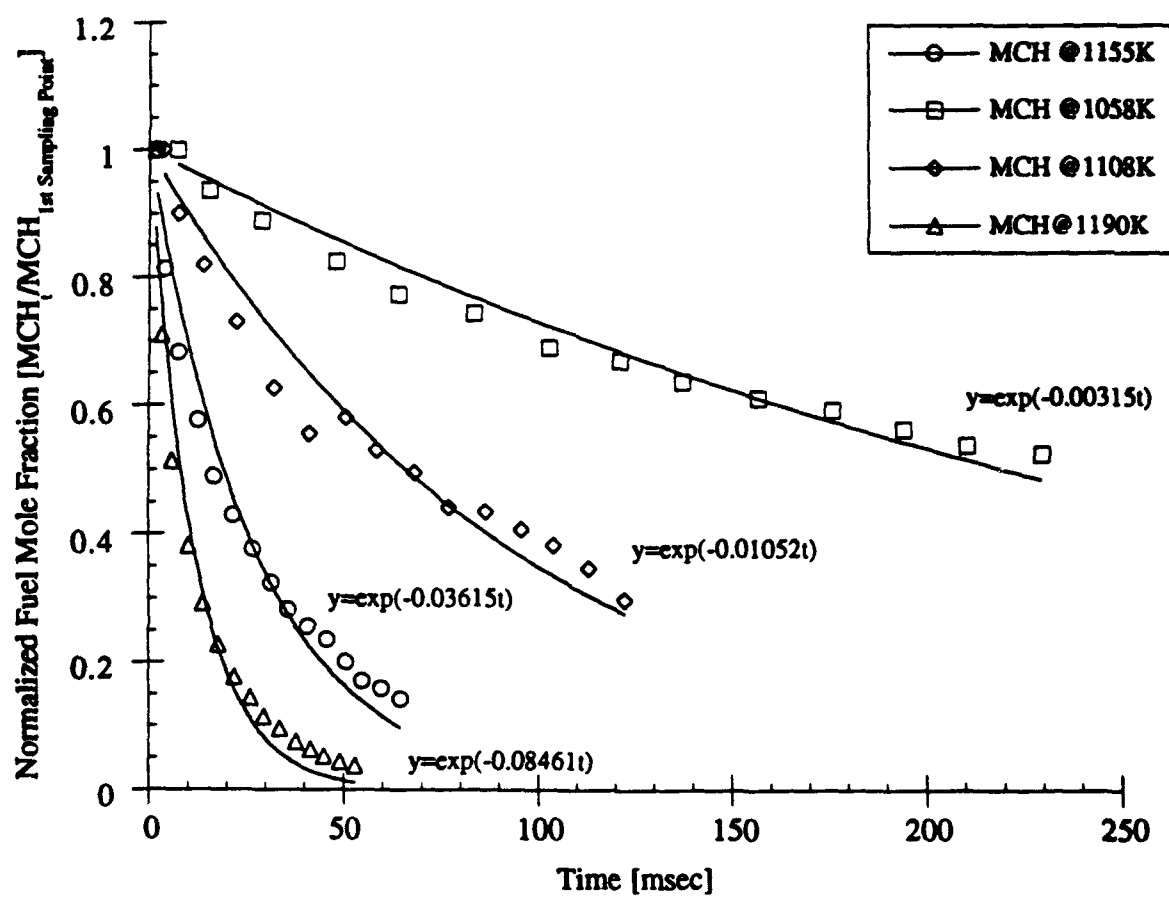


Figure 1: Normalized MCH Pyrolysis Profiles at Various Temperatures

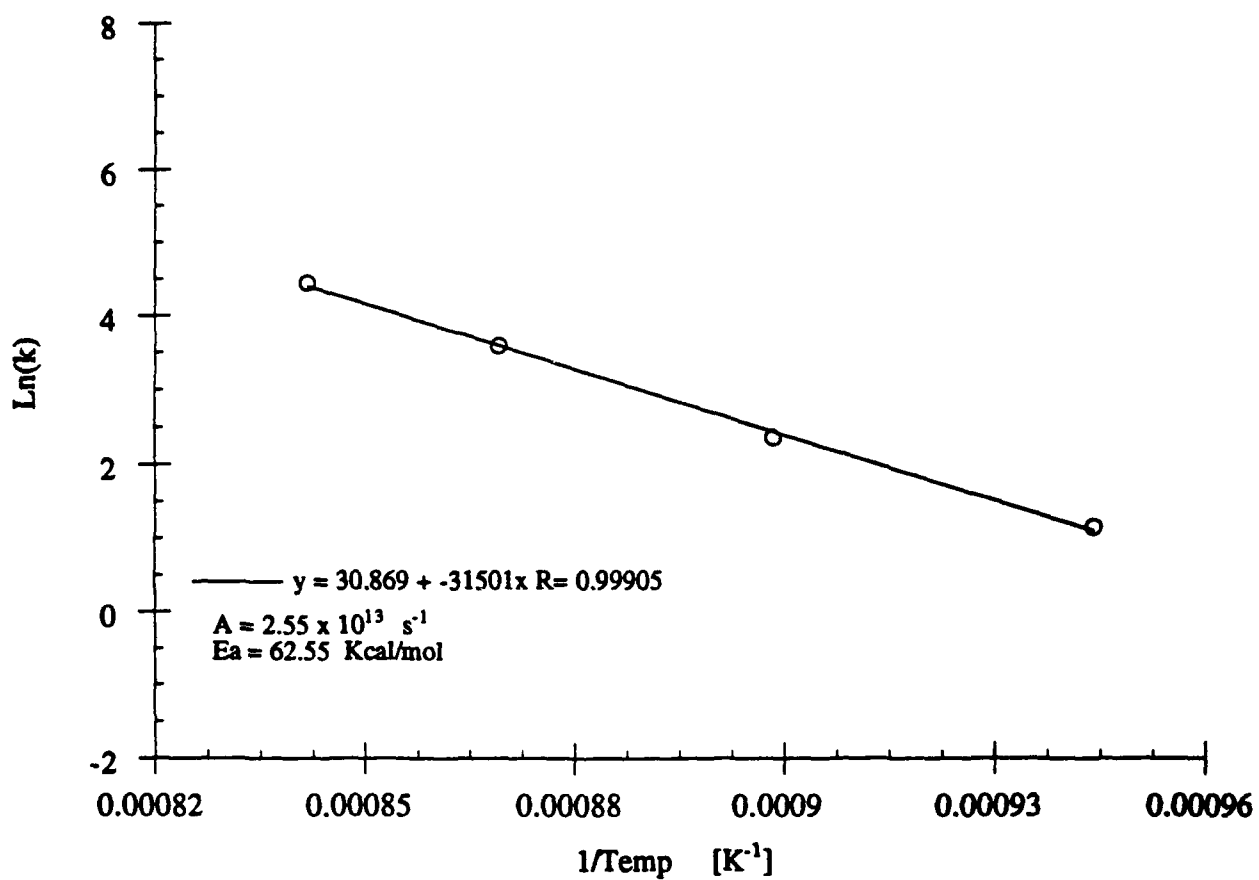


