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1. REPORT DATE (DD-MM-YYYY) 21-04-2010		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Thermal Decomposition of RP-2 with Stabilizing Additives				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) J.A. Widgren & T.J. Bruno (National Institute of Standards and Technology)				5d. PROJECT NUMBER	
				5f. WORK UNIT NUMBER 33SP0840	
				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RZ-ED-TP-2010-201	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSA 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-TP-2010-201	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048					
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (PA #10189).					
13. SUPPLEMENTARY NOTES For presentation at the 57 th JANNAF Joint Subcommittee Meeting, Colorado Springs, CO, 3-7 May 2010.					
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Mr. Matthew Billingsley
Unclassified	Unclassified	Unclassified	SAR	14	19b. TELEPHONE NUMBER (include area code) N/A

THERMAL DECOMPOSITION OF RP-2 WITH STABILIZING ADDITIVES

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ABSTRACT

The thermal decomposition of RP-2 and mixtures of RP-2 with four different additives has been investigated. The mixtures with RP-2 contained one of the following: 5 % *trans*-decahydronaphthalene (decalin); 5 % 1,2,3,4-tetrahydronaphthalene (tetralin); 5 % 1,2,3,4-tetrahydroquinoline (THQ); 1 % THQ; 0.5 % THQ; 0.1 % THQ; or 256 mg/L of the additive used to make JP-8+100 (the "+100 additive"). Decomposition reactions were performed in stainless steel ampoule reactors at temperatures from 375 °C to 450 °C (648 K to 723 K). All of the reactions were run with an approximate initial pressure of 34.5 MPa (5000 psi). After each reaction, the thermally stressed liquid phase was analyzed by gas chromatography. The increase in a suite of light decomposition products was used to monitor the extent of decomposition. The addition of THQ and tetralin had a significant effect on the decomposition of RP-2. Compared with neat RP-2, the addition of 5 % THQ slowed the decomposition by about an order of magnitude, while the addition of 5 % tetralin slowed the decomposition by approximately 50 %. At the concentrations tested, decalin and the +100 additive had little effect on the decomposition of RP-2.

INTRODUCTION

A large-scale project¹⁻¹³ involving the thermophysical properties of kerosene-based rocket propellants is in progress at the National Institute of Standards and Technology (NIST) as well as other facilities. This work is meant to enhance design and operational specifications for these fluids and facilitate new applications.^{14,15} The thermophysical properties that are being measured include equilibrium properties (such as the fluid density, vapor pressure, volatility, speed of sound and heat capacity) and transport properties (such as viscosity and thermal conductivity). Some of these property data for RP-1 and RP-2 have already been reported.^{2,3,5,8-10,12,16} The ultimate goal of the thermophysical property measurements at NIST is the development of equations of state to describe the properties.^{3,11,17,18}

The thermal stability of kerosene-based rocket propellants is important for their performance.^{4,19-26} The rocket propellant serves the dual roles of fuel and coolant in modern rocket engines. 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 kerosene-based rocket propellant RP-1 has been studied extensively.^{4,19,20,22-26} The thermal stability of the relatively new rocket propellant, RP-2, has been the subject of fewer studies.^{20,22} 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 is lower in RP-2 (1 vol %, compared to 2 vol % for RP-1), and the use of the red dye is not allowed in RP-2. All three of these differences were intended to increase the thermal stability of RP-2 and facilitate reusable rocket motors.

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.^{25,27} Much of the work on jet fuels has focused on additives that are "hydrogen donors", such as

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This work was performed under the sponsorship of the Air Force Research Laboratory (MIPR F1SBAA8022G001).

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1,2,3,4-tetrahydroquinoline (THQ),²⁸⁻³⁰ 1,2,3,4-tetrahydronaphthalene (tetralin),^{28,30-35} decahydronaphthalene (decalin),^{33,35} and benzyl alcohol.^{28,36-38} 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).²⁵ The use of such stabilizing additives has been suggested²⁶ for rocket propellants, but little work has been done.^{22,25}

This paper constitutes a review of three recent studies of the thermal stability of neat RP-2 and of mixtures of RP-2 with four potential stabilizers.^{6,7,13} Aliquots of each sample were thermally stressed in sealed stainless steel reactors at temperatures between 375 °C and 450 °C (648 K to 723 K). 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 effectiveness of each stabilizer was determined by comparing the amount of decomposition in the mixture to the amount of decomposition in neat RP-2.

EXPERIMENTAL

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), tetralin (99.5 % purity), and decalin (99 % 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 RP-2 was also obtained from the AFRL (Edwards Air Force Base).

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 on carbon rods in the center of an insulated box. A proportional-integral-derivative 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 ampoule reactors could be placed into tight-fitting holes in each of the 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 316L stainless steel tubing that was sealed on one end with a 316L 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 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 was determined gravimetrically from the mass of toluene required to fill it (approximately 0.11 mL).

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 reactors that we 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. 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.

