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Thermal Decomposition Kinetics of Kerosene-Based Rocket Propellants. 2. RP-2 with Three Additives[†]

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The thermal decomposition of RP-2 with three potential stabilizing additives was investigated. The additives were 1,2,3,4-tetrahydroquinoline (THQ), 1,2,3,4-tetrahydronaphthalene (tetralin), and the additive package that is used to make JP-8 + 100 (herein referred to as the "+100 additive"). For mixtures of RP-2 with THQ and tetralin, the concentration of additive was 5% by mass. The mixture of RP-2 with the +100 additive contained only 256 mg/L of the additive (the same concentration used to make JP-8+100). Decomposition reactions were performed at 375, 400, 425, and 450 °C in stainless steel reactors. At each temperature, the extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by gas chromatography. The results with each additive were compared to the decomposition of neat RP-2 under the same conditions. The addition of 5% THQ slowed the rate of decomposition by approximately an order of magnitude. The addition of 5% tetralin slowed the rate of decomposition by approximately 50%. At the low concentration tested, the +100 additive did not significantly change the thermal stability of the RP-2.

Introduction

Kerosene-based rocket propellant serves the dual roles of fuel and coolant in modern rocket engines.[1,2] Prior to combustion, the rocket propellant circulates through channels in the wall of the thrust chamber. Thus, the fuel carries heat away from the wall and maintains a safe wall temperature. This process, commonly referred to as regenerative cooling, exposes the fuel to high temperatures. For this reason, the thermal stability of the fuel is a key design parameter for specifying its performance.[1,2] The thermal stability of the kerosene-based rocket propellant RP-1 has been studied extensively.[1−7] The thermal stability of a relatively new rocket propellant, RP-2, has been the subject of fewer studies.[3,7,8] The specification for RP-2, along with an updated specification for RP-1, was published in 2005 as MTL-DTL-25576D. The primary differences between the specifications for RP-1 and RP-2 are that the allowed sulfur content is much lower in RP-2 (0.1 mg/kg, compared to 30 mg/kg in RP-1), the allowed olefin concentration of is lower in RP-2 (1 vol %, compared to 2 vol % for RP-1), and the use of the red dye is currently not allowed in RP-2. All three of these differences were intended to increase the thermal stability of RP-2.

A potential approach for further improvements in the thermal stability of RP-2 is to use stabilizing additives. The use of additives has a long history with kerosene-based jet fuels.[1,9] Much of the work on jet fuels has focused on additives that are "hydrogen donors", such as 1,2,3,4-tetrahydroquinoline (THQ),[10−13] 1,2,3,4-tetrahydronaphthalene

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(tetralin),[10,12–18] decahydronaphthalene (decalin),[13,17,18] and benzyl alcohol.[12,13,19–21] In related work, a major research effort initiated by the U.S. Air Force culminated in the formulation of the stabilizing additive package used to make JP-8 + 100 (herein referred to as the "+100 additive"). The +100 additive contains three components: an antioxidant (hydrogen donor), a metal deactivator, and a dispersant (surfactant).[1] The use of such stabilizing additives has been suggested[2] for rocket propellants, but little work has been done.[1,7]

The goal of this study is to extend the work on jet fuel stabilizers to find an additive that will significantly improve the thermal stability of RP-2. Herein, we report the thermal decomposition of RP-2 with three potential stabilizing additives: THQ, tetralin, and the +100 additive. We observed changes in thermal stability by monitoring the formation of light, liquid-phase decomposition products in the thermally stressed fuel. Decomposition reactions were performed at 375, 400, 425, and 450 °C in stainless steel ampule reactors. At each temperature, the extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by gas chromatography. In addition to this quantitative assessment of thermal stability, we also made qualitative observations about the color of the thermally stressed fuel and the formation of a pressurized vapor phase in the sealed reactors.

