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A high pressure plug flow reactor designed for supercritical hydrocarbon reaction studies was applied to the analysis and fuel fouling aspects of the endothermic fuel methylcyclohexane (MCH). At a reduced pressure of 1.3 (4.5 MPa), a residence-time of 0.9 minutes, and temperatures from 750-844 K, conditions typical of the most extreme aircraft conditions envisioned for the future, gaseous and liquid MCH products were analyzed. At the lower temperatures examined conversion of MCH to polynuclear aromatic hydrocarbons (PAH) was essentially zero. At higher temperatures, above 820 K, significant PAH formation was observed, as was particulate formation, a very important practical result and a trend established for soot formation in gaseous diffusion flames. Operation in the supercritical region revealed varying temperature to be significantly more important than pressure with regard to PAH and particulate formation. Chromatograms of MCH reactor products established that there were hundreds of gaseous and liquid intermediates under both the sub- and supercritical conditions of operation. In gas phase experiments at 1 atm and temperatures around 1100 K in the Princeton Turbulent Flow Reactor, explicit equations for the rate of decay of MCH and another endothermic fuel decalin were determined. Significantly, product compositions of both fuels were found to be very different from those observed by others for the catalytic decomposition of these fuels.

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FUELS COMBUSTION RESEARCH

For the period 1 October 1994 to 30 September 1997

Written by:

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February 1998

FUELS COMBUSTION RESEARCH

(AFOSR GRANT F49620-95-1-0016)

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I. Executive Summary

Princeton's Fuels Combustion Research grant concentrated on the characteristics of endothermic fuels necessary as coolants in the Air force's next generation aircraft and on the challenging condition of fuel fouling under sub- and super-critical conditions.

A high pressure plug flow reactor designed for supercritical hydrocarbon reaction studies was applied to the analysis and fuel fouling aspects of the pyrolysis of the prototype endothermic fuel methylcyclohexane (MCH). At a reduced pressure of 1.3 (4.5 MPa), a residence time of 0.9 minutes and temperatures from 750-844 K, conditions typical of the most extreme aircraft conditions envisioned by the Air Force for the future, gaseous and liquid pyrolysis products of MCH were analyzed. At the lower temperatures examined, conversion of MCH to polynuclear aromatic hydrocarbons (PAH), and thus particulate formation, was essentially zero. At higher temperatures, above 820 K, significant PAH and particulate formation was observed. This point is of significant practical importance. Operation in the supercritical region revealed varying temperature to be significantly more important than varying pressure with regard to PAH and particulate formation Chromatograms of MCH reactor products established that hundreds of gaseous and liquid products existed under sub- and super-critical conditions. In all cases benzene and cyclohexane were the major products. Results under similar conditions revealed the important fundamental result that, whereas pure toluene and heptane pyrolysis did not cause particulate fouling similar to MCH, toluene and heptane mixtures did.

In gas-phase experiments at 1 atm and around 1100 K in the Princeton Turbulent flow reactor explicit rates of decay of MCH and another endothermic fuel, decalin, were determined. For MCH pyrolysis the pre-exponential rate factor was found to be $3.7 \times 10^{13} s^{-1}$ and the activation energy 265 kJ/mol. Similar results for decalin were $7.7 \times 10^{10} s^{-1}$ and 204 kJ/mol. Significantly, the

product composition of methane, ethene, butadiene and benzene, were found for both fuels to be very different from those observed, particularly naphthalene, for the catalytic decomposition of these endothermic fuels.

II. Technical Discussion

Methylcyclohexane (MCH) has long been considered as a prototype endothermic fuel for the next generation aircraft of interest to the Air Force. Thus its pyrolysis characteristics under sub- and super-critical conditions were chosen for study in an effort to determine the chemistry of particulate formation (fouling) in fuel lines. Considering that, as a coolant, MCH and other endothermic fuels must eventually undergo pyrolysis and oxidation in the engine combustion chamber, gas phase kinetic studies of these compounds were also undertaken. Results of this integrated research effort are reported next as Supercritical Fuel Degradation and Endothermic Fuel Kinetics.

A) Supercritical Fuel Degradation

Experiments were conducted in a newly designed silica-lined laminar high pressure flow reactor system, illustrated in Fig. 1. The reactor was designed to approach plug-flow idealization, and pressures as high as 15 MPa and temperatures as high as 860 K could be obtained. In typical operation of this reactor, a high pressure HPLC pump forced reactants through a capillary tubing coil immersed in a heated, fluidized, isothermal alumina bath. Uncertainty in manual temperature control of the alumina bath was ±3K. The tubing coil (1.59 mm OD, 0.051mm ID) was constructed of silca-lined stainless steel (Silico-steel by Restek). Pressure was regulated by a dome-loaded back pressure regulator located downstream of a six position sampling valve. Uncertainty in pressure control was ± 0.02 MPa. A water-cooled heat exchanger at the entrance and exit of the alumina bath quenched reaction upon exiting the heated zone and ensured a controlled thermal history and residence time. A 0.5 micron frit was located immediately downstream of the heat exchanger to indicate and collect any solid formation.

