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Thermal Stability of Energetic Hydrocarbon Fuels for Use in Combined Cycle Engines

K. Wohlwend,* L. Q. Maurice,† and T. Edwards†
U.S. Air Force Research Laboratory, Wright–Patterson Air Force Base, Ohio 45433
R. C. Striebich‡ and M. Vangsness§
University of Dayton, Dayton, Ohio 45469-0132
and
A. S. Hill¶
University of Toledo, Toledo, Ohio 43606

Greater ease of use and higher density make energetic hydrocarbon fuels an attractive alternative to cryogenic fuels. The use of high-energy hydrocarbons in rocket and combined-cycle propulsion systems is being explored. In addition to its obvious use for propulsive purposes, fuel is used to cool system structures regeneratively to temperatures commensurate with presently available materials. Fuel thermal stability unfortunately limits the use of hydrocarbon fuels. In the present contribution, the thermal stability of RP-1, JP-10, and quadricyclane is assessed using a system for thermal diagnostic studies. It is found that, whereas JP-10 and RP-1 exhibit reasonable thermal stability, the highly strained quadricyclane rapidly degrades under high-pressure, condensed-phase thermal stress.

Introduction

CRYOGENIC propellants offer attractive performance advantages for launch vehicles.[1–4]** Liquid hydrogen (LH_2) and liquid oxygen (LO_2) are used in the high-efficiency main engines of the space shuttle, which has a high specific impulse I_{sp} rating of 455 s. Specific impulse is a measure of the thrust per mass flow rate of propellant at the nozzle; even small increases in specific impulse can have large potential benefits in the payload weight able to be placed into orbit. LH_2 and LO_2 also powered the upper stages of the Saturn 1B and Saturn V rockets as well as the second stage of the Atlas/Centaur launch vehicle, the first U.S. LH_2/LO_2 rocket.** The RL-10 engines on the Centaur, a first-stage LH_2/LO_2 rocket, have an I_{sp} of 444 s. I_{sp} ratings for hydrocarbon rockets can be 30% less than I_{sp} values for cryogenic propellants. For example, the RP-1-fueled/LO_2 Atlas G/Centaur rocket has an I_{sp} of 257 s (Ref. 4).

Regrettably, significant operational disadvantages are also associated with the use of LH_2: its low density (71 kg/m^3) translates into large storage tanks, increasing the dry (unfueled) mass of the launch vehicle. Also, cryogenic propellants require considerable thermal insulation, thus further increasing the potential weight of the structure used to carry the propellant. Moreover, the additional logistics and safety concerns of cryogenic propellants and the high cost of LH_2 (70 times that of JP-8 on a volume basis) limit its use.[1] Despite these drawbacks, the high efficiency of LH_2/LO_2 makes these problems worth consideration when reaction time and storability are not critical.

Hydrocarbons, however, remain the fuel of choice for rapid response, storable systems. The advantages of energetic hydrocarbons over conventional JP-8 (aircraft) and RP-1 (rocket) fuels as well as cryogenic propellants are considerable and have been reviewed.[1–4] The higher density of liquid hydrocarbons, such as JP-8 (0.80 g/ml) and RP-1 (0.81g/ml), over LH_2 (0.071 g/ml) provide a real incentive to consider the high-energy density materials. The higher energy densities of energetic hydrocarbons can overcome the lower I_{sp} values as compared to LH_2.

The higher energy content of high-energy hydrocarbons is a result of the high angle strain of the bonds in energetic compounds. Table 1 shows an example of how energy content (heat of combustion) for similar hydrocarbons increases with increased bond strain, normalized for carbon number. Cyclopropane, for example, with 60-deg bond angles, has a higher heat of combustion per CH_2 group than a straight chain alkane. High-energy density hydrocarbons such as quadricyclane (Fig. 1) feature total heats of combustion exceeding not only those of conventional rocket fuel (RP-1) (Fig. 2) but even moderately strained missile fuel (JP-10).

There exist a variety of other hydrocarbons that derive their high-energy density due to a compact molecular structure, such as aromatics or cycloalkanes, for example, cis–decalin, density = 0.897 g/ml. Other compounds such as cubane (C_8H_8), first synthesized in 1964, is both dense and strained.[5] Highly strained compounds were the only materials considered in this work because of their perceived thermal instability.