Experimental Section

Chemicals. Reagent-grade acetone, toluene, and dodecane were used as solvents in this work. They were obtained from commercial sources and used as received. All had stated purities of no less than 99%, which is consistent with our own routine analyses of such solvents by gas chromatography. The THQ (98% purity) and tetralin (99.5% purity) were also obtained from commercial sources and used as received. The +100 additive was obtained from the Fuels Branch of the Air Force Research Laboratory (AFRL, Wright Patterson Air Force Base). The sample of RP-2, which was clear and colorless, was also obtained from the AFRL (Edwards Air Force Base).

Figure 1. Apparatus used to thermally stress and decompose RP-1 and RP-2.

Apparatus. The apparatus used for the decomposition reactions is shown in Figure 1. Two thermostatted blocks of 304 stainless steel (AISI designation) were used to control the reaction temperature. Each block was supported in the center of an insulated box on carbon rods, which were chosen for their low thermal conductivity. A proportional−integral−derivative (PID) controller used feedback from a platinum resistance thermometer to maintain the temperature within 1 °C of the set value. As many as six stainless steel ampule reactors could be placed into tight-fitting holes in each of the two thermostatted blocks. Each reactor consisted of a tubular cell with a high-pressure valve. Each cell was made from a 5.6 cm length of ultrahigh-pressure 316 L stainless steel tubing (0.64 cm external diameter and 0.16 cm internal diameter) that was sealed on one end with a 316 L stainless steel plug welded by a clean tungsten-inert-gas (TIG) process. The other end of each cell was connected to a valve with a 3.5 cm length of narrow-diameter 316 stainless steel tubing (0.16 cm external diameter and 0.08 cm internal diameter) that was TIG-welded to the larger diameter tube. The valves were appropriate for high temperature in that the seats were stainless steel, and the packings were flexible graphite. Each cell and valve was capable of withstanding a pressure of at least 100 MPa (15000 psi) at the temperatures used. The internal volume of each cell, including the short length of narrow connecting tubing but not including the relatively small noxious volume (i.e., swept dead volume) of the valve, was determined gravimetrically from the mass of toluene required to fill it. Each cell volume was determined several times, and the average value (approximately 0.11 mL) was used for subsequent calculations.

It is possible that the surface properties of the reactors change with age and use. This could potentially change the amount of surface-catalyzed decomposition and shift the observed rate constants for decomposition. Our experimental design accounts for such a possibility in the following way. At any one time, we have a set of 15 reactors that are used for decomposition studies. Individual reactors occasionally fail (by developing a leak, etc.) and are replaced by new reactors. Consequently, the set of reactors used for this decomposition study were of varying ages. Additionally, the different temperatures and reaction times were done in a randomized order. Consequently, any effects of reactor aging should already be observable as scatter in the data (and, therefore, included in the uncertainty estimates for the rate constants). Since scatter in the data is small, we conclude that surface aging in the reactors is not very important in this system. This conclusion also suggests that surface catalysis is not very important for these fluids.

Decomposition Reactions. The procedure used to fill the reactors was designed to achieve an initial target pressure of 34.5 MPa (5000 psi) for all of the decomposition reactions.[22]

