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13. Abstract (Maximum 200 words)

AASERT support permitted an additional graduate student to be added to AFOSR's "Fuels Combustion Research" program at Princeton. This support allowed fuel pyrolysis and combustion to be studied under both sub and supercritical conditions. This newly integrated program, with AASERT support, proved to be an enormous success. It was found that under supercritical conditions the pyrolysis rate of fuels have a pre-exponential rate A factor order of magnitudes greater than results obtained at 1 atm. The activation energies of the complete energy range tested remained the same. Further, due to the phenomenon known as "caging" for the fuels studied, cyclic hydrocarbons formed under supercritical conditions, but not at 1 atm, and these cyclic hydrocarbons led to polynuclear aromatics (PAH) that are the precursors to particulate formation.

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FINAL REPORT

AASERT GRANT

(AFOSR GRANT F49620-95-1-0406)

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Princeton, NJ 08544

A. Summary

The ASSERT supported graduate students had worked on the investigation of the thermal and combustion characteristics of fuels at conditions of special interest to the Air Force. The efforts had concentrated on the characteristics of endothermic fuels necessary as coolants in next generation aircraft and fuel fouling under sub- and super-critical conditions. The students are presently writing their Ph.D. thesis.

B. Technical Discussion

Princeton's efforts in its AFOSR research program, "Fuels Combustion Research" (AFOSR Grant F49620-98-1-0134) concentrated on the pyrolysis and combustion of endothermic fuels under subcritical conditions and the pyrolysis of the same endothermic fuels and components of JP fuel under supercritical conditions. The motivation for the new approach in this program had been the Air Force's interest in advanced cooling techniques for high speed aircraft and its plan for the next generation aircraft gas turbines whose compression ratios would be increased to the extent that the fuel lines feeding the combustors would enter the supercritical range. This new motivation led to an integrated research effort under AFOSR's Princeton grant to study in detail the pyrolysis and combustion of methylcyclohexane (MCH) and decalin at 1 atm pressure and the pyrolysis of these fuels and tetralin under supercritical conditions. The experimental approach required continuation of 1 atm studies in the Princeton Turbulent Flow Reactor, which have been described in numerous AFOSR progress reports and archival papers (1-4) and the development of a unique, new supercritical flow reactor (5-7). The new supercritical experimental work required the addition of another graduate student to the program. Since support of graduate students had been one of the major contributing costs to the budget of the primary AFOSR program, it would have been impossible to add another student to the effort because of cost limitations. The awarding of the AASERT Grant that is the subject of this final report made it possible to enlist a new student, pursue the supercritical efforts and make some significant contribution to the understanding of the pyrolysis of aircraft fuels under supercritical conditions.

The overall approach allowed by the AASERT grant of having different students working in different pressure ranges with the same fuels had proved to be an enormous success. The global kinetic rates of MCH, decalin and tetralin for their first order decomposition were determined. Figure 1 summarizes the kinetic results at both 1 atm and the supercritical condition of 45 atm and Figure 2 reports the kinetic rate constants and major products found under these two different pressure conditions. These results were obtained from detailed experimental chemical analysis and for the supercritical case from numerous histograms typified by Figure 3. The significance of obtaining histograms of the type represented by Figure 3 is worth emphasizing. All the supercritical results were obtained by the graduate student supported by this AASERT Grant.

To be noted in Figure 2 is that dimethylcyclopentane is not formed in the 1 atm studies with respect to methylcyclohexane and methylhexahydroindane is not formed in the 1 atm studies of decalin. If one examines the activation energies of all systems reported in Figure 2, one notes that all except the subcritical study of decalin are in the 270 kJ/mole range. The statistical analysis of the experimental subcritical results requires reporting the results stated; however, since all the other results report values around 270 kJ/mole, one would expect similar initial bond breaking under the subcritical decalin condition compared to the other cases and thus one would expect that the true experimental activation energy value would also be in the 270 kJ/mole range. This modification is significant in that to keep the actual energy values within the proper range the pre-exponential A factor would have to be of the order $10^{13}sec^{-1}$, as exists for the subcritical results for methylcyclohexane. The significance is that then the subcritical results report an A factor of $10^{13}sec^{-1}$, the supercritical results report an A factor of $10^{15}sec^{-1}$ and all the activation energies are essentially similar. This two order of magnitude difference in the A factor may be significant.