High-energy fuels may be used to cool system structures regeneratively to temperatures commensurate with presently available materials in combined-cycle engines. Thermal stability unfortunately limits the use of hydrocarbons as coolants.[1,6] Liquid-phase pyrolysis reactions have been shown to be indicative of a fuel's propensity to form undesirable deposits under thermal stress at high temperatures.[7,8] Whereas detailed gas-phase pyrolysis of energetic materials has enabled an understanding of strained-ring hydrocarbons decomposition pathways under combustion conditions,[9–12] study of the liquid-phase pyrolysis of these fuels has not been undertaken to date. Strained-ring hydrocarbon fuels have shown a propensity to soot,[3] and soot formation pathways have been shown to be analogous to pyrolytic deposition mechanisms in fuels systems.[8] Thus, the development of liquid-phase pyrolysis experiments is the logical foundation for beginning to assess the potential use of energetic hydrocarbons as coolants.

Table 2 shows some selected properties of hydrocarbons (also see Refs. 13 and 14).

Description of Experiment

The thermal stability of fuel is often characterized by the mass of deposits that a particular fuel forms under thermal stress. However,

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*Fuels Chemist, Propulsion Directorate, Propulsion Sciences and Advanced Concepts Division, 1790 Loop Road North. Member AIAA.

†Fuels Chemist, Propulsion Directorate, Propulsion Sciences and Advanced Concepts Division, 1790 Loop Road North. Associate Fellow AIAA.

‡Research Engineer, Research Institute, Environmental Sciences, 300 College Park.

§Associate Research Physicist, Research Institute, Aerospace Mechanics Division, 300 College Park.

¶Research Assistant, Department of Chemical Engineering.

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such measurements do not provide insight into the initiation chemistry of the deposition process. An understanding of deposition precursor processes is crucial to devising deposition mitigation techniques, as well as evaluating a candidate fuel's thermal stability.

In the present work, thermal decomposition is studied in a system for thermal diagnostic studies (STDS).[15] The STDS is a versatile system for investigating thermal degradation in the gaseous or condensed phase (Fig. 3). It requires only small volumes of reactants (~5 ml) and, therefore, is an ideal tool for evaluating synthesized, strained hydrocarbons. The STDS is capable of accurately controlling experimental variables such as residence time, temperature, reactive atmosphere, and pressure (supercritical conditions).

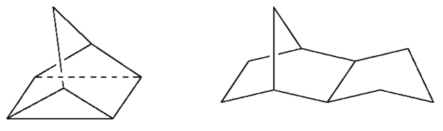
A membrane-diffusion solvent degasser was used to remove dissolved oxygen from the liquid reactant. Removing dissolved oxygen mitigated thermal-oxidative reactions, so that pyrolytic degradation could be examined without concern for oxygenated products acting as pyrolysis initiators or suppressors. A high-performance liquid chromatography (HPLC) pump delivered the liquid-phase material to the high-temperature reactor, with a backpressure regulator (500 psig) used downstream of the reactor to keep the material in the condensed phase, even at high temperature. Reactors were made using stainless-steel HPLC tubing with an internal diameter of 0.0254 cm, making exposures closer to near-isothermal conditions. Experiments consisted of exposing the reactant to high-temperature conditions and examining the decomposition of the reactant and products to determine reactant stability and speculate on the decomposition mechanism.

The thermal reaction compartment of the STDS is a gas chromatograph (GC) (Hewlett-Packard-5890A) with a separately controlled, high-temperature furnace inside. The high-temperature reactor is controlled isothermally at temperatures of between 200 and 650°C, with the GC oven around it held constant at 200°C for quantitative transport of reactants and products. Each experiment is completed at near-isothermal conditions, due to the small reactor and low flow rate of the reactants. High-pressure argon flows through the reactor while liquid flow is established and oxygen is removed by solvent degassing. When dissolved oxygen is fully removed, a high-pressure HPLC sampling valve switches the degassed liquid stream into the reactor leg, replacing the high-pressure argon gas. All experiments were conducted with a constant flow rate of 0.5 ml/min (laminar flow), giving a residence time of 1.8 s at 200°C. Backpressure regulators keep the system pressure at 34 atm. After the flow through, the high-temperature reactor is stabilized for 1 min, the decomposed reactant stream is sampled using a high-temperature, high-pressure sampling valve connected to a GC system (HP-5890). The GC is operated to separate and identify the thermal reaction products using a flame ionization detector. A 0.32-mm-i.d. Gas Pro column (Astec, Inc.) was used to separate the C_1–C_8 components of the sampled stream. A parallel 0.25-mm-i.d. DB-5 (J and W Scientific) capillary column was used in conjunction with a mass selective detector (HP-5970B) to help identify compounds of interest online.