Figure 2: Arrhenius Plots of Overall MCH Pyrolysis Decay

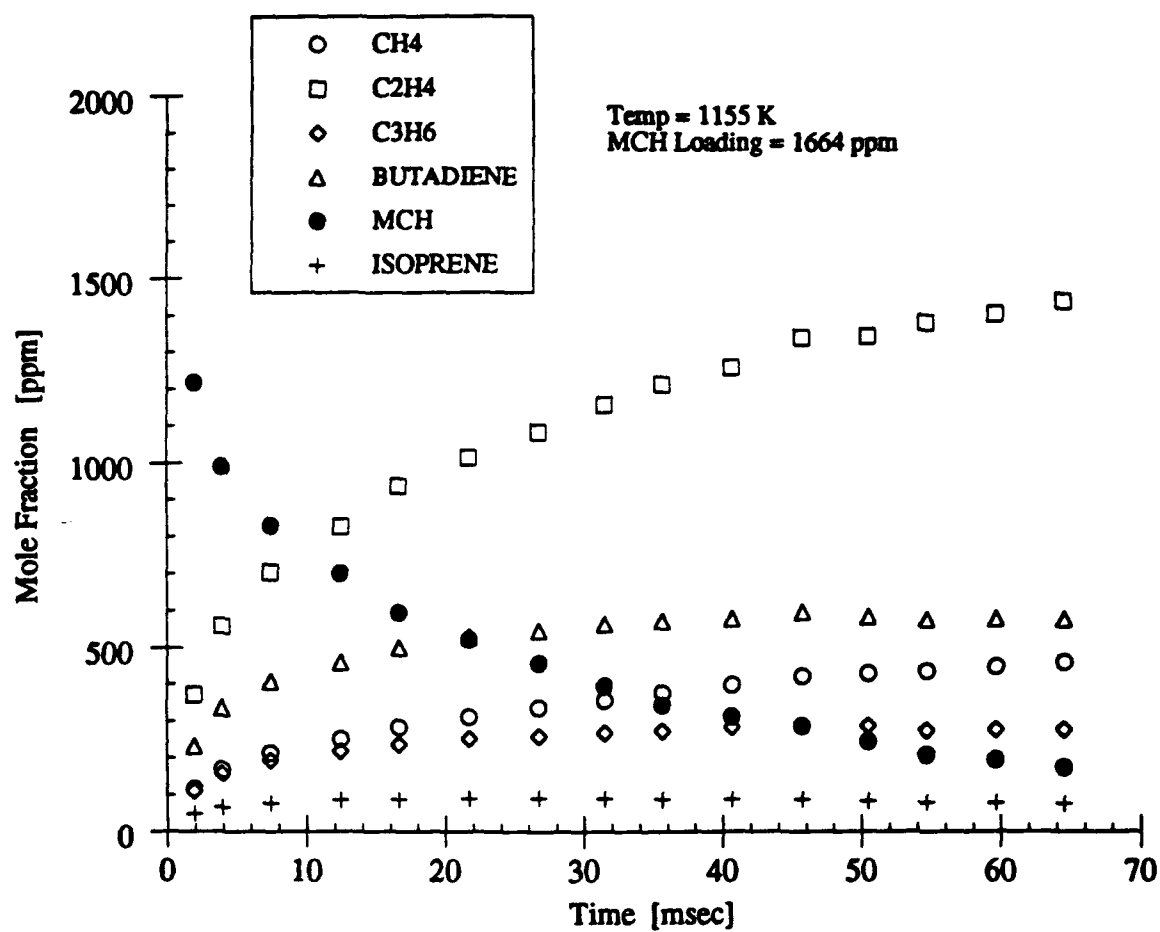


Figure 3: Typical MCH Pyrolysis Major Intermediate Profiles

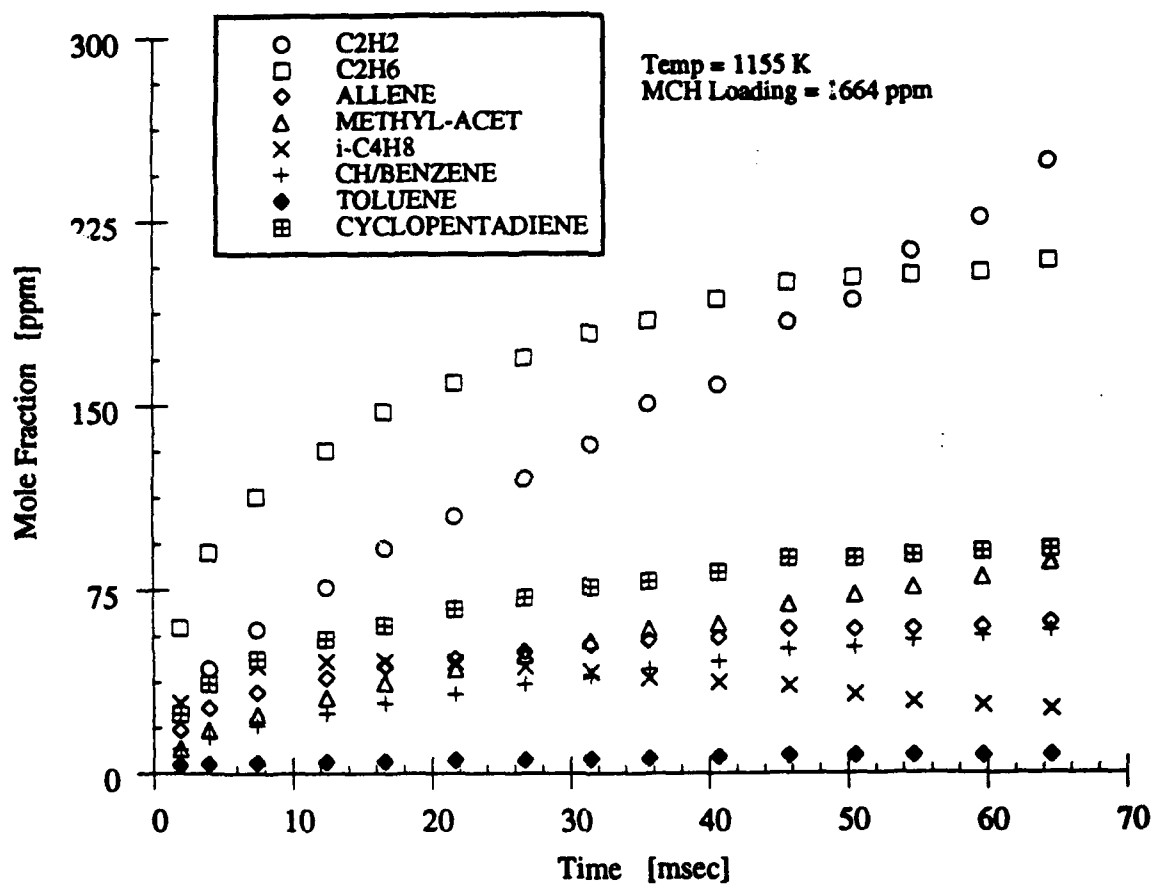


