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# FUELS COMBUSTION RESEARCH: SUPERCRITICAL FUEL PYROLYSIS

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## SUMMARY/OVERVIEW:

The fuels used in the next generation of hypersonic aircraft [1] will have to operate under very high pressures (beyond the critical pressures of most hydrocarbons) and will have to sustain very high heat loads in order to meet aircraft cooling requirements. Potential candidates for meeting these stringent cooling requirements are "endothermic" fuels, fuels that can undergo a controlled heat-absorbing chemical reaction (*e.g.*, dehydrogenation) prior to combustion. Critical to the development of the fuel systems in these aircraft is an understanding of the fuel pyrolysis reaction mechanisms under the conditions that the fuels will be operating. Of particular interest are the reactions leading to polycyclic aromatic hydrocarbons (PAH), which can serve as precursors to fuel-line deposits, a problem of critical importance to avoid, for safe aircraft operation. In order to better elucidate the mechanisms and kinetics of the reactions of endothermic fuel pyrolysis and PAH formation under supercritical conditions, supercritical pyrolysis experiments are being conducted, under the present research program, with model fuels, over a range of supercritical pressures and temperatures. The model fuels include two endothermic fuels, methylcyclohexane and decalin, as well as toluene and heptane, hydrocarbons representative of the aromatic and aliphatic components of jet fuels. The reaction products are analyzed by high-pressure liquid chromatography with diode-array ultraviolet-visible absorbance detection (HPLC/UV), an isomer-specific technique ideally suited for the analysis of PAH [2]. It is anticipated that the results from this study will provide information of critical importance to the design and development of fuel systems for high-speed aircraft.

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## TECHNICAL DISCUSSION

Pyrolysis experiments have been conducted with the model endothermic fuel methylcyclohexane (critical temperature 299 °C, critical pressure 34 atm) at a residence time of 30 sec; at temperatures of 330, 370, 430, 470, 530, and 570 °C; and at pressures of 20, 40, 60, 80, and 100 atm. Collection and analysis of the methylcyclohexane reaction products from these experiments reveals that for the 30-sec residence time employed and the entire range of pressures investigated, PAH are not produced at detectable levels at temperatures  $\leq 430$  °C. At the highest temperatures of 530 and 570 °C, PAH are produced at all pressures. At the intermediate temperature of 470 °C, PAH are detected at all pressures but in only minimally detectable amounts at the lowest pressure of 20 atm.

The methylcyclohexane pyrolysis experiments show that an increase in pyrolysis temperature brings about an increase in PAH production as well as an increase in the molecular sizes of the PAH formed. Figure 1 depicts an HPLC chromatogram of the products from methylcyclohexane pyrolysis at 570 °C and 100 atm, the highest temperature and pressure examined so far. Included in Figure 1 are the structures of the twenty-two PAH unequivocally identified by matching the chromatographic retention time and UV absorption spectrum of each sample component with those of authentic reference standards. The HPLC/UV technique is ideally suited for PAH analysis since each PAH exhibits a unique UV absorption spectrum. Compounds of similar chemical structure (*e.g.*, benzo[*a*]pyrene and benzo[*e*]pyrene) are thus easily distinguished, one from another—a distinction very important in determining chemical reaction pathways. The UV spectral matches confirming the identities of two of the methylcyclohexane products of Figure 1, benzo[*a*]pyrene and anthanthrene, are displayed in Figure 2.

As illustrated in Figure 1, supercritical pyrolysis at 570 °C and 100 atm produces a variety of PAH, ranging in size from one to seven aromatic rings, and including several classes of compounds: 10 benzenoid PAH (those with only six-membered rings), 3 fluoranthene benzologues (those with an internal five-membered ring), 3 indene benzologues (those with a five-membered ring containing a methylene carbon), and 6 methylated PAH. The high abundance of methylated PAH distinguishes these methylcyclohexane products from products of purely aromatic fuels [3] and undoubtedly results from the abundance of methyl fragments readily produced from pyrolysis of a hydrogen-rich endothermic fuel such as methylcyclohexane. Additional methylated PAH are thought to be among the products not yet identified in Figure 1 due to the coelution of species and the consequent superposition of peaks in the product components' UV spectra.

Just as pyrolysis temperature has a large effect on PAH production from supercritical methylcyclohexane pyrolysis, so does pressure. Figures 3 and 4 illustrate the effect of pressure on the yields of 2-, 3-, and 4-ring PAH produced from methylcyclohexane pyrolysis at 530 °C and 30 sec. As these figures indicate, all PAH increase in yield as pressure is increased—the greatest jump occurring in the interval from 80 to 100 atm. Figures 3 and 4 also demonstrate that the 2-ring species naphthalene and indene are produced in greatest abundance, followed closely by the two methyl naphthalenes. Compared to these 2-ring species, the 3- and 4-ring species are roughly an order of magnitude lower in yield. The trend of decreasing yield with increasing molecular size is characteristic of pyrolytic molecular growth processes [2].