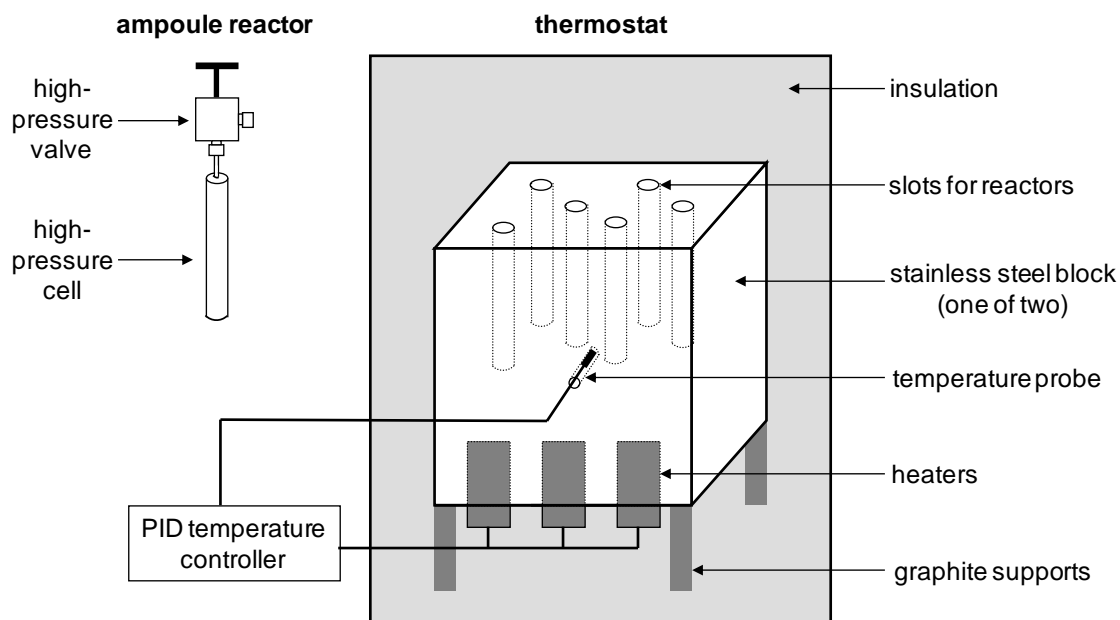


Figure 1. Apparatus Used to Thermally Stress RP-2.

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 decomposition reactions.⁴ This is important because it helps ensure that differences in observed decomposition rates are due only to differences in temperature (and not to differences in pressure). With an equation of state for n-dodecane, a computer program calculated the mass of n-dodecane needed to achieve a pressure of 34.5 MPa at a given temperature and cell volume.³⁹ We then assumed that the same mass of each fuel would yield a pressure close to our target pressure. This is a reasonable assumption because, although the rocket propellants are complex mixtures, models derived from the properties of n-dodecane have been used successfully to approximate the physical properties of kerosene-based fuels.^{40,41} The calculated mass of rocket propellant was added to the cell (sample masses were typically on the order of 0.06 g and varied depending on the experimental temperature and measured cell volume). The valve was then affixed to the cell and closed. Cells were then 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 re-closed, and the cell was warmed to room temperature. The single freeze-pump-thaw cycle should remove 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, can change the fuel composition by removing some of the more volatile components. 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.⁴²

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.⁴³ 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 in the next section.

After each run, the cells and valves were rinsed extensively with a mixture of acetone and toluene. The cells were also sonicated for about five minutes (while filled with the solvent 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 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

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 extent 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 highly thermally stressed samples. The valve was then removed from the reactor and any liquid remaining in the cell was transferred to the glass vial with a needle and syringe. 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). The liquid sample was then immediately diluted with a known amount of n-dodecane and refrigerated 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. The reasons for using n-dodecane are that it does not interfere with the GC analysis of early eluting decomposition products, and it serves as an effective storage medium (keeper) for the sample.

Aliquots 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.⁴⁴ The temperature program 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. Chromatograms of unheated fuel 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 corrected total peak area (arbitrary units) of this suite of decomposition products was used to monitor the extent of decomposition. Peak areas were corrected for dilution in n-dodecane by multiplying by the dilution factor. Peak areas were 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 decomposition samples. The simple use of peak area (i.e., without calibration) is possible only 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.⁴⁵ Consequently, calibrating the detector for each individual compound is not expected to significantly change the comparisons of additive effectiveness.

RESULTS AND DISCUSSION

Aliquots of RP-2, or of a mixture of RP-2 + additive, were thermally stressed in stainless steel ampoule reactors at an initial pressure of 34.5 MPa (5000 psi). Reaction temperatures of 375 °C, 400 °C, 425 °C, and 450 °C were used, although not every temperature was used for every mixture of RP-2 + additive. This temperature range was chosen, in part, because it allowed for reaction times of a convenient length. At 375 °C, the decomposition reaction is relatively slow, so reaction times ranged from 6 h to 24 h. At 450 °C, the reaction is much faster, so reaction times ranged from 10 min to 40 min. The thermally stressed liquid phase of every decomposition reaction was analyzed by a gas chromatograph equipped with a flame ionization detector (GC-FID).