Additional offline analyses were performed by GC–mass spectrometry (GC–MS). Once chromatographic samples are taken, valves are used to restore argon flow back through the reactor to reduce pyrolytic deposition and tube plugging.

Table 1 Hydrocarbon structure and stored energy

Hydrocarbon type	Molecular structure	Bond angle	Heat of combustion (per CH_2 group) kcal/mol
Open chain	—	109.5	157.4
Cyclohexane	⬡	109.5	157.4
Cyclopentane	⬠	108	158.7
Cyclobutane	□	90	164.0
Cyclopropane	△	60	166.6



Quadricyclane

JP-10
exo-tetrahydro-dicyclopentadiene

Fig. 1 Chemical structure of pure hydrocarbons considered.

Results and Discussion

The decomposition profiles of the three reactants are shown in Fig. 4. Decomposition profiles are defined by percent of reactant remaining vs temperature as measured on the GC–MS. Clearly, quadricyclane degrades at much lower temperatures than either JP-10 or RP-1. JP-10 is more stable than quadricyclane, but appears to be less stable than RP-1. From the perspective of regenerative cooling using these hydrocarbons, it is important to consider parent

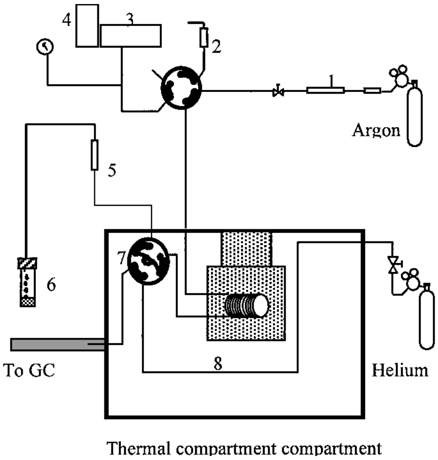


Fig. 3 STDS schematic: 1) check valve/filter, 2) restrictor, 3) HPLC pump, 4) solvent degasser, 5) backpressure regulator (500 psig), 6) sample collection, 7) sampling valve, and 8) furnace.

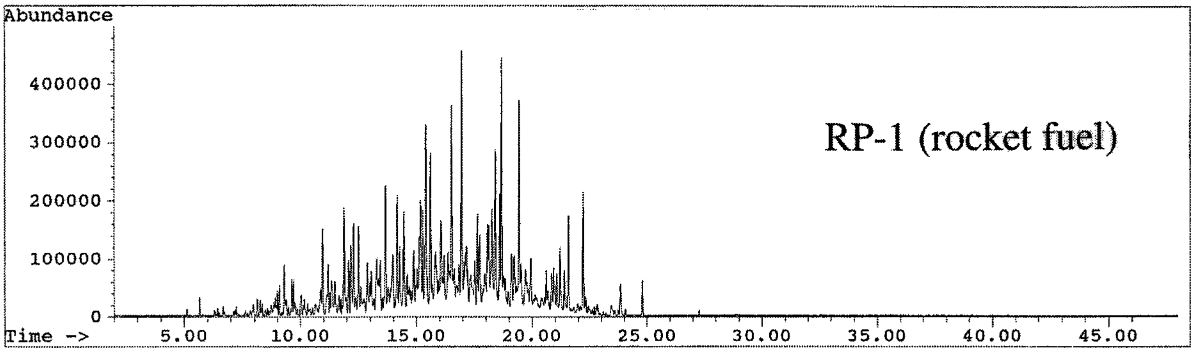


Fig. 2 RP-1 gas chromatogram.

Table 2 Selected properties of hydrocarbons[13,14]

Physical and chemical properties	JP-8	RP-1	JP-10	Quadricyclane	LH_2
Molecular weight	152	170.7	136	92	2.02
Molecular formula	$C_{10.9}H_{20.9}$	$C_{12.1}H_{23.42}$	$C_{10}H_{16}$	C_7H_8	H_2
Density, g/ml	0.80	0.81	0.95	0.98	0.071
Heat of combustion					
Btu/lb	18,494	18,600	18,130	19,061	49,900
kJ/mol	6,538	7,385	5,735	4,114	234
Boiling point, K (°F)	448–543 (347–518)	453–543 (354–518)	455 (360)	381 (226)	20 (−423)
Flash point, K (°F)	311 (100)	343 (158)	327 (130)	284 (52)	——