Figure 4: Typical MCH Pyrolysis Intermediate Profiles

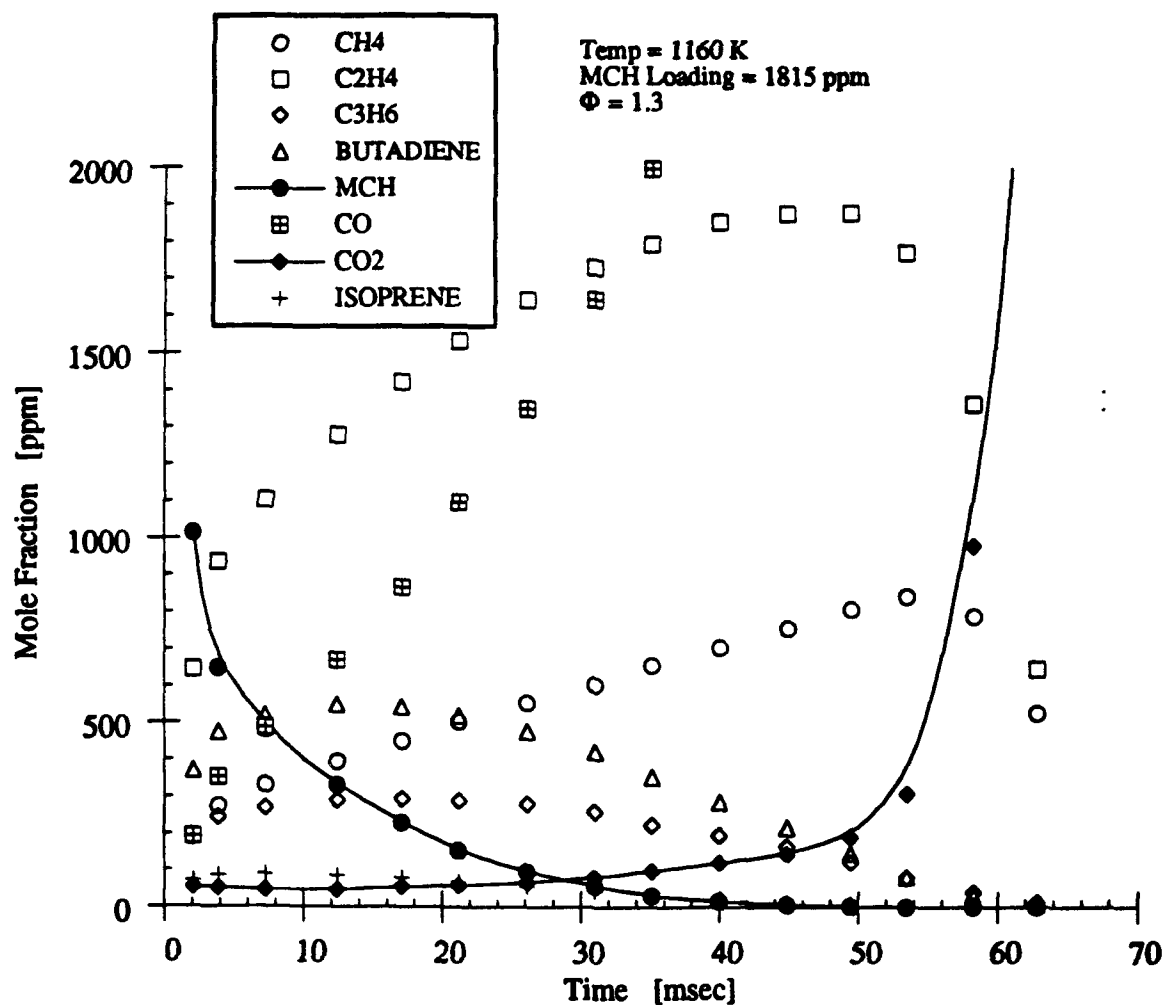


Figure 5: Typical MCH Oxidation Major Intermediate Profiles