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, a simplifying assumption is necessary in order to gain insight into the overall thermal stability of such a fuel. In this work, we assumed that a suite of light, liquid-phase decomposition products is representative of all the decomposition products. In Figure 2, which shows the early part of the chromatograms obtained for both thermally stressed and unstressed RP-2, the suite of decomposition products used for the kinetic analysis is circled. Importantly, this set of chromatographic peaks occupies a region of the chromatogram that is essentially vacant for the unheated fuel, which simplifies data analysis.

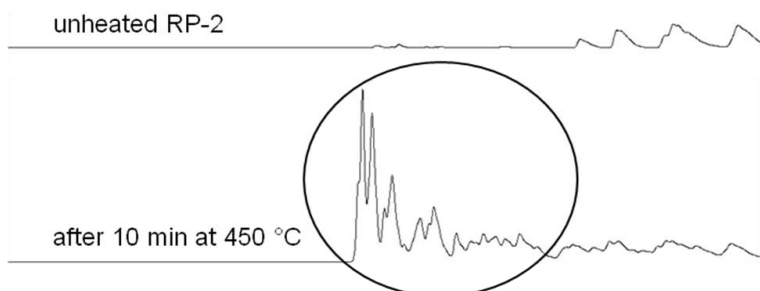
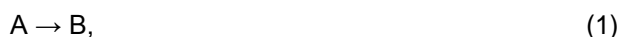


Figure 2. The Initial Part of the Chromatograms for Heated and Unheated RP-2.

THE THERMAL STABILITY OF NEAT RP-2

For neat RP-2, we monitored the increase in concentration of light, liquid-phase decomposition products as a function of time, t , at temperatures of 375 °C, 400 °C, 425 °C, and 450 °C.⁶ At each temperature, data were collected at four different reaction times, with 3 to 5 replicate decomposition reactions at each reaction time. These data were fit to a first-order rate law, equations 1–3, where $[B]_t$ is the concentration of products at time t and $[B]_\infty$ is the concentration of products at $t = \infty$:



$$-d[A]/dt = d[B]/dt = k t, \quad (2)$$

$$[B]_t = [B]_{\infty}(1 - \exp^{-kt}). \quad (3)$$

A pseudo-first-order rate constant for decomposition, k' , was obtained from the fit. The half-life, $t_{0.5}$, at each temperature (i.e., the time required for one-half of the fuel to decompose) was then calculated from k' by use of eq 4,

$$t_{0.5} = 0.6931/k'. \quad (4)$$

A related quantity is the interval required for 1 % of the fuel to decompose, $t_{0.01}$. For first-order reactions, $t_{0.01}$ is calculated from the rate constant by use of eq 5,

$$t_{0.01} = 0.01005/k'. \quad (5)$$

Figure 3 shows a plot of the corrected peak area (arbitrary units, see the Experimental section) of the suite of light decomposition products as a function of time for the decomposition of RP-2 at 450 °C. The value of k' was determined from the nonlinear fit to the data (shown as a solid line in Figure 3). For RP-2 at 450 °C, $k' = 5.47 \times 10^{-4} \text{ s}^{-1}$ with an uncertainty of $0.80 \times 10^{-4} \text{ s}^{-1}$. The decomposition rate constants for RP-2 at all four temperatures, along with values of $t_{0.5}$ and $t_{0.01}$, are presented in Table I. The uncertainty for each value of k' in Table I is the standard error in the nonlinear fit.

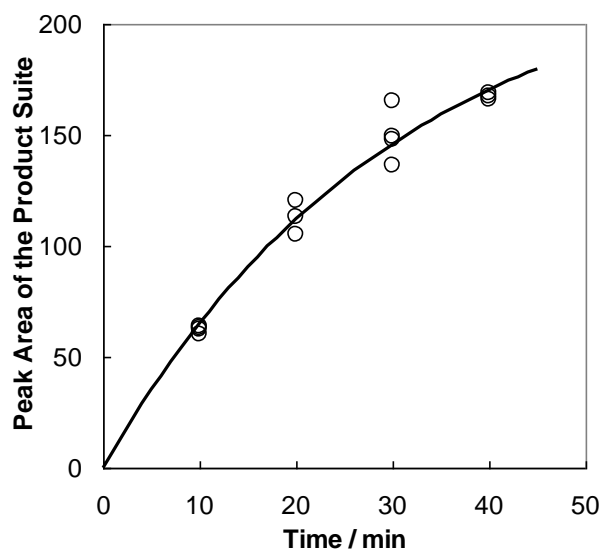


Figure 3. A Plot of the Kinetic Data for RP-2 at 450 °C.

Table I. Kinetic Data for the Thermal Decomposition of RP-2.