The subcritical (gas phase) methylcyclohexane pyrolysis results revealed that methylcyclopentane pyrolysis was to be β scission dominated and, little, if any, PAH is found during the pyrolysis. The major pyrolysis products were ethene, 1,3 butadiene, methane and propane. It has been concluded that under supercritical conditions while β scission processes are still important, they are significantly slower at 1 atm. Further, dimethylpentane and methylcyclopentane are major products not found under subcritical conditions (Fig. 2). Thus, it had been proposed that dimethylpentane develops from an intermediate methylhexedienyl radical (MHDL). The process by which the initial 6-member ring is converted to a 5-member ring is most apparently due to the phenomenon of caging, a phenomenon frequently discussed in the supercritical chemical process literature(8).

Thus, it appears quite evident that under supercritical conditions, methylcyclohexane pyrolysis creates MHDL which then follows two possible routes to further change: β scission leading essentially to innocuous products or a cyclization due to the phenomenon called caging and possibly leading to significant PAH formation. Obviously, the extent of either route depends on the physical parameters of the set of experiments reported in Figs. 1 and 2.

To understand the phenomenon of caging, it is best to consider both routes simultaneously. To offer a simple phenomenological approach, consider that in the dissociative β scission process, the products of any β scission step must diffuse away in competition with a collision process that would cause a radical such as MHDL to form a new bond instead of breaking one and create a cyclohydrocarbon compound. One can visualize that this process would most likely occur under very high pressures. Thus it is quite apparent that in a practical system the amount of PAH and subsequent particulates that form are due to the competitive "rate processes", one controlled by the diffusion of dissociated species (β scission) and the other by a collision rate process that forms a new bond (caging).

In order to estimate the effect of caging with respect to a chemical process, the general approach had been to apply transition state theory(8,9) . What essentially has been considered is the rate of formation of a product through an intermediate (complex) in competition with the intermediate reforming the initial reactant. However, Princeton's work with respect to pyrolysis has extended the concept in that the intermediates do not proceed back to the reactant, but have two possible routes to form different products, one a β scission route to innocuous products and the other a caging process leading to products which could cause fuel line fouling.

Now, following the classical chemical approach to evaluating the extent of a given route, the argument has been presented that under supercritical conditions the extent of PAH formation would be determined by the ratio of the collisional rate of formation of the new cyclohydrocarbon due to caging to the diffusion rate of the β scission products "to get out of the cage". This ratio can be represented by the following expression

$$\frac{\nu d^2 \exp(-E/RT)}{D} \quad \text{or} \quad \frac{\nu \exp(-E/RT)}{\left(D/d^2\right)}$$

where ν is the crossing frequency (sec^{-1}), d^2 the collision cross section, E the activation energy and D the mass diffusivity (cm^2/sec)(8). Essentially νd^2 is the pre-exponential kinetic A factor of the rate expression in the numerator. The second representation above is formulated so that a ratio of characteristic times is presented. This time rate will be recognized as a Damkohler number(8). Further, for the pyrolysis processes under consideration in this effort, the caging institutes a bond formation process and thus the activation energy is zero. The relevant Damkohler number is then $[\nu/(D/d^2)]$.

Typical small molecular diffusivities have been reported to be from 10^{-1} cm^2/sec for gases to 10^{-5} cm^2/sec in liquids(8). One would estimate that under the supercritical conditions of the experiments discussed here that the diffusivities of a supercritical fluid would be somewhere between the two values, say of the order 10^{-3} cm^2/sec. It is very tempting to speculate that the two order of magnitude differences in A factor found between the subcritical and supercritical conditions reported in this research is due to two orders of magnitude difference between the diffusion under subcritical and supercritical conditions, but there is no real justification for this comparison. However, it is relevant to point out that, although supercritical fluids have in may instances greater similarity to liquids than gases, their diffusivities act more like gases in that they are inversely proportional to pressure. The diffusivities of liquids are independent of pressure. Certainly, these statements were true for the range of supercritical pressures in the reported work. Thus caging products should increase with pressure. Due to this concept, the ratio of caging intermediate methylhydroindane found for decalin compared to its β scission route was measured as a function of pressure at a given temperature. A substantial increase in methylhydroindane with pressure, nearly an order of magnitude increase with an increase from 1 to 85 atm in pressure was observed. These results are of great significance, not only for their application to practical considerations in that a small amount of particulates could play havoc in an aircraft gas turbine fuel line, but also that they offer fundamental confirmation of the conceptual processes proposed and illustrate the important parameters which a design engineer must consider.