The chemical inertness of the silica-lined stainless steel of the reactor coil in the temperature range investigated was demonstrated by means of comparison of the product yields and distributions of supercritical methylcyclohexane pyrolysis both in a silica-lined stainless steel and in chromatography-grade 316 stainless steel. Identical results from each material were found up to 840 K (the highest temperature examined) and indicated that only homogeneous fluid phase reactions were occurring. The nitrogen sparge system indicated in Fig. 1 reduced the dissolved oxygen in all experimental fuels used to less than 1 PPM.

Product samples were analyzed post-experiment. Quenched products were collected in five sample loops of a multi-position valve. The liquid and gaseous products were subsequently separated in a specially designed apparatus. Separate gaseous and liquid analyses were performed using Gas Chromatograph Fourier Transform Infrared (FTIR) Spectroscopy equipment. The liquid samples were injected by means of a calibrated syringe onto a DB-5 column (J&W Scientific, 30m, 0.32mm i.d., 0.025mm film) of a HP 5890 chromatograph. For the gaseous samples, a 1 cc sample loop was injected onto the column. C_4 and smaller species were separated by means of a PORAPlot-Q column (Chrompack, 25m, 0.32mm i.d., 10 mm film) in conjunction with a DB-5 column. A flame ionization detector (FID) was used to quantify the mole fractions of product yield. FID signals were converted to mole fraction by means of an extensive calibration. FTIR spectroscopy, along with known standards, were used to identify product temperatures from 750 to 844 K. At the lower temperatures examined, conversion of reactants to PAH was zero or negligible. At the higher temperatures, above 820 K, significant PAH formation was observed, along with formation of solids. This result is, indeed, of great practical significance.

A qualitative histogram of the uncondensed (gaseous) products found at 820 K (Fig. 2) revealed that uncondensed products at 830 K were nearly identical to those found at 820 K. The uncondensed products consisted primarily of C_1 to C_4 aliphatics. The presence of these light molecules in the quenched products suggested that at the temperature of the reaction, 820 K, a significant radical pool from these light C_1 to C_4 species existed.

A typical gas chromatogram of the condensed (liquid) products obtained at 820 K, at a reduced pressure of 1.3 and a residence time of 0.9 minutes is given in Fig. 3. As the chromatograph illustrates, hundreds of condensed products were formed, most in concentrations too small to be identified. The major products were identified using GC-FTIR analysis. Relative product yields were compared on the basis of percentage of the total flame-ionization detector count of all products for a given injection. In these studies, some quantification of product yields was obtained, but comparison was made between relative product yields of different experiments. The quantitative yield data would be the focus of a proposed continuing effort.

Relative yields of the major condensed products were obtained at 820 and 844 K (Fig. 3). Yields of these major products increased exponentially with increasing temperature. This exponential behavior is illustrated by the relative yields of toluene as a function of temperature (Fig. 4). Benzene and cyclohexane were identified as major products; however, to date their relative yields have been unknown because the two molecules could not be separated -- they co-eluted from the gas-chromatograph. The overall ratio of the yields of the PAH species in the 844 K sample to those in the 822 K sample were determined to be about 6. Further, the PAH yields at the higher temperature were possibly also slightly depressed due to the agglomeration of PAH into small amounts of solids. PAH yields were nearly undetectable below 820 K.

In addition to the observation of rapidly increasing PAH yields above 820 K in supercritical methylcyclohexane, solids were also observed to form at temperatures above 820 K and at the conditions of pressure and residence times investigated. Based on analogous gas-phase soot-formation studies, PAH were presumed to be the precursors to homogeneous solid formation (where surface effects are insignificant). The observation of homogeneous solid inception coincident with that of substantial PAH formation would appear to support this hypothesis.

To investigate the effects of pressure on PAH formation, deoxygenated methylcyclohexane was pyrolyzed at 780 K and reduced pressures from 0.5 to 2.0. This temperature was chosen in order to minimize the pronounced effects of the +/- 5 K uncertainty in temperature on the product yields at temperatures above 810 K. At these higher temperatures, a 5 K difference in temperature could result in a difference in product yield of more than an order of magnitude. However, at lower temperatures (near 780 K), variations in product yields due to the uncertainty in temperature were minimized, and effects due to the pressure variation could be isolated. It was postulated that one effect of a higher pressure on the chemistry involved in methylcyclohexane pyrolysis was due to an increased density and its corresponding effect on supercritical kinetic phenomena. Over the range of reduced pressures examined, the density increased by a factor of about 6.