RP-2					
$T / \text{°C}$	k' / s^{-1}	Uncertainty in k'		$t_{0.5} / \text{h}^{-1}$	$t_{0.01} / \text{min}^{-1}$
		$/ \text{s}^{-1}$			
375	1.33×10^{-5}	0.30×10^{-5}		14.5	12.6
400	9.28×10^{-5}	2.01×10^{-5}		2.07	1.80
425	1.33×10^{-4}	0.33×10^{-4}		1.45	1.26
450	5.47×10^{-4}	0.80×10^{-4}		0.35	0.31

THE THERMAL STABILITY OF RP-2 + THQ

THQ is the most effective stabilizing additive that we have found to date.^{7,13} We have completed two studies with THQ. In the first study,⁷ a mixture of RP-2 + 5 % THQ was thermally stressed at temperatures of 375 °C, 400 °C, 425 °C and 450 °C. In the second study,¹³ mixtures of RP-2 with five different concentrations (0 %, 0.1 %, 0.5 %, 1 % and 5 %) of THQ were thermally stressed at 400 °C. In both studies, the kinetics of decomposition was monitored by GC-FID.

For the mixtures of RP-2 with THQ, we again monitored the increase in the suite of light, liquid-phase decomposition products as a function of time. At each temperature, data were collected at three or four different reaction times, with 3 to 5 replicate decomposition reactions run at each reaction time. The addition of THQ to RP-2 can dramatically affect the amount of decomposition, as illustrated in Figure 4.

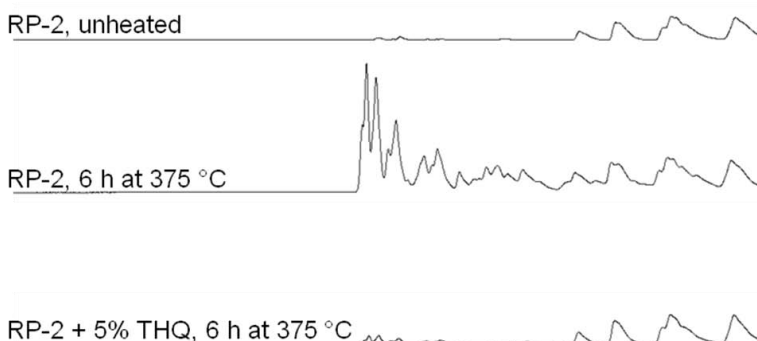


Figure 4. Comparison of the Initial Part of the Chromatograms for Unheated RP-2 and Thermally Stressed Samples of RP-2 and RP-2 + 5 % THQ.

Figure 5 summarizes all of the kinetic data at 375 °C for neat RP-2 (○) and for RP-2 + 5 % THQ (■). The kinetic curves for RP-2 + 5 % THQ are not well fit by a first-order rate law, so we cannot compare first-order rate constants to determine the effectiveness of the stabilizer. Instead, we simply compare the corrected peak areas of the early eluting decomposition products at different time-points. For neat RP-2, after 6 h of thermal stress at 375 °C, the corrected peak area of these decomposition products was 22.0 (with a standard deviation, σ , of 1.7). For comparison, the corrected peak area for RP-2 + 5 % THQ after 6 h of thermal stress at 375 °C was 1.8 ($\sigma = 0.3$). In other words, the addition of 5 % THQ slowed the initial rate of decomposition by more than an order of magnitude. At longer reaction times, the 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 + 5 % THQ.

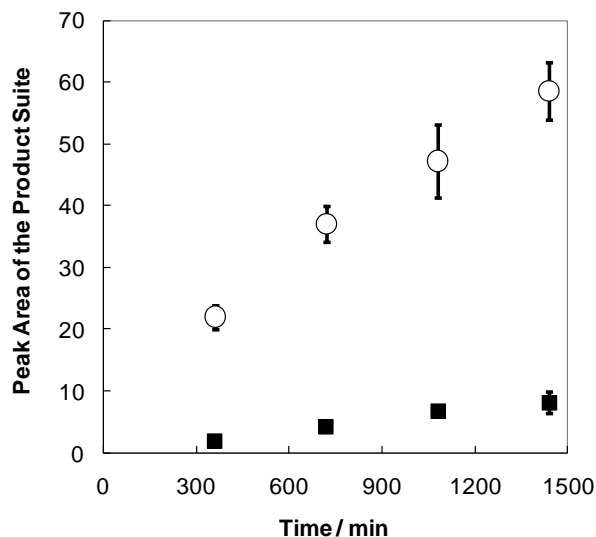


Figure 5. Kinetic Data for Neat RP-2 (○) and for RP-2 + 5 % THQ (■) at 375 °C.

Similar results were obtained at higher temperatures. That is, the stabilizing effect did not seem to vary much with temperature in the range studied. For example, Figure 6 summarizes the data at 425 °C for neat RP-2 (○) and for RP-2 + 5 % THQ (■).