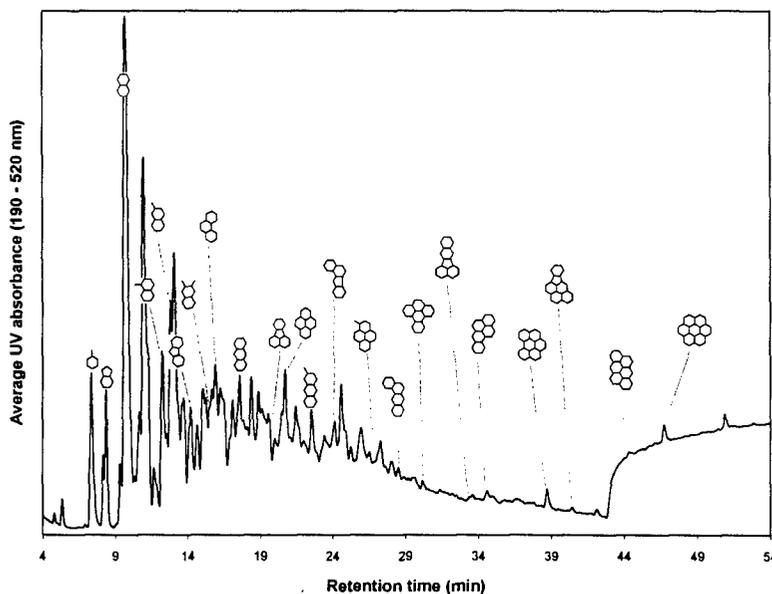
The increase of PAH production with increasing pressure can be tied to the findings of Stewart [4]. As proposed by Stewart [4] and demonstrated in Figure 5, methylcyclohexane pyrolysis produces an intermediate, the methylhexenyl radical, which either in the gas phase at atmospheric pressure or in the supercritical phase produces  $\beta$ -scission products such as ethene and propene. In the very dense environments characteristic of supercritical pressures, however, diffusion of  $\beta$ -scission products (away from one another) is impaired and collision processes are favored, enhancing carbon-carbon bond formation and facilitating the production of cyclic structures. Under supercritical conditions, therefore, the intermediate methylhexenyl radical produces dimethylcyclopentane [4], a hydrocarbon containing a methylated five-membered ring. Such five-membered-ring species have been shown [4 and references therein] to undergo facile conversion to structures containing six-membered aromatic rings. It thus makes sense that the higher pressures that enhance production of five-membered-ring species also enhance production of PAH, as demonstrated in the methylcyclohexane experiments (Figures 3 and 4).

Figure 6 illustrates the reaction [5] of two five-membered-ring species to give naphthalene, one of the most abundant PAH produced in the methylcyclohexane supercritical pyrolysis experiments. Figure 6 also shows how the 1-naphthyl radical, formed from hydrogen-abstraction of naphthalene, can combine [6] with benzene, also present in the supercritical methylcyclohexane pyrolysis products [4], to form the 4-ring product fluoranthene, another of the PAH observed in the methylcyclohexane experiments.

The results obtained so far highlight the importance of temperature and pressure on PAH formation from the pyrolysis of endothermic fuels under supercritical conditions. Future work will include: methylcyclohexane experiments at additional temperatures and residence times, supercritical pyrolysis experiments with other model fuels, and work on the reaction mechanisms of PAH formation in the supercritical context. Since PAH are precursors to carbon solids, determination of the reaction conditions and pathways responsible for PAH formation during the supercritical pyrolysis of endothermic fuels should provide information of critical value to the prevention of fuel-line fouling in high-speed aircraft.

## REFERENCES

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**Figure 1.** Reverse-phase HPLC chromatogram of products of methylcyclohexane supercritical pyrolysis at 570 °C and 100 atm. The rise in baseline at ~43 minutes corresponds to a change in mobile-phase composition to UV-absorbing dichloromethane. Identified components in order of elution from left to right, are: toluene, indene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, fluorene, 2,3-dimethylnaphthalene, phenanthrene, anthracene, fluoranthene, pyrene, 2-methylanthracene, benzo[a]fluorene, 1-methylpyrene, benz[a]anthracene, benzo[e]pyrene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, anthanthrene, coronene.

