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The formation of polycyclic aromatic hydrocarbons from the supercritical pyrolysis of 1-methylnaphthalene ☆

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Abstract

In order to better understand the pyrolytic reactions leading to the formation of polycyclic aromatic hydrocarbons (PAH) and carbonaceous solids under supercritical conditions, we have pyrolyzed the model fuel 1-methylnaphthalene (critical temperature, 499 °C; critical pressure, 36 atm) in an isothermal silica-lined stainless-steel reactor coil at 585 °C, 110 atm, and 140 s. Analysis of the reaction products by high-pressure liquid chromatography with diode-array ultraviolet-visible absorbance detection and mass spectrometric detection has led to the identification of 37 individual 2- to 7-ring PAH—fifteen of which have never before been reported as products of 1-methylnaphthalene pyrolysis. The absence, among the reaction products, of single-ring aromatics and acetylene indicates that there is no aromatic ring rupture in this reaction environment, and the structures of each of the 5- to 7-ring PAH products reveal the intactness of the two 2-ring naphthalene units required in their construction. Proposed reaction pathways involving species plentiful in the reaction environment—1-naphthylmethyl radical, methyl radical, 1-methylnaphthalene, naphthalene, and 2-methylnaphthalene—account for the formation of the observed 5- to 7-ring PAH products. These reaction pathways, along with consideration of bond dissociation energies and relative abundances of reactant species, account for the extremely high product selectivity exhibited by the observed product PAH. The detection of seven 8- and 9-ring PAH, each requiring construction from three naphthalene or methylnaphthalene units, provides evidence that the types of reaction mechanisms outlined here—for the combination of two naphthalene entities to form 5- to 7-ring PAH—are also likely to apply to the combination of three and more such entities in the formation of larger-ring-number PAH and eventually carbonaceous solids.

Keywords: Polycyclic aromatic hydrocarbons; Supercritical fuel pyrolysis; 1-Methylnaphthalene

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1. Introduction

Ever-increasing demands for higher speeds and engine efficiencies in high-speed aircraft are placing increasingly stringent demands on the fuels themselves [1]. It is anticipated that within the fuel lines and injection systems of future high-speed aircraft [2,3], fuels may be subjected (for periods of minutes) to temperatures of up to 600 °C and pressures of up to 150 atm—conditions that are supercritical for most pure hydrocarbons as well as jet fuels [1,3]. At these

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☆ Supplementary data for this article can be accessed online. See Appendix A.

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temperatures and pressures, the fuel can undergo pyrolytic reactions, which have the potential of forming carbonaceous solid deposits that can clog fuel lines, foul fuel injectors, and lead to undesirable or even disastrous effects for the aircraft [1]. Critical to the development of reliable fuel systems in these aircraft, therefore, is an understanding of the fuel pyrolysis reaction mechanisms pertinent to the supercritical conditions under which these fuels will be operating. Of particular interest are the reactions leading to polycyclic aromatic hydrocarbons (PAH), which can serve as precursors to the carbonaceous fuel-line deposits [4].

In order to better elucidate the reactions responsible for PAH formation under supercritical pyrolysis conditions, we have conducted supercritical pyrolysis experiments with the model fuel 1-methylnaphthalene (critical temperature, 499 °C; critical pressure, 36 atm), a 2-ring aromatic component of jet fuels [5]. Gas-phase pyrolysis [6–8] and oxidation [9,10] of 1-methylnaphthalene have been previously investigated, but the work of Stewart et al. with other fuels [4,11] has demonstrated that pyrolysis reaction pathways and kinetics in the supercritical phase differ substantially from those in the gas phase. Distinctions between the supercritical phase and gas phase are particularly pronounced for the reactions of PAH formation and growth. Recent studies in our laboratory with toluene demonstrate that acetylene-addition mechanisms [12–14]—widely applicable to high-temperature, gas-phase combustion systems—do not hold for the lower temperatures and higher pressures of our supercritical fuel pyrolysis environment, as no acetylene is formed [15,16].

A critical element in our experimental effort to discern PAH reaction pathways is the ability to analyze large PAH with as much structural specificity as possible. We thus employ high-pressure liquid chromatography (HPLC) combined with diode-array ultraviolet-visible absorbance and mass spectrometric detection—a technique ideally suited for isomer-specific PAH analysis. In the following, we present the results of our supercritical 1-methylnaphthalene pyrolysis experiments at 585 °C, 110 atm, and 140 s. We report the identities of 37 individual 2- to 7-ring PAH products—fifteen of which have never before been observed as products of 1-methylnaphthalene pyrolysis or combustion. We propose reaction pathways for the formation of these PAH, accounting for the high degree of product selectivity experimentally observed. Evidence is also presented for the presence of 8- and 9-ring PAH products whose exact identities are not yet known but whose presence helps establish the link between PAH formation and carbonaceous solids formation in the supercritical fuel pyrolysis context.

2. Experimental equipment and techniques

The supercritical 1-methylnaphthalene pyrolysis experiments are conducted in an isothermal, isobaric reactor designed by Davis [17] and previously used by Stewart [4,11] and Ledesma et al. [15,16] for supercritical pyrolysis of other model fuels. The reactor system is illustrated and described in detail elsewhere [15].

Prior to an experiment, liquid 1-methylnaphthalene is sparged with nitrogen to remove any dissolved oxygen that could introduce auto-oxidative effects [4]. The sparged fuel is then loaded into a high-pressure pump, which delivers the fuel to the reactor, a silica-lined stainless-steel coil of 1-mm i.d., 1.59-mm o.d. capillary tubing. The reactor coil is immersed in a temperature-controlled fluidized-alumina bath, which ensures isothermality throughout the reactor length. The entrance and exit lines of the reactor are passed through a water-cooled (25 °C) heat exchanger to ensure a controlled thermal history and residence time. Exiting the heat exchanger, the quenched reaction products pass through a stainless-steel filter (hole size, 10 μm) and on to a high-pressure valve, for liquid product collection. Gaseous products are collected in a Teflon sampling bag following the high-pressure valve. A dome-loaded back-pressure regulator, downstream of the valve, controls the system pressure, to within ±0.2 atm, up to a maximum of 110 atm.

The 1-methylnaphthalene pyrolysis experiments are conducted at a fixed residence time of 140 s, at temperatures of 550, 575, and 585 °C, and at pressures of 40 to 110 atm. At the conclusion of each pyrolysis experiment, the gaseous reaction products are removed and injected into a gas chromatograph (GC) with flame-ionization detector. The liquid products are removed from the high-pressure collection valve and transferred to a vial. A 20-μL aliquot of the liquid product mixture is removed for injection onto an Agilent Model 6890 GC with a flame-ionization detector, in conjunction with an Agilent Model 5973 mass spectrometer.

An additional 20-μL aliquot of the liquid product mixture is dissolved into 200 μL of dimethylsulfoxide, and two separate aliquots of the resulting product/dimethylsulfoxide solution are injected onto two separate high-pressure liquid chromatographs—one, a Hewlett-Packard Model 1050, coupled to a diode-array ultraviolet-visible (UV) absorbance detector; the other, an Agilent Model 1100, coupled to a diode-array UV detector in series with a mass spectrometer (MS). Employing atmospheric-pressure photo-ionization, the MS monitors mass-to-charge ratios up to 700. As detailed elsewhere [18], each HPLC uses a reversed-phase Restek Pinnacle II PAH octadecylsilica column (particle size, 5 μm; inner diameter, 4.6 mm; and length, 250 mm), through