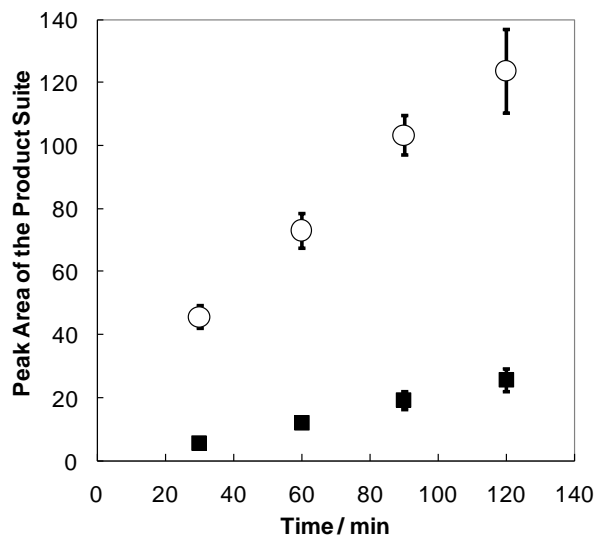


Figure 6. Kinetic Data for Neat RP-2 (○) and for RP-2 + 5 % THQ (■) at 425 °C.

For RP-2 + 5 % THQ, we also monitored the concentration of THQ during thermal stress. For example, Figure 7 shows concentration of THQ as a function of reaction time at 425 °C. Even after 4 h at 425 °C, a small amount of the THQ remains. Approximately one half of the initial THQ remains after 2 h (the maximum reaction time shown in Figure 6). This is consistent with the fact that significant stabilization of the RP-2 is still observed after 2 h at 425 °C (Figure 6). It also shows that lower concentrations of THQ still provide effective stabilization of the fuel. Finally, the curve in Figure 7 is also consistent with our observation that the maximum stabilizing effect occurs at the beginning of thermal stress.

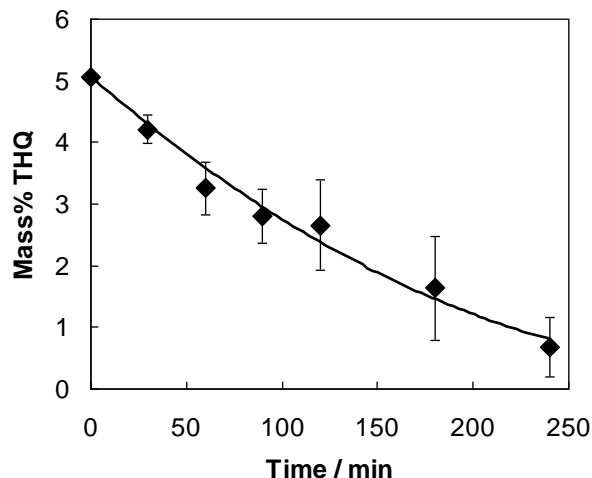


Figure 7. The Mass % of THQ Remaining in the RP-2 as a Function of Time at 425 °C.

We also did a series of experiments at 400 °C with different concentrations of THQ.¹³ Figure 8 summarizes the data for neat RP-2 (○), RP-2 + 0.1 % THQ (◆), RP-2 + 0.5 % THQ (□), RP-2 + 1 % THQ (◇), and RP-2 + 5 % THQ (■). For neat RP-2, after 1 h of thermal stress at 400 °C, the corrected peak area of the light, liquid-phase decomposition products was 21.1 (with a standard deviation, σ , of 3.0). For comparison, the corrected peak areas after 1 h of thermal stress at 400 °C were 17.9 ($\sigma = 1.0$) for RP-2 + 0.1 % THQ, 8.1 ($\sigma = 1.0$) for RP-2 + 0.5 % THQ, 5.0 ($\sigma = 0.1$) for RP-2 + 1 % THQ, and 2.4 ($\sigma = 0.4$) for RP-2 + 5 % THQ. The corrected peak areas after 4 h of thermal stress at 400 °C were 62.1 ($\sigma = 5.5$) for neat RP-2, 58.9 ($\sigma = 4.6$) for RP-2 + 0.1 % THQ, 41.4 ($\sigma = 5.7$) for RP-2 + 0.5 % THQ, 20.9 ($\sigma = 1.4$) for RP-2 + 1 % THQ, and 8.7 ($\sigma = 1.0$) for RP-2 + 5 % THQ. Clearly, the extent of decomposition depends on the concentration of THQ. The highest concentration, 5 %, showed the greatest stabilizing effect. However, substantial stabilization was also seen at lower concentrations of 1 % and 0.5 %.

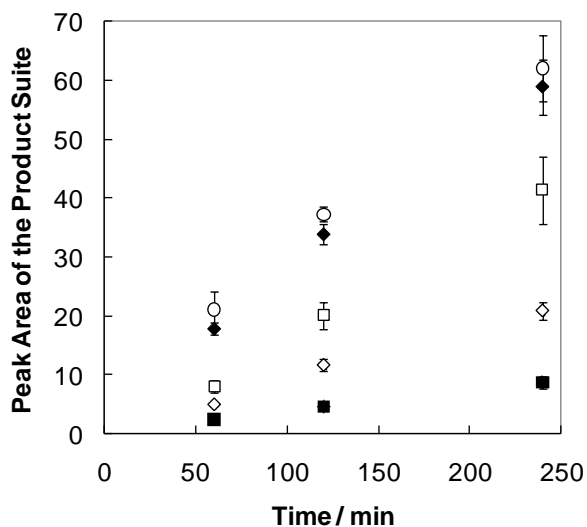


Figure 8. Kinetic Data for RP-2 with Varying Concentrations of THQ at 400 °C.