Relative product yields from the investigation of changing the pressure indicated that pressure variations could have a significant impact on product distributions and yields of products observed. Increasing pressure within the range of a reduced pressure between 0.5 and 2.0 reduced the conversion of the reactant, methylcyclohexane, to products. However, while the yields of all products were reduced as the pressure increased, heavier products were a greater fraction of the total yield at higher pressures. At a reduced pressure of 0.5, heavy (C7 and larger) products constituted 72% of the total yield, while at a reduced pressure of 2.0, they constituted 82% of the total yield. There was a shift toward heavier products at higher pressures - a result consistent with LeChatlier's principle.

To investigate the effects of molecular structure on PAH formation, preliminary experiments with three types of hydrocarbons with different molecular structures also were performed. Pyrolysis of supercritical methylcyclohexane, toluene, heptane, and a mixture of toluene and heptane was examined. Experiments were performed at reduced pressures of 1.3 and residence times on the order of 1 minute. Reaction temperatures in these experiments were as high as 840 K unless solid formation was observed at a lower temperature. The critical properties of these fuels and preliminary results of these experiments are summarized in Table 1.

An important practical result of these experiments was the revelation that a pure aromatic, toluene, and a pure straight chain aliphatic hydrocarbon, heptane, were not prone to fouling; however, the addition of a small amount of the aliphatic to the aromatic compound produced fouling tendencies. As indicated in the text and Fig. 3, MCH pyrolysis products confirmed the presence of both aromatics and aliphatics; thus MCH also was found to be prone to fuel line fouling. The conclusion is that under the supercritical fuel line conditions chosen, pure aromatics would not generate sufficient radicals to permit growth to PAH and solids could also be significant.

B. Endothermic Fuel Kinetics

In the 1 atm, gas phase MCH pyrolysis study in the lirinceton flow reactor throughout the temperature range (1050-1200K) studied, the major intermediates found were ethene, 1,3 butadiene, methane and propene. Unlike the liquid-phase catalytically driven reaction reported in the literature, no toluene or other aromatics were formed in these gas-phase reaction studies.

The assumption that the pyrolysis of the MCH occurred primarily by H abstraction and, to a lesser extent, by C-C bond homolysis, with the resulting fuel radicals decaying through ß-scission of both C-C and C-H bonds, permitted an analysis which predicted formation rates of intermediates that were in reasonable agreement with the experimentally obtained reaction rates. Without reporting all the specific measurements taken, MCH pyrolysis decay profiles were measured (Fig. 5) as functions of time at 1 atm pressure and four temperatures (1058, 1108, 1154 and 1192K), and the exponential curve fits of these data were calculated. When a first-order rate analysis was applied, the curves permitted the calculation of the rate constant for the overall MCH decomposition at each temperature. The experimental data were normalized by the fuel loading for each case, and first-order curve fits were obtained (Fig. 5). By linear regression of the data in this figure it was possible to determine the overall activation energy as 265 kJ/mol and the corresponding pre-exponential factor to be $3.7 \pm 0.5 \times 10^{13} s^{-1}$.

The MCH oxidation rates were found to be faster than the pyrolysis rate, but interestingly no new major intermediates were detected. Thus the presence of oxygen increased the rate of H abstraction from the fuel, but it did not affect the ß-scission paths of the radicals formed.

The results of the experiments in which MCH/toluene blends were oxidized indicated that, although the oxidation mechanism of each fuel was unaffected by the presence of the other fuel in the reactor, the oxidation of both fuels was related to the initial MCH concentration. Increasing MCH concentrations resulted in faster decay of both component fuels. The less stable MCH produced the majority of the radical pool for both MCH and toluene attack. Complete details of this MCH effort appeared in a recent publication (Combust. and Flame, 108, 266 (1997)).

Corresponding to the MCH pyrolysis, studies of decalin, another endothermic fuel, were undertaken, and a pyrolysis study was completed. This aspect of the research followed that of the MCH effort. Decalin pyrolysis profiles were obtained at four different temperatures (Fig. 6). From these data the kinetic parameters associated with the overall decay were determined to be $7.71 \times 10^{10} sec^{-1}$ and 203.9 kJ/mole for the pre-exponential and activation energy, respectively. The major products formed for all temperatures considered were methane, ethene, propene, 1,3 butadiene and benzene. Whereas very little naphthalene (less than 10 ppm) was formed in these gas phase studies, naphthalene is the dominant hydrocarbon formed during the catalytic dehydrogenation of decalin. This result corresponded to that found for MCH in that there was minimal production of the primary dehydrogenation product under vapor phase conditions.

III. Personnel

Prof. I. Glassman, Principal Investigator

Dr. K. Brezinsky, Co-Principal Investigator, 1 Oct. 1994 - 30 Sept. 1996

Mr. S. Klotz, Graduate Student

Mr. J. Stewart, Graduate Student

Mr. S. Zeppieri, Graduate Student

IV. Publications

Stewart, J., Brezinsky, K., and Glassman, I., "Pyrolytic Formation of Polycyclic Aromatic Hydrocarbons in Supercritical methlcyclohexane", Eastern States Section/The Combustion Institute Technical Meeting Proceedings, 1995.