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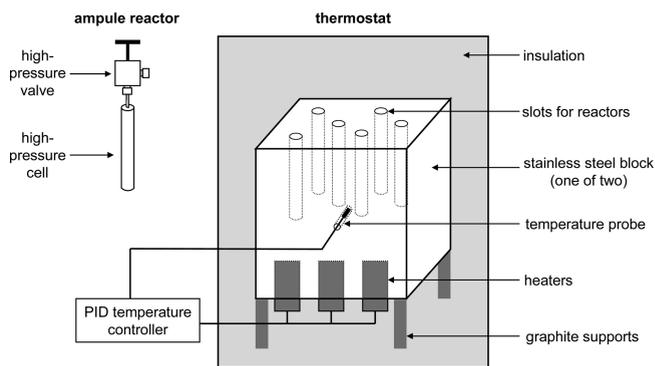
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This is important because it helps ensure that differences in observed decomposition rates are due only to differences in temperature and composition (and not to differences in pressure). With an equation of state for *n*-dodecane, a computer program[23] calculated the mass of *n*-dodecane needed to achieve a pressure of 34.5 MPa at a given reaction temperature and cell volume. We then assumed that the same mass of RP-2 + additive would yield a pressure close to our target pressure. This is a reasonable assumption because, although RP-2 is a complex mixture, models derived from the properties of *n*-dodecane have been used successfully to approximate the physical properties of kerosene-based fuels.[24,25] The calculated mass of fuel was added to the cell with a syringe equipped with a 26-gauge needle (sample masses were typically on the order of 0.06 g and varied depending on the experimental temperature and cell volume). The valve was then affixed to the cell and closed. The cell was chilled to 77 K in liquid nitrogen, and subsequently, the head space was evacuated to 10 Pa through the valve to remove air from the cell. The valve was then reclosed, and the cell was warmed to room temperature. This single freeze−pump−thaw cycle removes the air from the vapor space in the cell without removing dissolved air from the fuel itself. This mimics the conditions under which the fuels are actually used (i.e., they contain dissolved air). The other advantage of doing only one freeze−pump−thaw cycle is that it limits the chances of removing more volatile components from the fuel. More rigorous degassing procedures, such as bubbling inert gas through the fuel, were avoided. Such procedures will cause a change in fuel composition by removing some of the more volatile components from the fuel. It is also worth mentioning that the autoxidation reactions caused by dissolved oxygen are thought to be relatively unimportant for hydrocarbon fuel decomposition above 250−300 °C.[26]

The loaded reactors were then inserted into the thermostatted stainless steel block, which was maintained at the desired reaction temperature. Fluid reflux inside the cells was minimized by putting the entire reactor inside the insulated box (although only the cell tubing was inserted into the thermostatted block). The reactors were maintained at the reaction temperature for a specified period ranging from 10 min to 24 h. In order to minimize the time required for temperature equilibration, only one reactor at a time was placed in the thermostatted block if the reaction time was less than 30 min. With this procedure, we estimate that the effective thermal equilibration (warm-up) time is approximately 2 min for a reaction temperature of 450 °C.[27] After decomposition, the reactors were removed from the thermostatted block and immediately cooled in room-temperature water. The thermally stressed fuel was then recovered and analyzed as described below.

After each run, the cells and valves were rinsed extensively with a mixture of acetone and toluene. The cells were also sonicated for five minutes (while filled with the acetone/toluene mixture) between rinsings in order to remove any solid deposits that may have formed on their walls. Cleaned cells and valves were heated to 150 °C for at least 1 h to remove residual solvent.

Blank experiments were occasionally performed to check the effectiveness of this protocol for cleaning the cells. For these blank experiments, a cell was loaded with fuel as described above, but the cell was not heated above room temperature.

After a day, the fuel in the cell was removed and analyzed by gas chromatography (as described in the following section). The success of the cleaning procedure was confirmed by the visual absence of color or solids in the unheated fuel and by the absence of decomposition products in the resulting gas chromatogram.

Analysis of Liquid-Phase Decomposition Products by Gas Chromatography (GC). The production of light decomposition products caused the pressure in the reactors to increase during the decomposition reactions. After decomposition, the reactors contained a pressurized mixture of vapor and liquid, even at room temperature. Liquid-phase decomposition products in the thermally stressed fuel were used to monitor the kinetics of decomposition. Therefore, a sampling procedure was designed to minimize loss of the liquid sample when the reactors were opened. Specifically, a short length of stainless steel tubing was connected to the valve outlet on the reactor. The end of this tubing was placed inside a chilled (7 °C) glass vial, and the valve was slowly opened. Often, some of the reacted fuel was expelled into the vial, especially for the more thermally stressed samples. The valve was then removed from the reactor and any liquid remaining in the cell was transferred to the glass vial by use of a syringe with a 26-gauge needle. The vial was sealed with a silicone septum closure, and the mass of liquid sample was quickly determined (with an uncertainty of 0.0001 g). Then, the liquid sample was immediately diluted with a known amount of *n*-dodecane and refrigerated (at 7 °C) until the analysis was performed. The resulting *n*-dodecane solution was typically 5% reacted fuel (mass/mass). The purpose of this procedure was to prepare the samples for GC analysis and to minimize evaporative losses from the samples. One of the reasons for using *n*-dodecane is that it does not interfere with the GC analysis of early eluting decomposition products (see below).