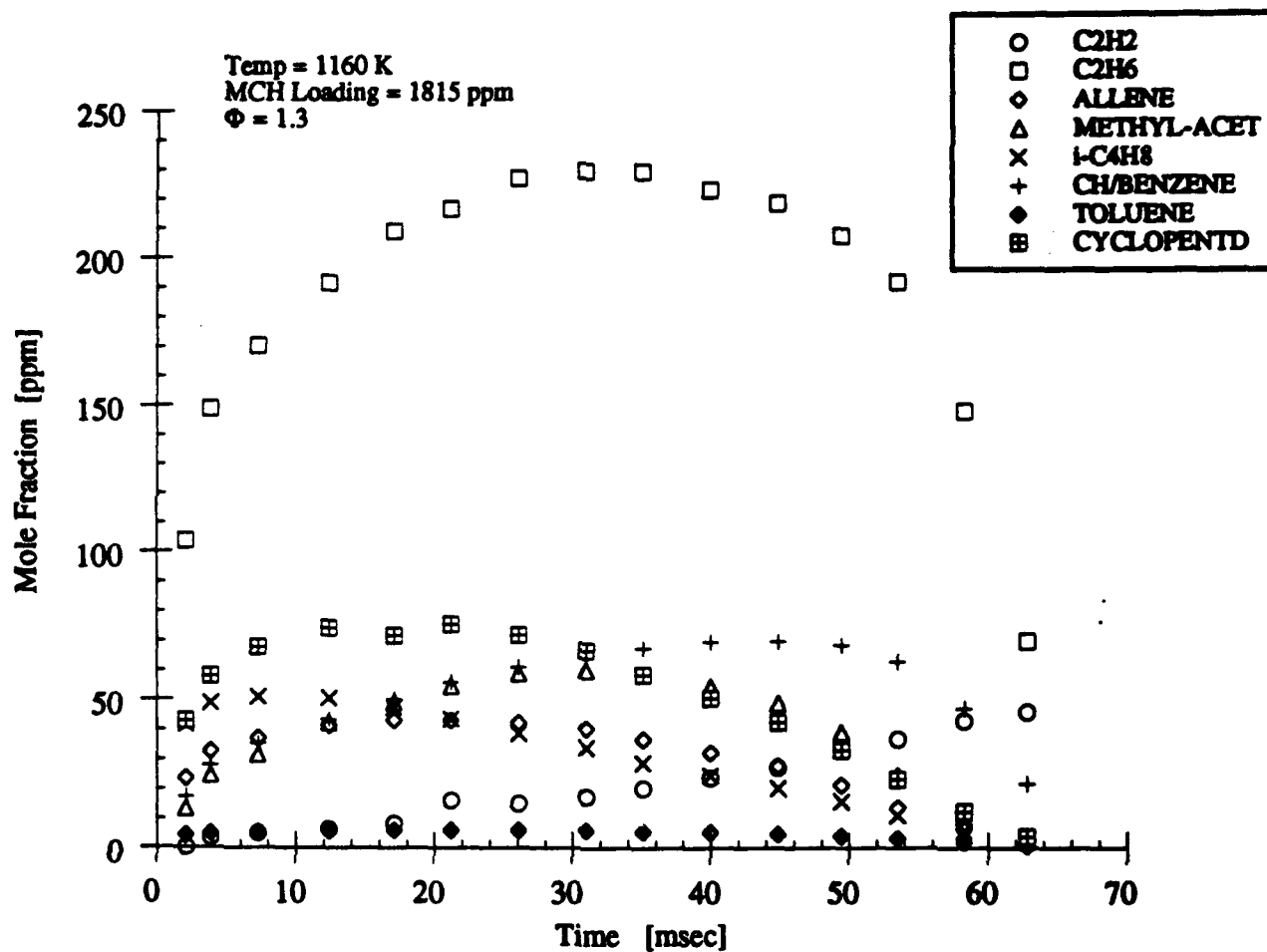


Figure 6: Typical MCH Oxidation Intermediate Profiles

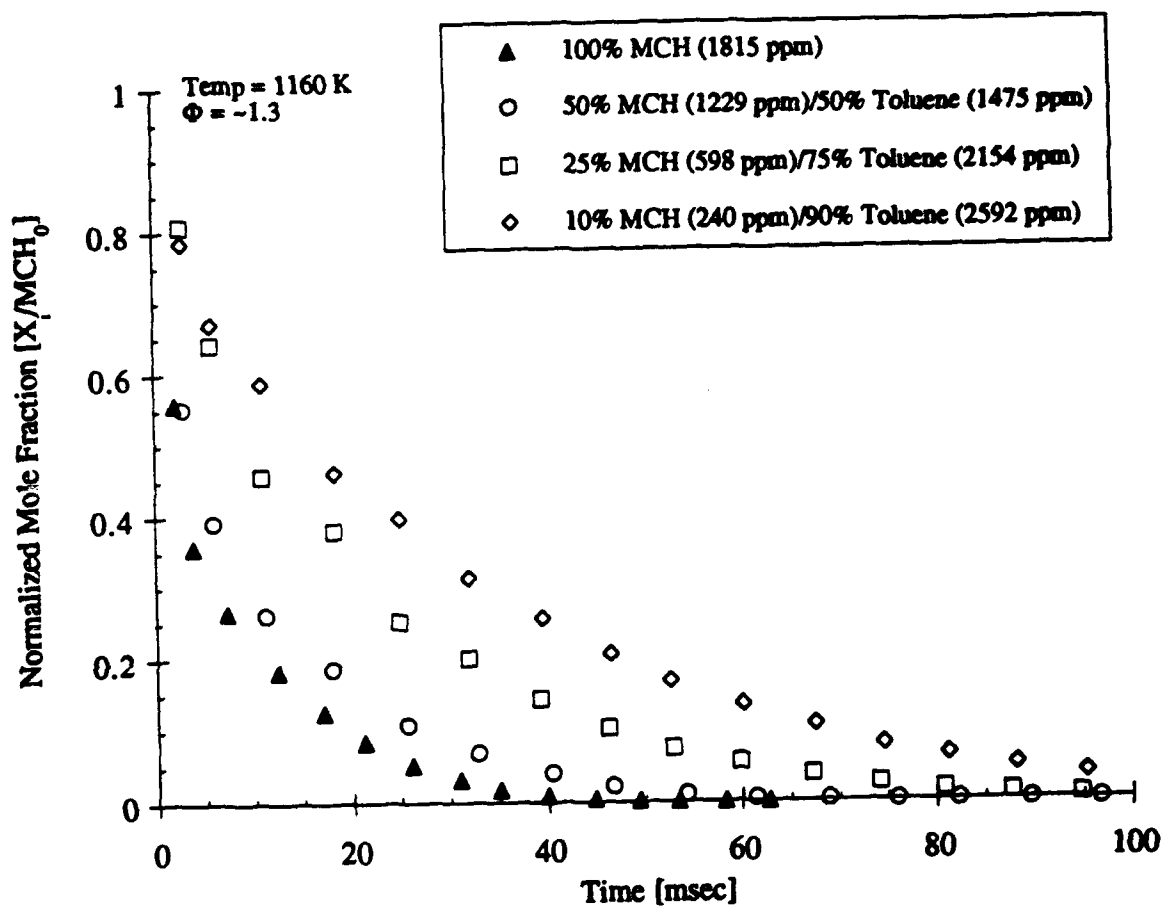


Figure 7: Normalized MCH Decay Profiles for