Glassman, I., "Plateau Region of Composite Propellants," AIAA Journal 12, 439 (1996).

Glassman, I., "Combustion, 3rd Ed.," Academic Press, San Diego, CA (1996).

Shaddix, C., Brezinsky, K., and Glassman, I., "Analysis of Fuel Decay Rates in High Temperature Oxidation of 1-Methylnaphthalene", Combustion. And Flame 108, 139 (1997).

Zeppieri, S., Brezinsky, K., and Glassman, I., "Pyrolysis Studies of Methylcyclohexane and Oxidation Studies of Methycyclohexane and Methylcyclohexane/Toluene Blends," Combust. And Flame 108, 226 (1997).

Stewart, J., Brezinsky, K., and Glassman, I., "Pressure and Temperature Effects on Supercritical Decalin Pyrolysis", Eastern States Section/The Combustion Institute Technical Meeting Proceedings, 1997.

Zeppieri, S., Brezinsky, K., and Glassman, I., "Atmospheric Pyrolysis and Oxidation Studies of Decalin," Eastern States Section/The Combustion Institute Technical Meeting Proceedings, 1997.

V. Interactions

Performer	-	I. Glassman
Customer	-	UTC/ARPA Active Combustion Control Program (Dr. T. Rosfjord)
Result	-	Continued advice to program
Application	-	Control of gas turbine instabilities

Performer	-	K. Brezinsky
Customer	-	G.E. Research Center (Dr. Sanjay Correa)
Result	-	Discussion of research results relevant to fuel fouling
Application	-	Gas turbine engine fuel lines

Performer - K. Brezinsky
Customer - Texaco (Bill Studzinski)
Result - Presentation of aromatics oxidation chemistry
Application - Automotive engine performance

Performer - I. Glassman, K. Brezinsky
Customer - NASA Lewis (D. Bittker)
Result - Toluene and Benzene Modelling
Application - Gas turbine combustion

Performer - I. Glassman, K. Brezinsky
Customer - UTRC (Dr. M. Colket)
Result - Toluene Modelling
Application - Gas turbine combustion

Performer - I. Glassman
Customer - UTRC (Dr. L. Spadaccini)
Result - Supercritical fuel results transfer
Application - Gas turbine fuel fouling

Performer - I. Glassman, K. Brezinsky
Customer - Imperial College (for U.S. WPAFB)(Prof. L. Lindstedt)
Result - Toluene modelling
Application - Gas turbine combustion

Table 1: Critical Properties

FUEL	Critical Temperature (K)	Critical Pressure (MPa)	PAH Formation	Solid Formation
Methylcyclohexane	572.2	3.471	Yes	Yes
Toluene	540.3	2.756	No	No
Heptane	591.8	4.104	Trace	Trace
10% Heptane, 90% Toluene (Molar)	577.5	3.610	Yes	Yes