Aliquots (3 µL) from crimp-sealed vials of each sample were injected into a gas chromatograph equipped with an automatic sampler and a flame ionization detector (FID). Research-grade nitrogen was used as the carrier and makeup gas. The split/splitless injection inlet was maintained at 300 °C, and samples were separated on a 30 m capillary column coated with a 0.1 µm film of (5%-phenyl)-methylpolysiloxane.[28] A temperature program was used that consisted of an initial isothermal separation at 80 °C for 4 min, followed by a 20 °C/min gradient to 275 °C. This final temperature was held constant for 2 min. The FID was maintained at 275 °C.

RP-2 decomposition was observed from the total increase in the chromatographic peak areas of the emergent suite of decomposition products. Chromatograms of unheated RP-2 (including RP-2 mixtures with the additives) exhibited only very small peaks with retention times of less than 3.2 min; however, following thermal stress, a suite of decomposition products was observed to elute earlier than 3.2 min. The total peak area of this suite of decomposition products was used to measure the extent of decomposition. The peak area was corrected for dilution in *n*-dodecane by multiplying by the dilution factor. The peak area was also corrected for drifts in detector response by analyzing an aliquot of a stock solution (pentane and hexane in *n*-dodecane) along with each set of fuel samples. These corrected peak areas (in arbitrary units) were used to compare the effectiveness of each additive. The simple use of peak area for the comparison is possible because of the types of compounds being analyzed and the use of a FID. For hydrocarbons, the relative sensitivity of the detector (based on moles of carbon) varies by only a few percent.[29] Consequently, calibrating the detector for each individual compound is not expected to significantly change the comparisons.

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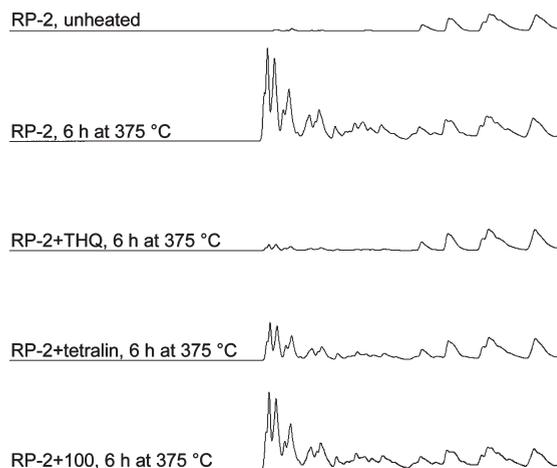(29) McNair, H. M.; Bonelli, E. J. *Basic Gas Chromatography*; Varian: Palo Alto, 1968.

Figure 2. First 4 min of the gas chromatograms for several RP-2 samples. There are only a few peaks in this early part of the chromatogram for the sample of unheated RP-2. The suite of early eluting decomposition products is prominent in the chromatogram for the sample of RP-2 that had been thermally stressed at 375 °C for 6 h. The other three chromatograms are for mixtures of RP-2 with the three different additives. All of the mixtures had been thermally stressed at 375 °C for 6 h and showed clearly differing amounts of decomposition.

Figure 3. Plot of the corrected peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 375 °C. The four different samples are the following: (○) neat RP-2; (▲) RP-2 with 256 mg/L of the +100 additive; (♦) RP-2 with 5% tetralin; (■) RP-2 with 5% THQ. The error bars indicate the standard deviation in replicate decomposition reactions at each time point.

Results and Discussion

The thermal decomposition of fuels like RP-2 is very complex. There are a large number of compounds in the fuel, each compound may decompose by more than one reaction pathway, the decomposition reactions may yield more than one product, and the initial decomposition products may further decompose to other products. Because of this complexity, some type of simplifying assumption is necessary in order to gain insight into the overall thermal stability of such a fuel. In this work, we assume that a suite of light, liquid-phase decomposition products (see Figure 2) is representative of all the decomposition products. This assumption is convenient for two reasons. First, the light decomposition products are produced in relative abundance. Second, the chromatographic peaks for these decomposition products occupy a region of the chromatogram that is essentially devoid of peaks for the unstressed fuel, so peak deconvolution is unnecessary. It would be possible—but much less convenient—to monitor heavier decomposition products.