Various MCH/Toluene Blends

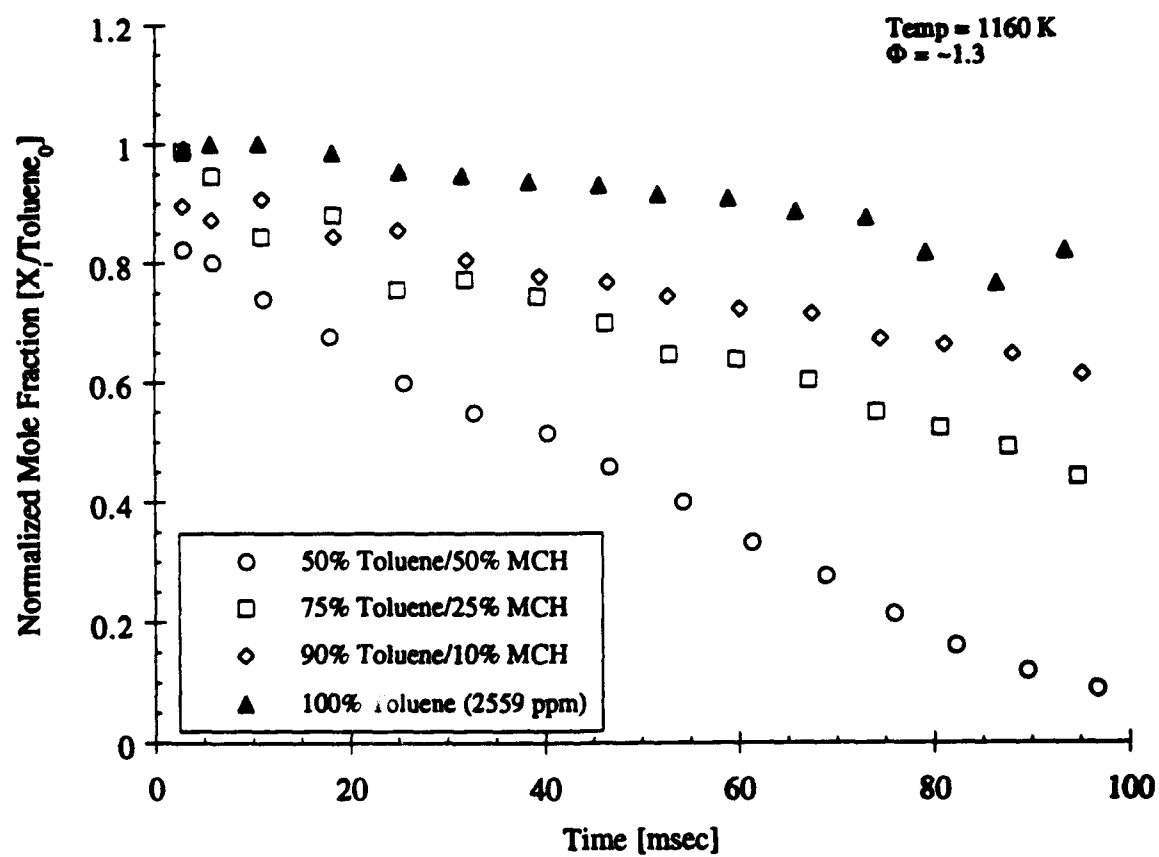


Figure 8: Normalized Toluene Decay Profiles for Various MCH/Toluene Blends

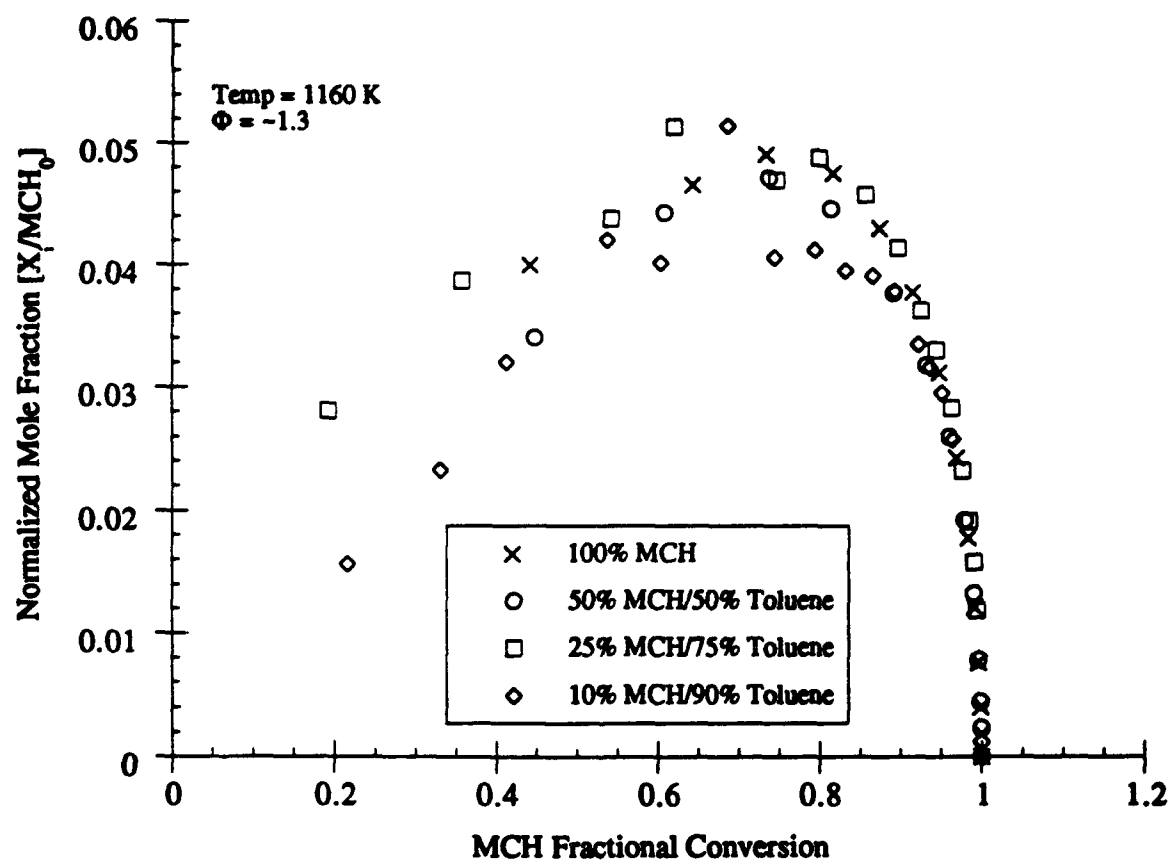