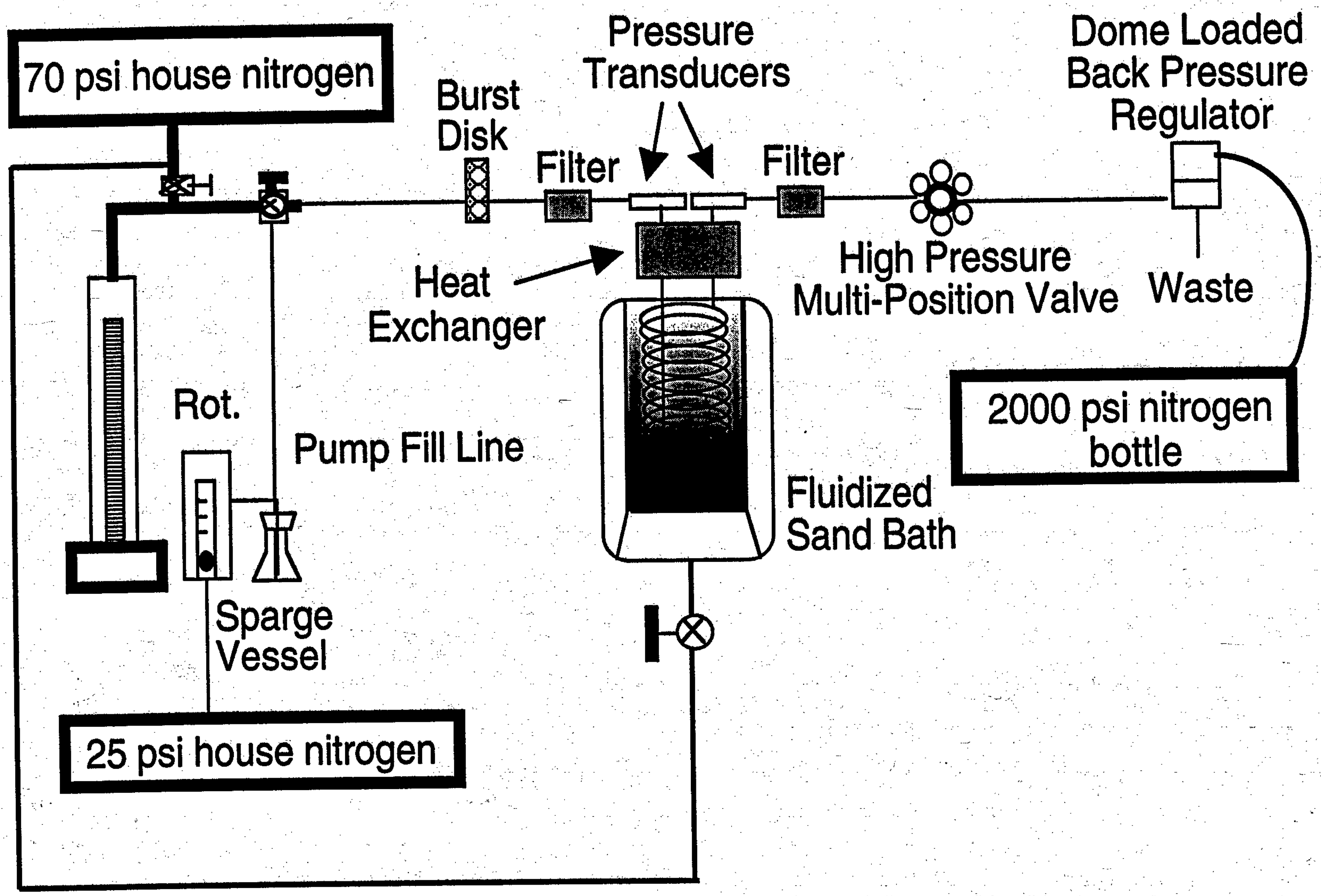

Figure 1: Experimental Apparatus

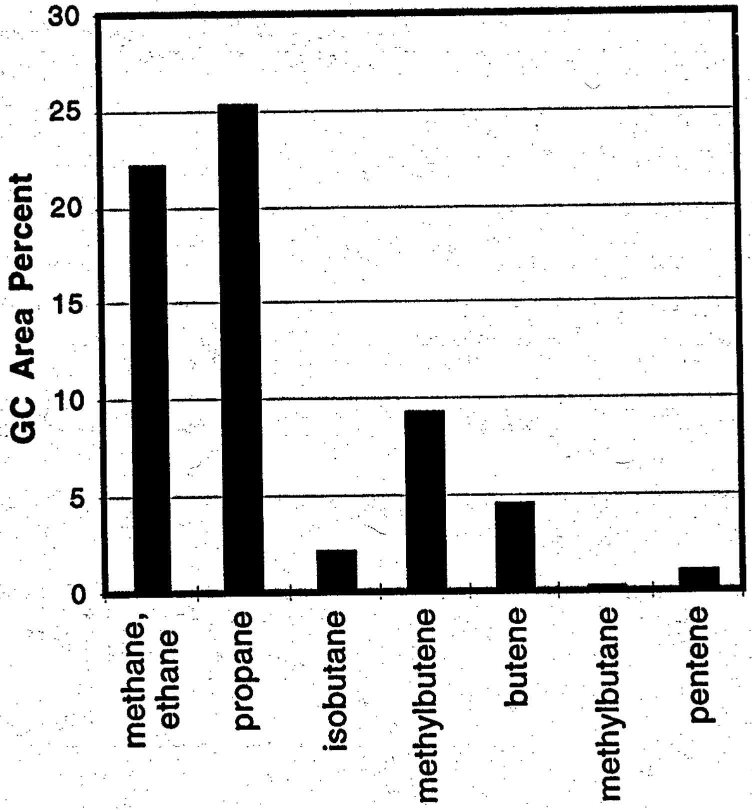

Figure 2: Major Uncondensed Products of Supercritical Methylcyclohexane Pyrolysis
T=820K, Pr=1.3, Residence Time=1 minute