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Global Kinetic Rates

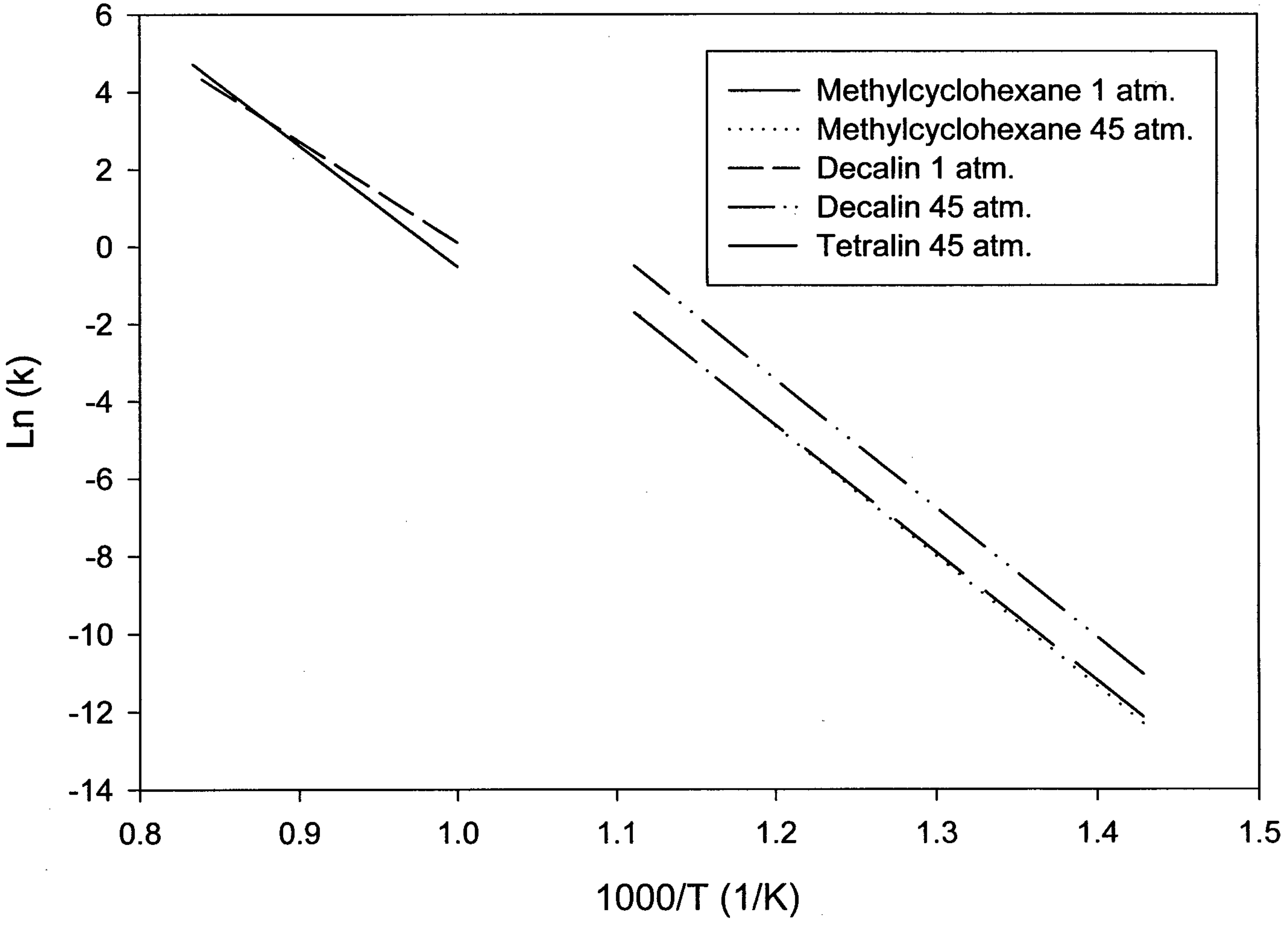


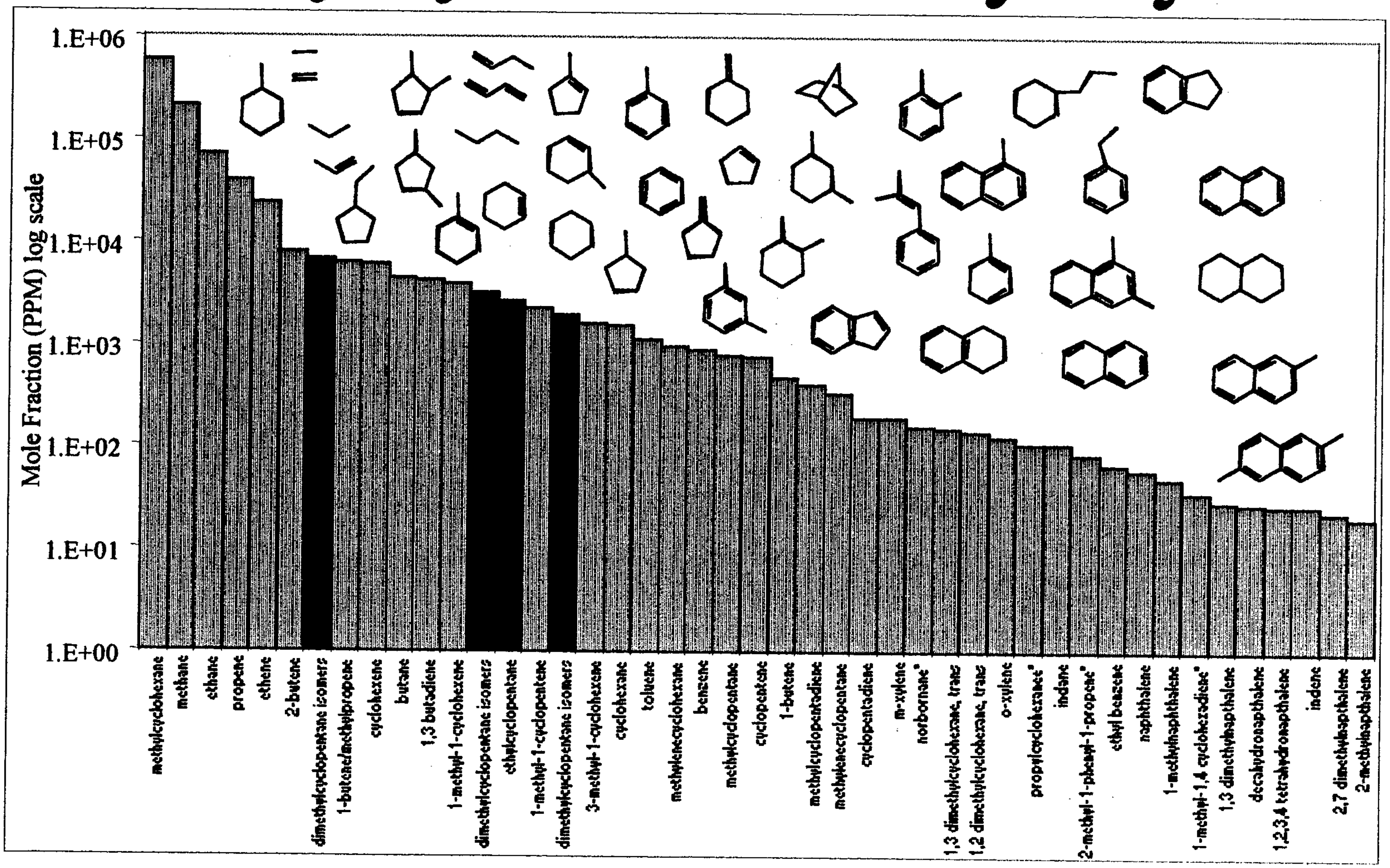
Fig 1

Integrated Research Summary

Fuel	*Phase*	*A (1/sec)*	*Ea (kJ/mole)*	*Major Products*
Methylcyclohexane	gas	2.55E+13	261	ethene, 1,3 butadiene, methane, propene
Methylcyclohexane	supercritical	2.51E+15	278	methane, ethane, propene, ethene, **dimethylcyclopentane**, propane, 1-methyl-1-cyclohexene, **ethylcyclopentane**
Decalin	gas	2.70E+11	218	methane, ethene, propene, 1,3 butadiene, benzene, toluene
Decalin	supercritical	6.31E+15	276	methane, propane, ethane, propene, ethene, butene, butane, **methylhexahydroindane** , indene
Tetralin	supercritical	1.26E+15	273	naphthalene, **methylindane** , ethane, methane, ethene, phenylbutane, propane, propene

Fig, 2

Major Products of Methylcyclohexane Pyrolysis



Fig, 3

Transition Under ASSERT Grant F49620-95-1-0406

Performer - I. Glassman
Customer - UTRC (Dr. M Colket)
Result - Insight into sooting problem
Application - Emissions for aircraft gas turbines

Performer - I. Glassman
Customer - Rocketdyne (Dr. R. Edelman)
Result - Sooting occurrence in rocket engines
Application - Emission from rocket engine