Figure 9: Normalize Isoprene Mole Fraction vs. MCH Fractional Conversion

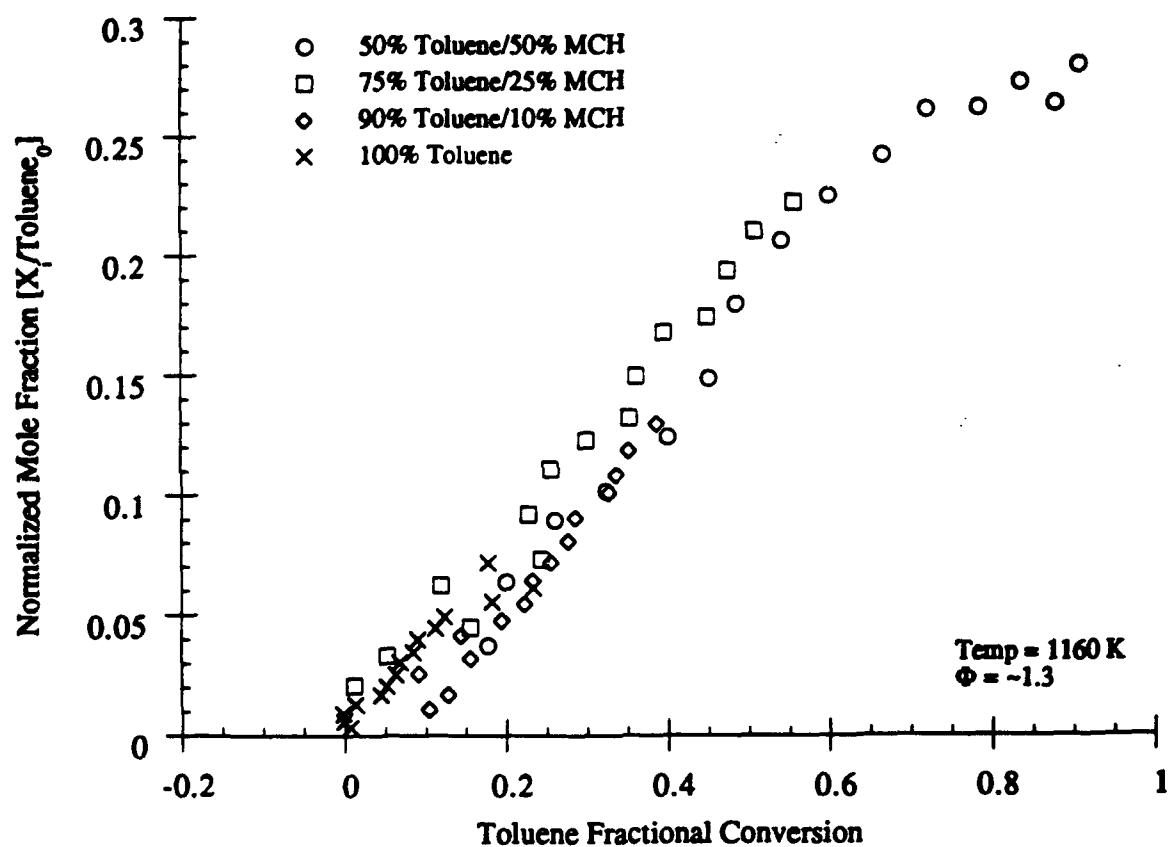


Figure 10: Normalized Benzene Mole Fraction