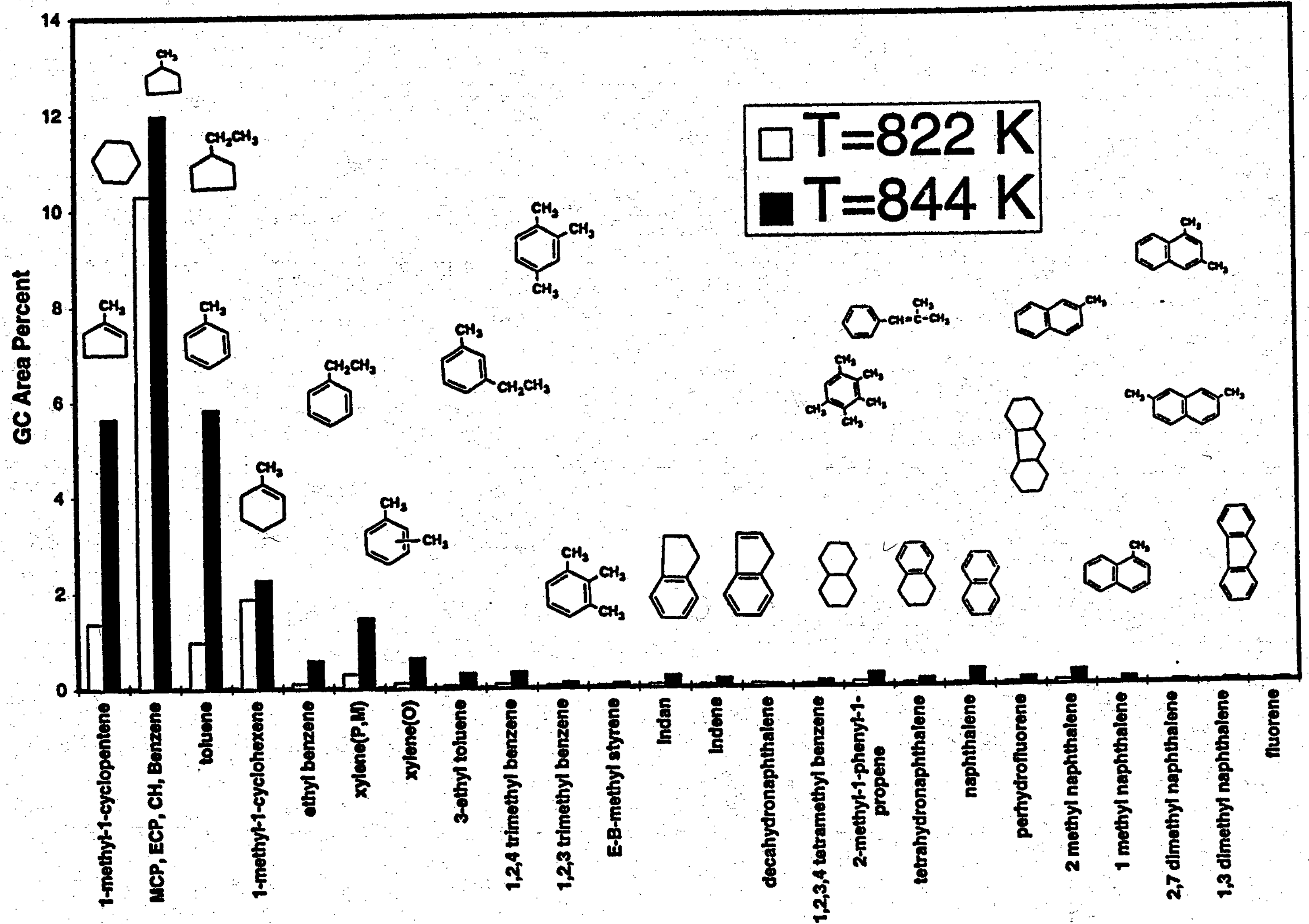

Figure 3: Methylcyclohexane Pyrolysis Major Condensed Products
T=820K, 844K, Pr=1.3, Residence Time=1 minute