Of the other potential stabilizers that we have tested, tetralin was the most successful. A mixture of RP-2 + 5 % tetralin was thermally stressed at temperatures of 375 °C, 400 °C, 425 °C and 450 °C. Figure 9 compares the kinetic data for neat RP-2 (○) and RP-2 + 5 % tetralin (◆) at 375 °C. For neat RP-2, after 6 h of thermal stress at 375 °C, the corrected peak area of the early eluting decomposition products was 22.0 ($\sigma = 1.7$). For RP-2 + 5 % tetralin, the corrected peak area after 6 h of thermal stress at 375 °C was 9.7 ($\sigma = 0.5$). In other words, the addition of 5 % tetralin slowed the decomposition by approximately 50 %. At higher temperatures, the stabilizing effect was smaller, but still significant.

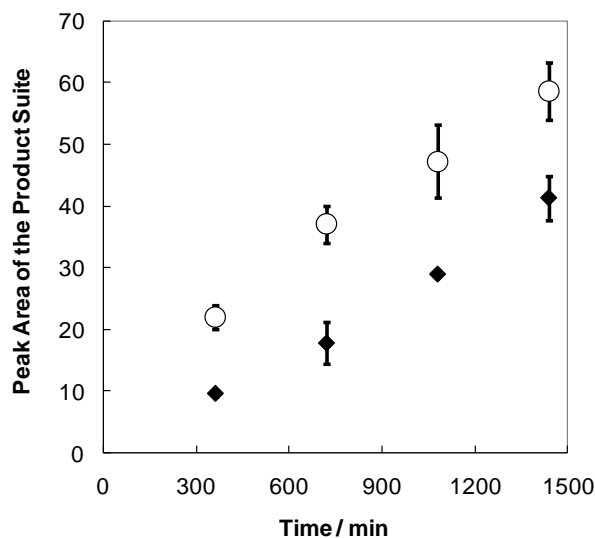


Figure 9. Kinetic Data for Neat RP-2 (○) and for RP-2 + 5 % Tetralin (◆) at 375 °C.

A mixture of RP-2 + 5 % decalin was thermally stressed at temperatures of 375 °C, 400 °C, 425 °C and 450 °C. This mixture showed little change in the amount of decomposition compared to neat RP-2. Similarly, the addition of 256 mg/L of the +100 additive did not significantly change the rate of decomposition, although we ran tests only at 375 °C and 425 °C with this additive.

THQ is a stronger hydrogen donor than tetralin and decalin, so it is not too surprising that it is a better thermal stabilizer for RP-2. Our results are consistent with work done on both jet fuel and biodiesel fuel, where THQ was found to be a particularly good stabilizer.^{30,46} THQ is also known to stabilize RP-1 at temperatures below ~975 °C.²² The ineffectiveness of the +100 additive may be due not simply 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.²⁵ Therefore, it is not too surprising that it is less effective at inhibiting the cracking reactions that dominate at the temperatures studied herein. It is possible that the active components of the +100 additive simply decompose too quickly to be effective in this higher temperature regime.

SUMMARY AND CONCLUSIONS

Based on the formation of light, liquid-phase decomposition products, we found that THQ was the most promising of the additives studied. The addition of 5 % THQ decreased the rate of decomposition by approximately an order of magnitude. Significant stabilization was also observed at initial THQ concentrations of 1 % and 0.5 %. The addition of 5 % tetralin decreased the rate of decomposition by approximately 50 %. The addition of 5 % decalin did not significantly change the thermal stability of the RP-2. At the low concentration tested, the +100 additive did not

significantly change the thermal stability of the RP-2. Finally, it is important to remember that the kinetics of decomposition may depend on the identity of the wetted surfaces of the apparatus, so these results are best applied when the wetted surface is constructed from 300 series stainless steels.

FUTURE WORK

It would be interesting to study the effect of a few other additives (e.g., benzyl alcohol). We would also like to test the effect of different reactor materials, particularly copper, on the thermal stability of these mixtures. In addition, we plan to measure the corrosivity of the thermally stressed fuel (and its mixtures with additives) by use of our improved copper strip corrosion test. It would also make sense to study the most promising additives for their effect on coke formation.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the AFRL (MIPR F1SBAA8022G001). We thank Matthew Billingsley (AFRL, Edwards Air Force Base) and Ronald Bates (CPIAC) for useful discussions, especially during the planning stages of these experiments, and for supplying the RP-2. We thank Tim Edwards (AFRL, Wright Patterson Air Force Base) for supplying the +100 additive.