vs. Toluene Fractional Conversion

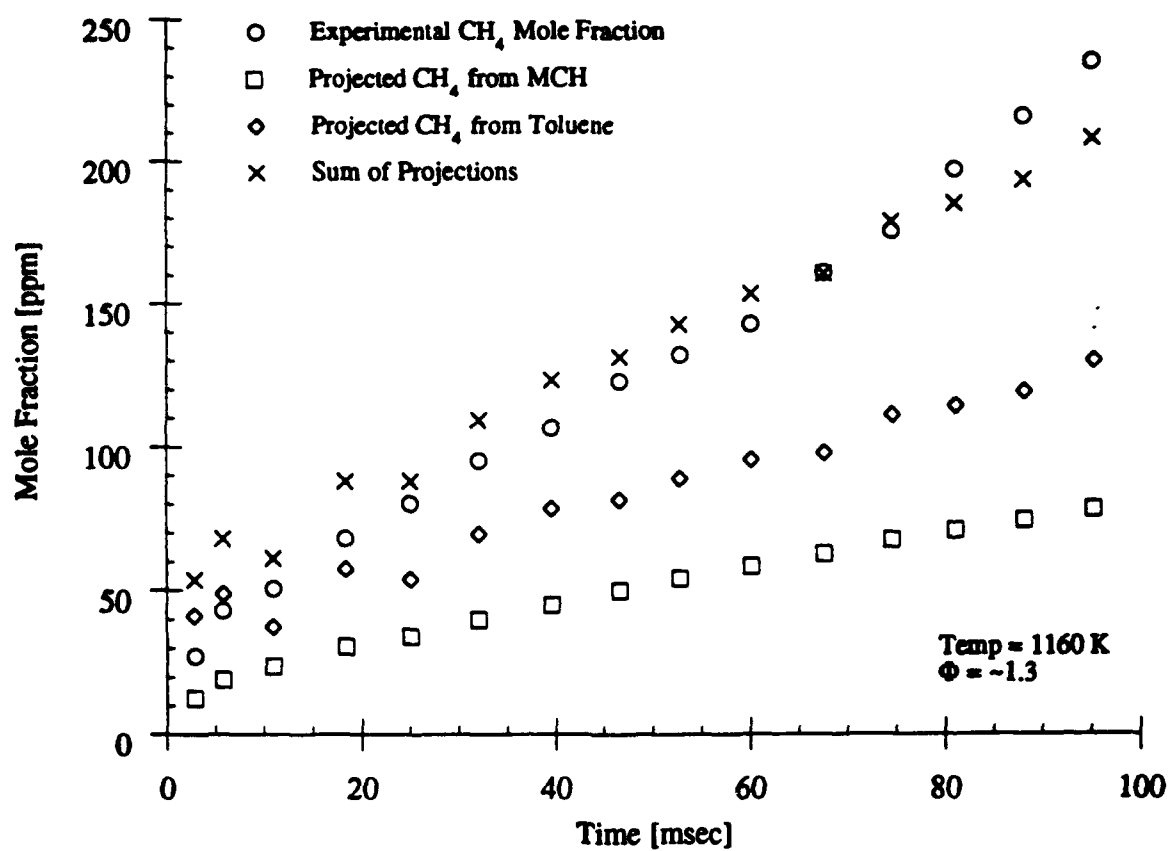


Figure 11: Methane Mole Fraction for 10% MCH/90% Toluene Blend

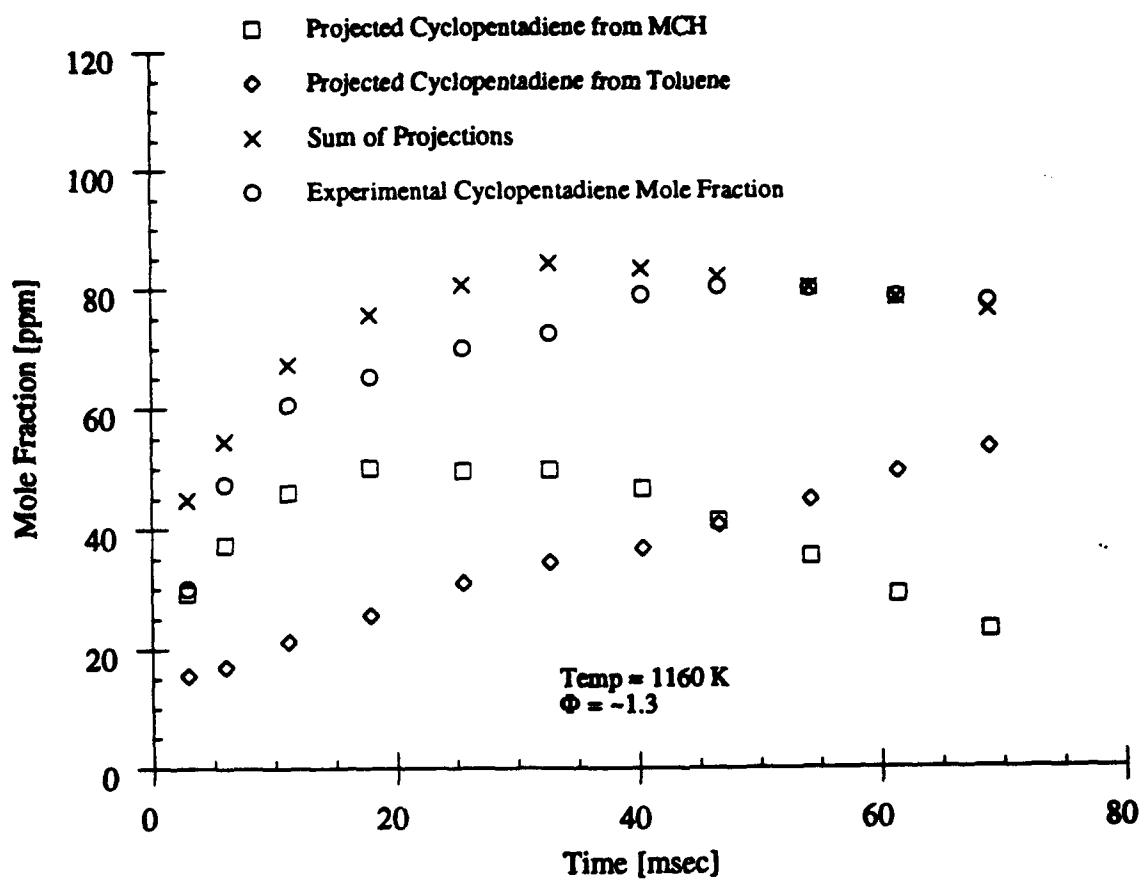