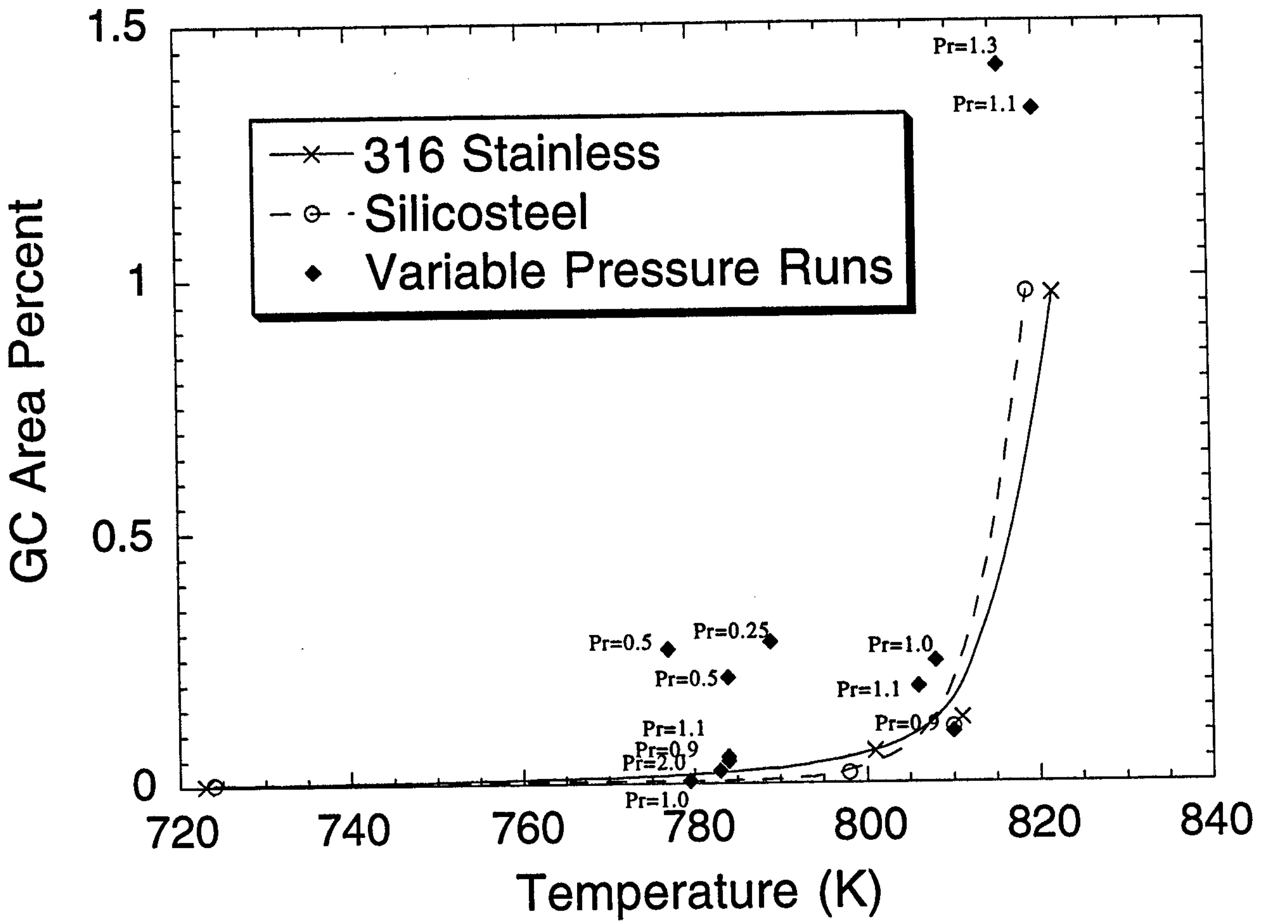

Figure 4: Toluene Yields in Methylcyclohexane Pyrolysis as a Function of Temperature and Pressure
Residence Time=1 minute