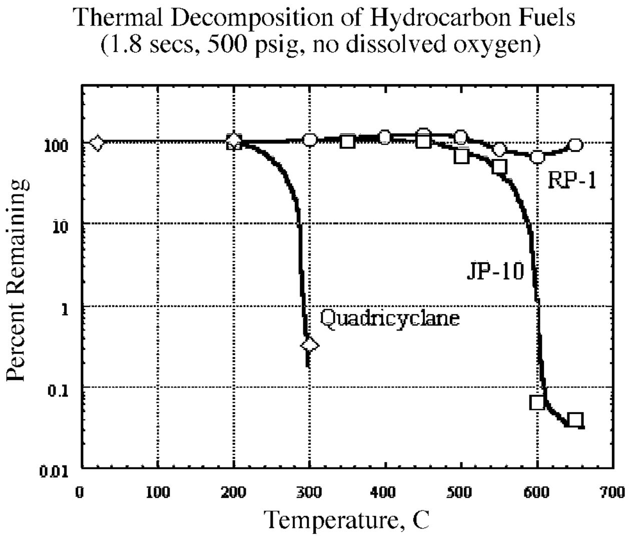


Fig. 4 RP-1, JP-10, and quadricyclane decomposition profiles.

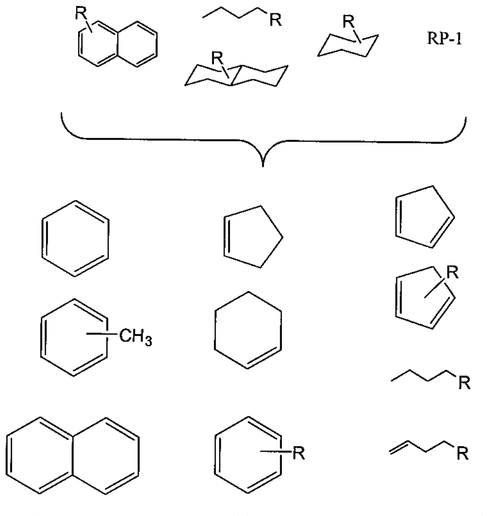


Fig. 5 RP-1 thermal decomposition products as determined by GC–MS.

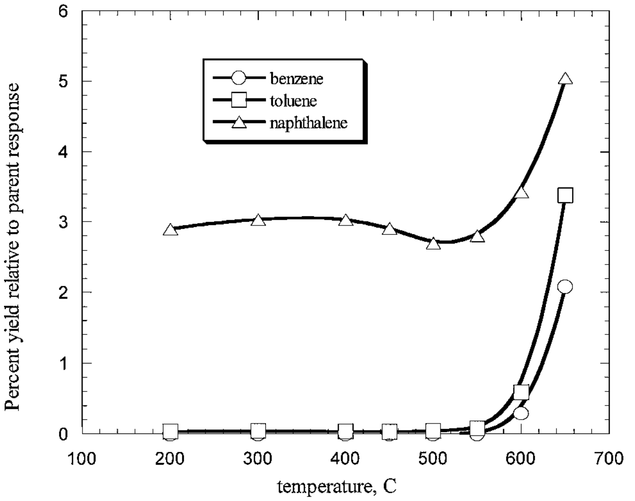


Fig. 6 Aromatic formation in RP-1 based on parent reponse to GC–MS detection at 200°C.

compound stability. If quadricyclane were used as a coolant and experienced temperatures above 200–300°C, some or all of the strain energy of the molecule would be lost because the quadricyclane would decompose before the combustor. Fuel system designers must consider the implications with regard to energy loss for a material to be used as a coolant and propellant.

The parent compound stability provides an indication of how much thermal stress a molecule may undergo before it degrades. After the molecule degrades, the products that form may indicate its propensity to form deposits[12] as well as to provide a possible decomposition mechanism as a function of temperature. Decomposition products for RP-1 are shown in Fig. 5, as determined by GC–MS results. The RP-1 parent material is composed of a wide range of compounds comprising primarily cycloparaffins and paraffins. A small amount of fragmentation is evident initially at 500°C. The RP-1 components experience more severe fragmentation at temperatures above 600°C. Product formation at 650°C appears from Fig. 4 to decrease (~95%) parent compound stability, but this response was difficult to determine accurately due to the complex nature of the RP-1. Cyclics and unsaturates dominate light product formation. Although RP-1 pyrolysis does not plug the reactor, the effluent turned yellow at 600°C and became even darker at 650°C. Higher temperature tests were not completed to avoid plugging the reactor. Benzene, toluene, and naphthalene formation occurred and became detectable between 600 and 650°C, as shown in Fig. 6. Single-ring and polycyclic aromatic hydrocarbon formation may be indicative of substantial parent compound degradation and subsequent molecular growth reactions to larger, more stable aromatic hydrocarbons. However, it must be noted that the RP-1 parent compounds may include small quantities (<3%) of aromatic compounds. As seen in Fig. 6, a small amount of naphthalene is already present in RP-1. No benzene or toluene were originally present in RP-1.