REFERENCES

1. Outcalt, S.L., Laesecke, A., and Brumback, K.J., "Thermophysical Properties Measurements of Rocket Propellants RP-1 and RP-2," *Journal of Propulsion and Power* 25, 1032-1040 (2009).
2. Bruno, T.J., and Smith, B.L., "Improvements in the measurement of distillation curves. 2. Application to aerospace/aviation fuels RP-1 and S-8," *Industrial & Engineering Chemistry Research* 45, 4381-4388 (2006).
3. Magee, J.W., Bruno, T.J., Friend, D.G., Huber, M.L., Laesecke, A., Lemmon, E.W., McLinden, M.O., Perkins, R.A., Baranski, J., and Widegren, J.A., *Thermophysical Properties Measurements and Models for Rocket Propellant RP-1: Phase I*, NISTIR 6646, National Institute of Standards and Technology, Boulder, Colorado (February 2007).
4. Andersen, P.C., and Bruno, T.J., "Thermal decomposition kinetics of RP-1 rocket propellant," *Industrial & Engineering Chemistry Research* 44, 1670-1676 (2005).
5. Bruno, T.J., *The Properties of RP-1 and RP-2*, Technical Report to AFRL/PRSA (Edwards Air Force Base), National Institute of Standards and Technology, Boulder, CO (March 2008).
6. Widegren, J.A., and Bruno, T.J., "Thermal Decomposition Kinetics of Kerosene-based Rocket Propellants. 1. Comparison of RP-1 and RP-2," *Energy & Fuels* 23, 5517-5522 (2009).
7. Widegren, J.A., and Bruno, T.J., "Thermal Decomposition Kinetics of Kerosene-based Rocket Propellants. 2. RP-2 with Three Additives," *Energy & Fuels* 23, 5523-5528 (2009).
8. Huber, M.L., Lemmon, E.W., and Bruno, T.J., "Effect of RP-1 Compositional Variability on Thermophysical Properties," *Energy & Fuels* 23, 5550-5555 (2009).
9. Akhmedova-Azizova, L.A., Abdulagatov, I.M., and Bruno, T.J., "Effect of RP-1 Compositional Variability on Thermal Conductivity at High Temperatures and High Pressures," *Energy & Fuels* 23, 4522-4528 (2009).
10. Lovestead, T.M., and Bruno, T.J., "A Comparison of the Hypersonic Vehicle Fuel JP-7 to the Rocket Propellants RP-1 and RP-2 with the Advanced Distillation Curve Method," *Energy & Fuels* 23, 3637-3644 (2009).
11. Huber, A.L., Lemmon, E.W., Ott, L.S., and Bruno, T.J., "Preliminary Surrogate Mixture Models for the Thermophysical Properties of Rocket Propellants RP-1 and RP-2," *Energy & Fuels* 23, 3083-3088 (2009).
12. Ott, L.S., Hadler, A.B., and Bruno, T.J., "Variability of The Rocket Propellants RP-1, RP-2, and TS-5: Application of a Composition- and Enthalpy-Explicit Distillation Curve Method," *Industrial & Engineering Chemistry Research* 47, 9225-9233 (2008).