Performer - I. Glassman
Customer - SRI International (Dr. G. Faris)
Result - Carbon fiber formation
Application - Strong materials

Honors Award

Propellant and Combustion Award Irvin Glassman American Institute of Aeronautics and Astronautics	1998
Distinguished Teaching Award Irvin Glassman Princeton University School of Engineering and Applied Science	1998
Election to National Academy of Engineering Irvin Glassman National Academy of Engineering	1996
Ralph Coats Roe Award Irvin Glassman American Society of Engineering Education	1984
Robt. H. Goddard Professorship Irvin Glassman Princeton University	1983
Sir Alfred Egerton Gold Medal Irvin Glassman The Combustion Institute	1982

Principal Investigator Annual Data Collection (PIADC) Survey Form

PI DATA

Name Irvin Glassman

Institution Princeton University

Contract/Grant No F49620-95-1-0406

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Project/Subarea

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NUMBER OF CONTRACT/GRANT CO-INVESTIGATORS

Faculty ______ Post Doctorates ______ Graduate Students ____ Other ______

PUBLICATIONS RELATED TO AFOREMENTIONED CONTRACT/GRANT

Name of Journal, Book, etc.

Combustion Science and Technology

Title of Article
"Supercritical Pyrolysis of Decalin, Tetralin and n-Decane at 700-800 K. Product Distributionand Reaction Mechanism"
Authors
J. Stewart, K. Brezinsky, and I. Glassman
Publisher
V. 136, pp. 373-390, June 1998
Name of Journal, Book, etc.
27th Symposium (Int'l.) on Combustion

Title of Article
"Sooting Laminar Diffusion Flames Effect of Dilution, Additives, Pressure and Microgravity"
Authors
I. Glassman
Publisher
The Combustion Institute, Pittsburgh, PA
Accepted for publication (1998)
Name of Journal, Book, etc.
27th Symposium (Int'l.) on Combustion

Title of Article
"Modeling the Combustion of Toluene-Butane Blends"
Authors
S. Klotz, K. Brezinsky and I. Glassman
Publisher
The Combustion Institute, Pittsburgh, PA
Accepted for publication (1998)

Name of Journal, Book, etc.
Journal of Propulsion and Power

Title of Article
"Combustion Thermodynamics of Metal-Complex Oxidizer Mixtures"
Authors
I. Glassman and P. Papas
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American Institute of Aeronautics and Astronautics
Accepted for publication (1998)
Name of Journal, Book, etc.
Journal of Physical Chemistry

Title of Article
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Submitted 1998