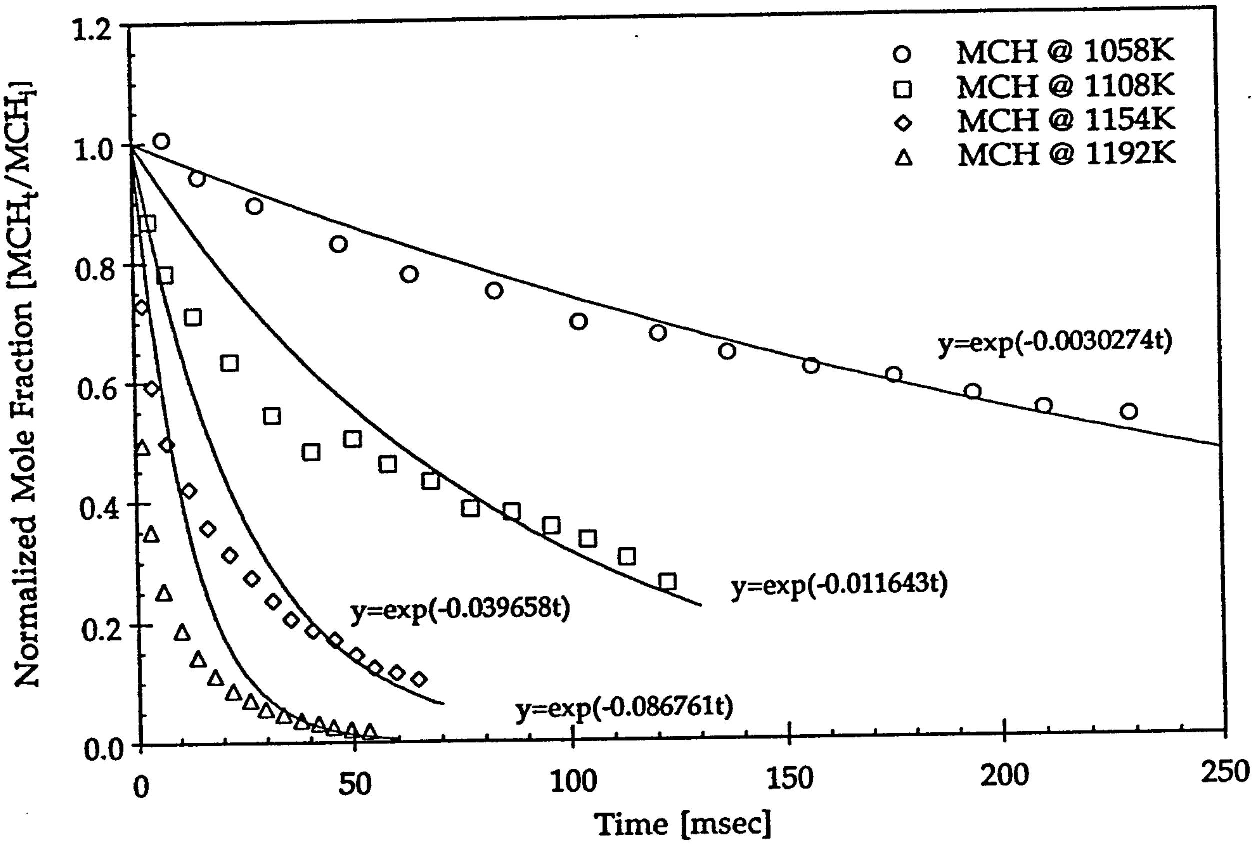

Figure 5. MCH Pyrolysis Profiles

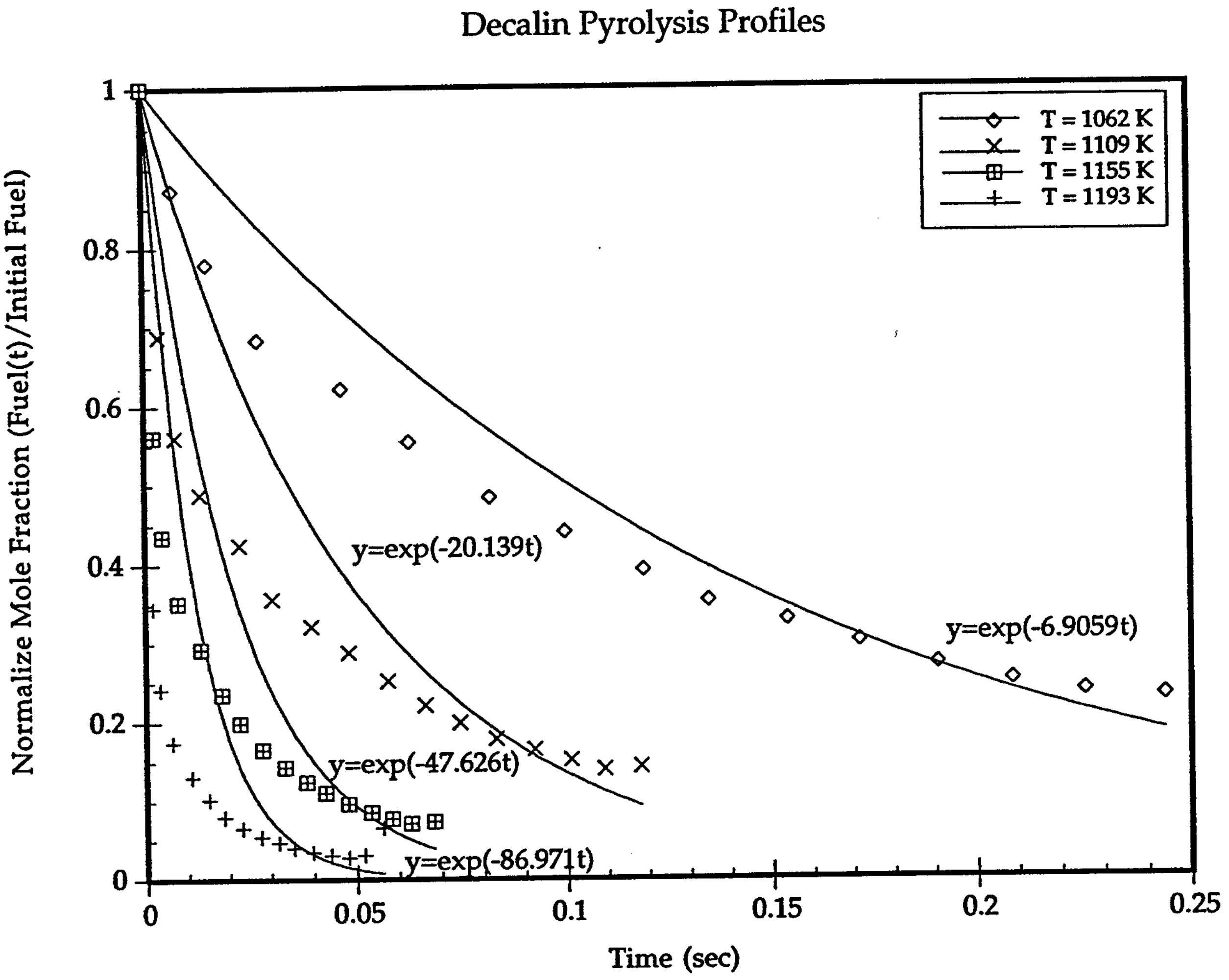

Figure 6. Decalin Pyrolysis Profiles