Figure 2

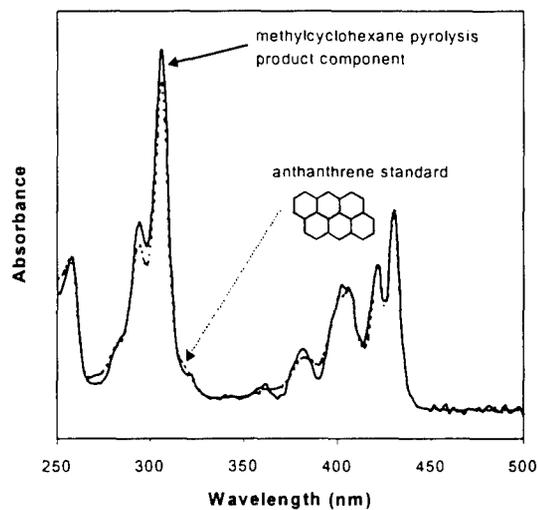
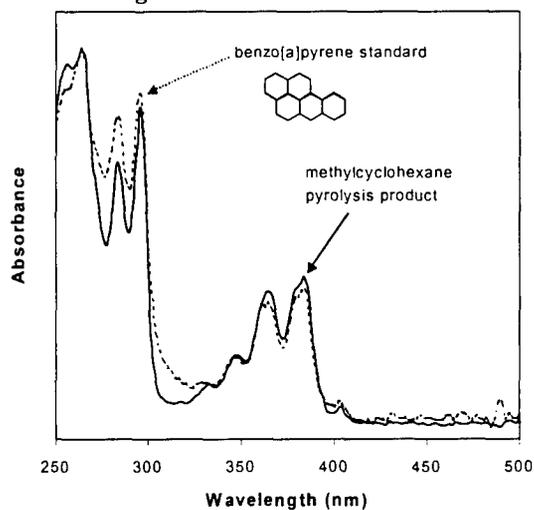


Figure 3

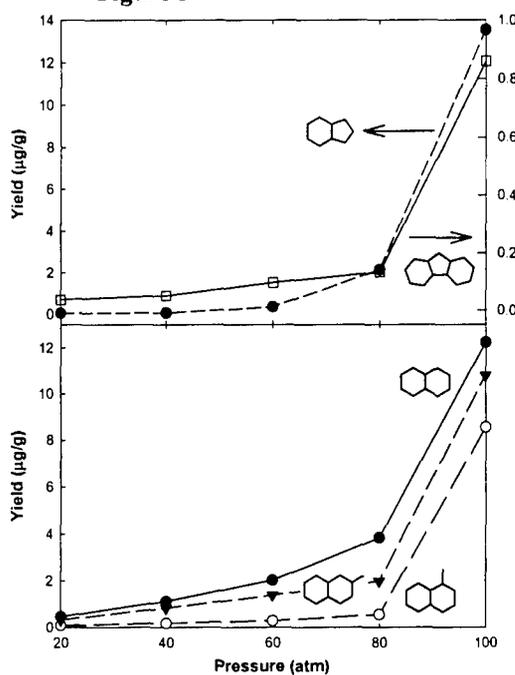
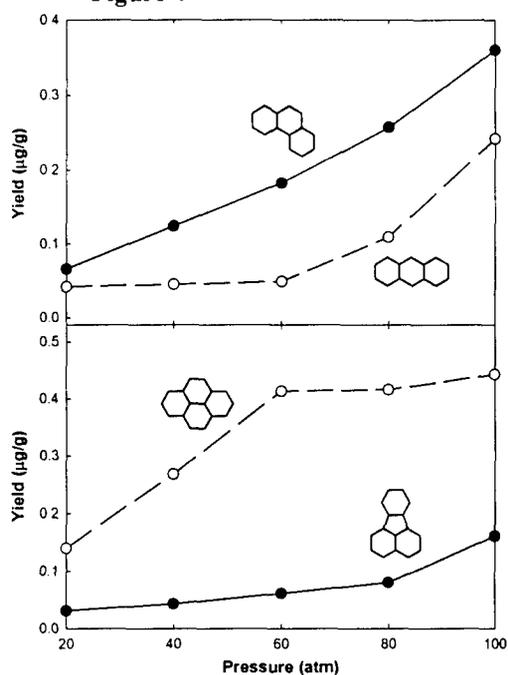


Figure 4



Gas-Phase and Supercritical Phase

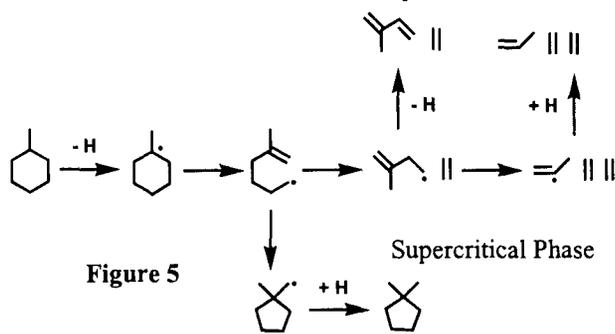


Figure 5

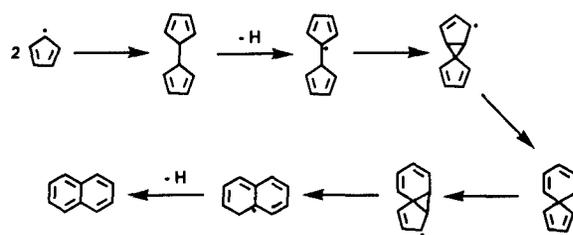


Figure 6