Aliquots of RP-2, RP-2 with 5% THQ, RP-2 with 5% tetralin, or RP-2 with 256 mg/L of the +100 additive (hereafter the mixtures are referred to as, RP-2 + THQ, RP-2 + tetralin, and RP-2 + 100) were thermally stressed in sealed stainless steel reactors. For RP-2 + 100, reaction temperatures of 375 and 425 °C were used. For the other three samples, reaction temperatures of 375, 400, 425, and 450 °C were used. This temperature range was chosen because it allowed for reaction times of a convenient length. At 375 °C, the decomposition is relatively slow, so reaction times ranged from 6 to 24 h. At 450 °C, the decomposition is much faster, so reaction times ranged from 10 to 40 min. For all of the decomposition reactions, the initial pressure at the reaction temperature was 34.5 MPa (5000 psi).

The thermally stressed liquid phase of every decomposition reaction was analyzed by a gas chromatograph equipped with a flame ionization detector (GC-FID). Figure 2 shows the early part of the chromatograms obtained for unheated RP-2 and for thermally stressed samples of RP-2, RP-2 + THQ,
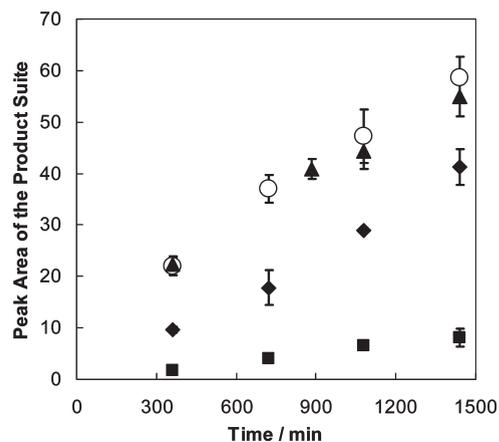
RP-2 + tetralin, and RP-2 + 100. All of the thermally stressed samples had been heated at 375 °C for 6 h and showed clearly differing amounts of decomposition (Figure 2). When compared to the chromatogram for thermally stressed RP-2, the chromatogram for RP-2 + THQ shows almost no decomposition, the chromatogram for RP-2 + tetralin shows significantly reduced decomposition, and the chromatogram for RP-2 + 100 shows little change in the amount of decomposition. Interestingly, the suite of decomposition products was essentially the same for each of the samples, and even the ratios of decomposition products were similar for each sample. Hence, it would appear that these additives slow the rate of decomposition without altering the decomposition pathways.

Figure 3 summarizes all of the data at 375 °C. It shows a plot of the corrected peak area (arbitrary units, see the Experimental Section) of the early eluting decomposition products as a function of time. For neat RP-2, the corrected peak area after 6 h of thermal stress at 375 °C was 22.0 (with a standard deviation, σ, of 1.7). For comparison, the corrected peak areas after 6 h at 375 °C were 1.8 ($\sigma = 0.3$) for RP-2 + THQ, 9.7 ($\sigma = 0.5$) for RP-2 + tetralin, and 22.3 ($\sigma = 1.5$) for RP-2 + 100. In other words, the addition of 5% THQ slowed the decomposition by approximately an order of magnitude, the addition of 5% tetralin slowed the decomposition by approximately 50%, and the addition of 256 mg/L of the +100 additive did not change the rate of decomposition. At longer reaction times, any stabilizing effect is smaller, presumably due to a decrease in the concentration of the stabilizer (see below). For example, after 24 h of thermal stress at 375 °C, the corrected peak areas were 58.6 ($\sigma = 4.0$) for neat RP-2, 8.1 ($\sigma = 1.8$) for RP-2 + THQ, 41.3 ($\sigma = 3.5$) for RP-2 + tetralin, and 54.9 ($\sigma = 3.9$) for RP-2 + 100. Figures 4–6 show that the trends observed at 375 °C are also seen at higher temperatures: (1) over the entire temperature range, 5% THQ is the most effective stabilizer; (2) 5% tetralin has a significant, but much smaller stabilizing effect; (3) the +100 additive has no significant effect at 256 mg/L; and (4) the stabilizing effect is greatest at the beginning of the reaction.