Figure 12: Cyclopentadiene Mole Fraction for 50% MCH/50% Toluene Blend

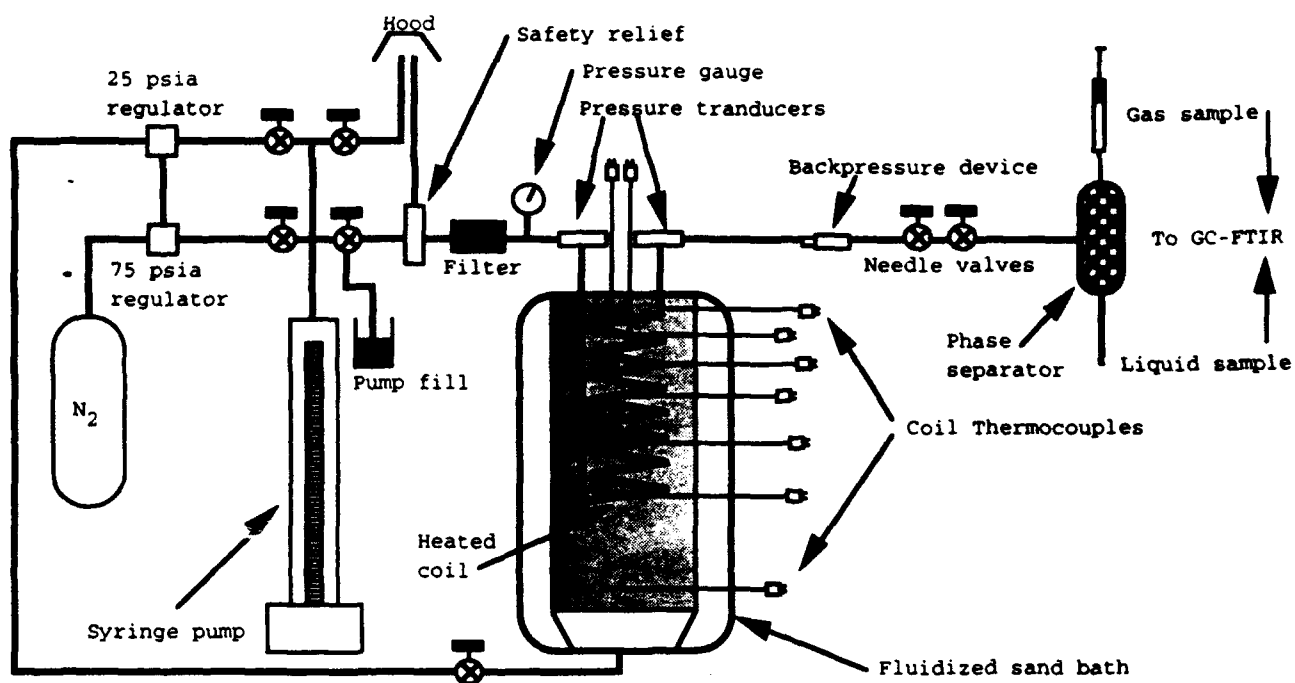


Figure 13 Schematic of the Supercritical Flow Reactor