Decomposition products observed in JP-10 exposure are shown in Fig. 7, as determined by GC–MS. Because JP-10 is essentially a pure compound, its product distribution is more straightforward than is RP-1. JP-10 starts to fragment slightly at 450°C and decomposes readily by 600°C. The major decomposition products observed are cyclopentene and cyclopentadiene. Minor products include substituted cyclopentene and substituted cyclopentadiene. Tetrahydrodicyclo-pentadiene is also formed, possibly via JP-10 isomerization. Benzene, toluene, and naphthalene formation is observed between 550 and 600°C, as shown in Fig. 8. None of these

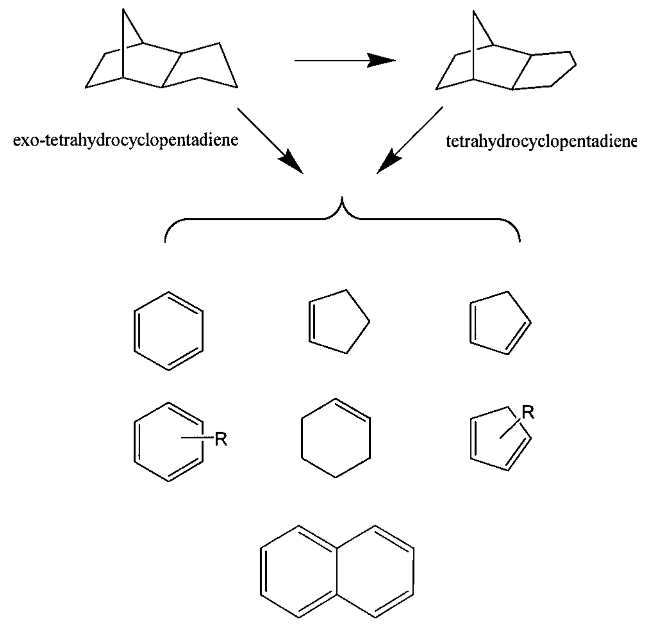


Fig. 7 JP-10 thermal decomposition products.

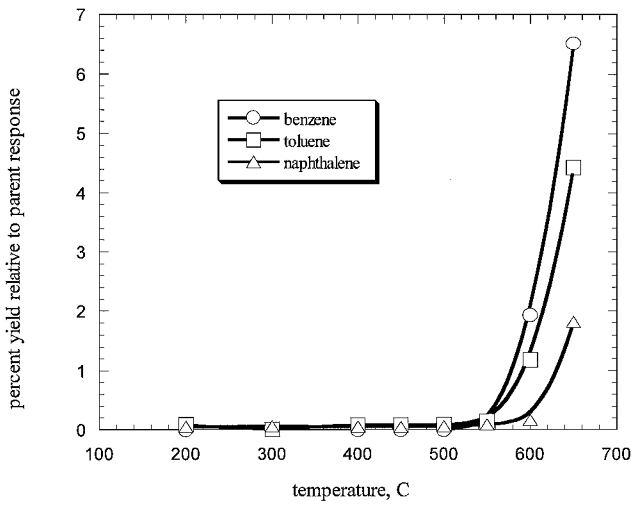


Fig. 8 Aromatic formation in JP-10 based on parent reponse to GC–MS detection at 200°C.

compounds were present in the original JP-10. Because of the slightly lower temperatures at which initial fragmentation is observed for JP-10 when compared to RP-1, the former is considered slightly less stable. However, aromatic formation was more prevalent in RP-1 than observed for JP-10, probably due to the initial concentration of aromatic components in the RP-1. These aromatics may have acted as seed components to form the aromatic decomposition products. JP-10 degradation products did not plug the reactor, but the fuel became discolored at 600–650°C.