Figure 7 shows a plot of the concentration of THQ as a function of reaction time. Even after 4 h at 425 °C, a small amount of the THQ remains. Approximately one-half of the
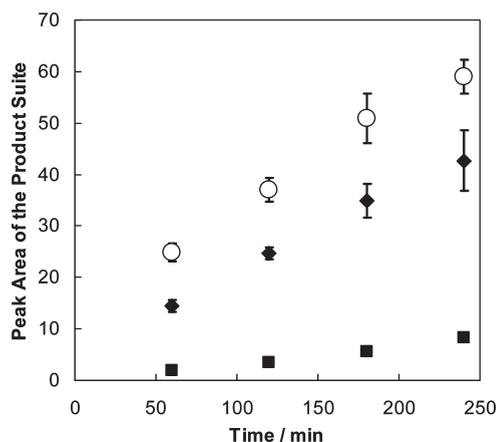
Figure 4. Plot of the corrected peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 400 °C. The four different samples are the following: (O) neat RP-2; (♦) RP-2 with 5% tetralin; (■) RP-2 with 5% THQ. The error bars indicate the standard deviation in replicate decomposition reactions at each time point.
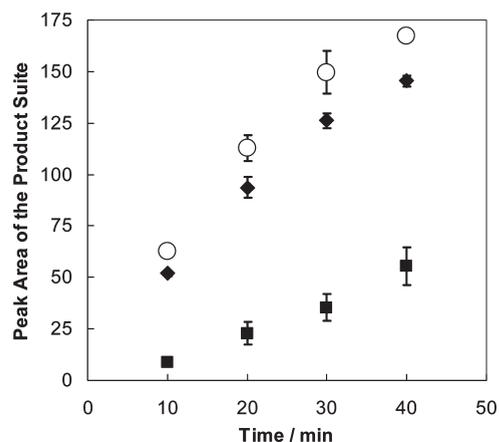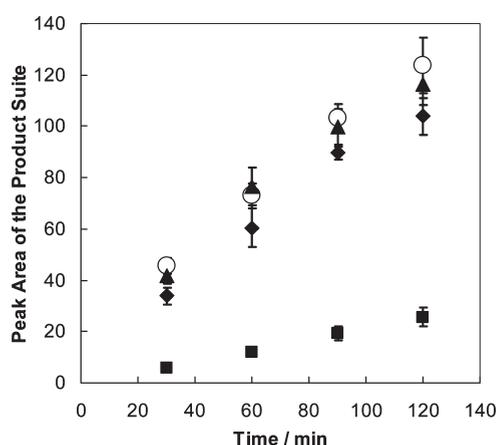

Figure 6. Plot of the corrected peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 450 °C. The four different samples are the following: (O) neat RP-2; (♦) RP-2 with 5% tetralin; (■) RP-2 with 5% THQ. The error bars indicate the standard deviation in replicate decomposition reactions at each time point.

Figure 5. Plot of the corrected peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 425 °C. The four different samples are the following: (O) neat RP-2; (▲) RP-2 with 256 mg/L of the +100 additive; (♦) RP-2 with 5% tetralin; (■) RP-2 with 5% THQ. The error bars indicate the standard deviation in replicate decomposition reactions at each time point.

Figure 7. Plot of the mass percent of THQ remaining in the fuel as a function of reaction time at 425 °C. These data show that approximately one-half of the initial THQ remains after 2 h (the maximum reaction time shown in Figure 5). The error bars indicate the standard deviation in replicate decomposition reactions at each time point. The solid line is a polynomial fit that is intended only to guide the eye.

initial THQ remains after 2 h (the maximum reaction time shown in Figure 5). This is consistent with the fact that significant stabilization of the RP-2 is still observed after 2 h at 425 °C (Figure 5). It also shows that lower concentrations of THQ still provide effective stabilization of the fuel. Finally, the curve in Figure 7 is consistent with our observation that the maximum stabilizing effect occurs at the beginning of thermal stress.

In addition to the quantitative assessment of thermal stability described above, we made two types of qualitative observations related to thermal stability: (1) changes in the color of the thermally stressed fuel and (2) the development of a pressurized vapor phase in the sealed reactors, which is caused by the formation of low-molecular-weight decomposition products. Before being heated, the neat RP-2 was clear and colorless. After 10 min at 450 °C, it was still colorless. After 40 min at 450 °C, the liquid was yellow-brown in color. After thermally stressing neat RP-2 for 10 min at 450 °C, approximately half of the entire liquid sample was expelled under pressure when the
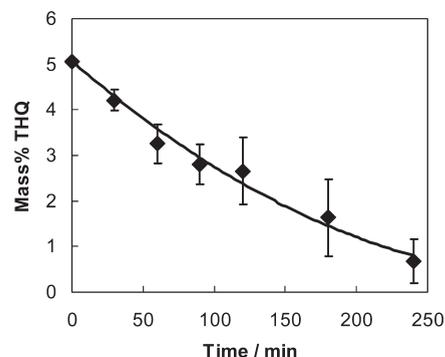
reactor valve was opened. After 40 min at 450 °C, the entire liquid sample was expelled under pressure when the reactor valve was opened. The addition of 5% THQ to the RP-2 suppressed the development of color—the fuel was still light yellow after 40 min at 450 °C. The THQ also suppressed the formation of a pressurized vapor phase—nothing was expelled from the reactor after 10 min at 450 °C, and approximately 75% of the sample was expelled after 40 min at 450 °C. The addition of 5% tetralin to the RP-2 did not have such definite effects, although it did seem to slightly suppress the development of color and the formation of a pressurized vapor phase. The addition of 256 mg/L of the +100 additive did not have an observable effect on the development of color or the formation of a pressurized vapor phase.

The superiority of THQ as a stabilizer is not surprising. THQ is a stronger hydrogen donor than tetralin, and it has been shown to be a superior stabilizer for both jet fuel and biodiesel fuel.[10,13,30] It is also known to stabilize RP-1 at

(30) Bruno, T. J.; Wolk, A.; Naydich, A. Stabilization of Biodiesel Fuel at Elevated Temperature with Hydrogen Donors: Evaluation with the Advanced Distillation Curve Method. *Energy Fuels* **2009**, *23*, 1015–1023.

temperatures below ~975 °C.[7] The ineffectiveness of the +100 additive may not be simply due to its relatively low concentration, but rather to the high temperatures used in our experiments. The +100 additive was designed to work at temperatures of less than 220 °C, where autoxidation reactions (from oxygen dissolved in the fuel) are the dominant mechanism of fuel decomposition.[1] Therefore, it probably is not as effective at inhibiting the cracking reactions that dominate at the temperatures studied herein. Alternatively, the active components of the +100 additive may themselves decompose too quickly to be effective in this higher temperature regime.

Conclusions

The additives THQ and tetralin significantly increased the thermal stability of RP-2 with respect to the formation of light decomposition products (i.e., cracking). The addition of 5% THQ decreased the formation of light, liquid-phase cracking products by approximately an order of magnitude. The addition of 5% tetralin decreased the formation of light, liquid-phase cracking products by approximately 50%. At the low concentration tested, the +100 additive did not significantly change the thermal stability of the RP-2. It is important to remember that these results may depend on the identity of the wetted surfaces of the apparatus. Strictly speaking, these results may apply only when the wetted surface is a 300 series stainless steel. Nevertheless, the results with THQ are especially promising, and it would be interesting to study the effect of THQ concentration on the thermal stability of RP-2. Some other avenues for future work include testing more additives (e.g., decalin), testing different reactor materials (e.g., copper), and testing the more promising additives (e.g., THQ) for their effect on coke formation.