Because of its higher strain energy, quadricyclane was (predictably) more thermally unstable than either RP-1 or JP-10. Moreover, quadricyclane polymerized rapidly at 450°C, plugging the reactor tube. Quadricyclane isomerized to norbornadiene, even at temperatures below 300°C. The norbornadiene decomposition products indicate the eventual formation of aromatics, as shown in Fig. 9. Benzene and toluene formation is shown in Fig. 10; no naphthalene formation was observed at these lower (<450°C) temperatures. A small amount of toluene formation is observed at 200°C. The isomerization of quadricyclane to norbornadiene is consistent with observations in gas-phase studies.[10,11] Similar decomposition products are seen in both the gas-phase and condensed-phase studies. Because the reactor was plugged at such a low temperature, samples stressed to higher temperatures could not be collected. Polymerization-inhibiting additives may retard the decomposition process and will be studied in future work.

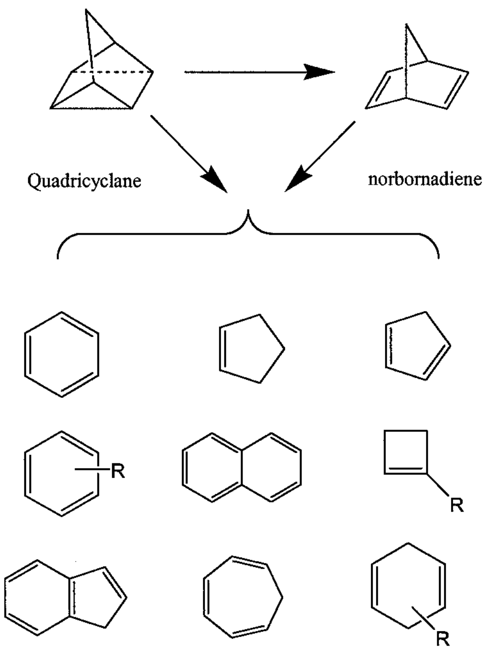


Fig. 9 Quadricyclane thermal decomposition pathways.

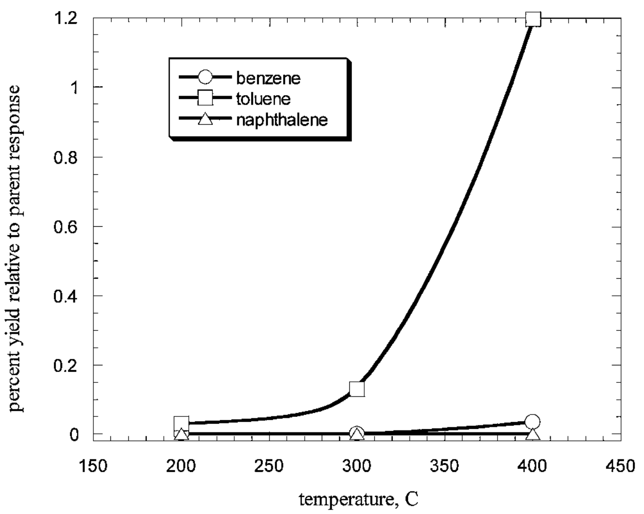


Fig. 10 Aromatic formation from quadricyclane based on parent reponse to GC–MS detection at 200°C.

Conclusions

The thermal decomposition behavior of high-energy density hydrocarbons under condensed-phase high-temperature conditions was examined. These experiments examine conditions more typical of fuel systems for combined-cycle engines than do gas-phase experiments previously conducted.

Stability measurements performed in this study indicated that RP-1 was the most stable at the conditions investigated, followed closely by JP-10. Quadricyclane is the least stable, degrading at relatively low temperatures compared to JP-10 and RP-1. Once substantial pyrolysis is observed, aromatic formation increases are observed for all three reactants. JP-10 degradation leads to the formation of small amounts of benzene and toluene whereas RP-1 yielded higher formation of benzene and toluene, along with naphthalene. Quadricyclane features slight formation of benzene and toluene, but substantial polymerization, which leads to reactor plugging even at low temperatures. Apparently, quadricyclane would not be capable of providing significant fuel system cooling (due to its thermal instability) if reaction times or temperatures were excessive. Product formation from the degradation of these reactants is helpful in speculating about the mechanism of decomposition and the propensity for deposition. The mitigation of undesirable pyrolytic deposition processes is predicated on the understanding of the inherent formation chemistry. Work to address pyrolytic deposition for strained hydrocarbons under condensed-phase high-temperature conditions is ongoing in our laboratory.

Acknowledgments

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