13. Widegren, J.A., and Bruno, T.J., "Thermal Decomposition Kinetics of Kerosene-based Rocket Propellants. 3. RP-2 with Varying Concentrations of the Stabilizer 1,2,3,4-Tetrahydroquinoline " *Energy & Fuels* submitted (2010).
14. Wang, T.S., "Thermophysics characterization of kerosene combustion," *Journal of Thermophysics and Heat Transfer* 15, 140-147 (2001).
15. Bruno, T.J., Billingsley, M., and Bates, R.W., *Findings and Recommendations from the Joint NIST/AFRL Workshop on Rocket Propellants and Hypersonic Vehicle Fuels*, National Institute of Standards and Technology, Boulder, CO (November 2008).
16. Outcalt, S.L., Laesecke, A., and Brumback, K.J., "Thermophysical Properties Measurements of Rocket Propellants RP-1 and RP-2," *Journal of Propulsion and Power* submitted (2008).
17. Bruno, T.J., *The Properties of S-8 and JP-10*, Technical Report to the Wright Laboratory Aero Propulsion and Power Directorate, National Institute of Standards and Technology, Boulder, CO (November 2007).
18. Bruno, T.J., Huber, M.L., Laesecke, A., Lemmon, E.W., and Perkins, R.A., *Thermochemical and Thermophysical Properties of JP-10*, NISTIR 6640, National Institute of Standards and Technology, Boulder, Colorado (June 2006).
19. Bates, R.W., Edwards, T., and Meyer, M.L., "Heat Transfer and Deposition Behavior of Hydrocarbon Rocket Fuels," *41st Aerospace Sciences Meeting and Exhibit*, Reno, NV, AIAA Paper 2003-123.
20. Brown, S.P., and Frederick, R.A., "Laboratory-scale thermal stability experiments on RP-1 and RP-2," *Journal of Propulsion and Power* 24, 206-212 (2008).
21. Edwards, T., and Zabarnick, S., "Supercritical Fuel Deposition Mechanisms," *Industrial & Engineering Chemistry Research* 32, 3117-3122 (1993).
22. MacDonald, M.E., Davidson, D.F., and Hanson, R.K., "Decomposition Rate Measurements of RP-1, RP-2, n-Dodecane, and RP-1 with Fuel Stabilizers," *44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, Hartford, CT, AIAA Paper 2008-4766 (July 2008).
23. Stiegemeier, B., Meyer, M.L., and Taghavi, R.A., "Thermal Stability and Heat Transfer Investigation of Five Hydrocarbon Fuels: JP-7, JP-8, JP-8+100, JP-10, RP-1.," *38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, Indianapolis, IN, AIAA Paper 2002-3873.
24. Wohlwend, K., Maurice, L.Q., Edwards, T., Striebich, R.C., Vangsness, M., and Hill, A.S., "Thermal stability of energetic hydrocarbon fuels for use in combined cycle engines," *Journal of Propulsion and Power* 17, 1258-1262 (2001).
25. Edwards, T., "Liquid fuels and propellants for aerospace propulsion: 1903-2003," *Journal of Propulsion and Power* 19, 1089-1107 (2003).
26. Irvine, S.A., Schoettmer, A.K., Bates, R.W., and Meyer, M.L., "History of sulfur content effects on the thermal stability of RP-1 under heated conditions," *40th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, Fort Lauderdale, FL, AIAA Paper 2004-3879.
27. Coleman, M.M., Schobert, H.H., and Song, C.S., "A New Generation of Jet Fuels," *Chemistry in Britain* 29, 760-762 (1993).
28. Coleman, M.M., Selvaraj, L., Sobkowiak, M., and Yoon, E., "Potential Stabilizers for Jet Fuels Subjected to Thermal Stress above 400 °C," *Energy & Fuels* 6, 535-539 (1992).
29. Yoon, E.M., Selvaraj, L., Eser, S., and Coleman, M.M., "High-temperature stabilizers for jet fuels and similar hydrocarbon mixtures. 2. Kinetic studies," *Energy & Fuels* 10, 812-815 (1996).
30. Yoon, E.M., Selvaraj, L., Song, C.S., Stallman, J.B., and Coleman, M.M., "High-temperature stabilizers for jet fuels and similar hydrocarbon mixtures. 1. Comparative studies of hydrogen donors," *Energy & Fuels* 10, 806-811 (1996).
31. Beaver, B., Sobkowiak, M., Clifford, C.B., Wei, Y.J., and Fedek, M., "High heat sink jet fuels. 3. On the mechanisms of action of model refined chemical oil/light cycle oil (RCO/LCO)-derived stabilizers for JP-8," *Energy & Fuels* 21, 987-991 (2007).
32. Sobkowiak, M., Clifford, C.B., and Beaver, B., "High heat sink jet fuels. 2. Stabilization of a JP-8 with model refined chemical oil/light cycle oil (RCO/LCO)-derived stabilizers," *Energy & Fuels* 21, 982-986 (2007).

33. Song, C.S., Eser, S., Schobert, H.H., and Hatcher, P.G., "Pyrolytic Degradation Studies of a Coal-Derived and a Petroleum-Derived Aviation Jet Fuel," *Energy & Fuels* 7, 234-243 (1993).
34. Song, C.S., Lai, W.C., and Schobert, H.H., "Hydrogen-Transferring Pyrolysis of Long-Chain Alkanes and Thermal-Stability Improvement of Jet Fuels by Hydrogen Donors," *Industrial & Engineering Chemistry Research* 33, 548-557 (1994).
35. Stewart, J., Brezinsky, K., and Glassman, I., "Supercritical pyrolysis of decalin, tetralin, and n-decane at 700-800 K. Product distribution and reaction mechanism," *Combustion Science and Technology* 136, 373-390 (1998).
36. McKinney, D.E., Bortiatynski, J.M., and Hatcher, P.G., "Use of C-13-Labeled Compounds to Trace Their Reactivity in Complex Systems: A Model Study of a Potential Antioxidant in Thermally Altered Jet Fuel," *Energy & Fuels* 7, 578-581 (1993).
37. Selvaraj, L., Sobkowiak, M., Song, C., Stallman, J.B., and Coleman, M.M., "A Model System for the Study of Additives Designed to Enhance the Stability of Jet Fuels at Temperatures above 400 °C," *Energy & Fuels* 8, 839-845 (1994).
38. Selvaraj, L., Stallman, J.B., Song, C.S., and Coleman, M.M., "In situ regeneration of the thermal stabilizer benzyl alcohol via ethanol in simulated jet fuels above 400 °C," *Fuel Processing Technology* 50, 153-162 (1997).
39. Lemmon, E.W., McLinden, M.O., and Huber, M.L., *NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP): Version 8.0*, NIST Standard Reference Database 23, National Institute of Standards and Technology, Gaithersburg, MD (2007).
40. Huber, M.L., Laesecke, A., and Perkins, R., "Transport properties of n-dodecane," *Energy & Fuels* 18, 968-975 (2004).
41. Lemmon, E.W., and Huber, M.L., "Thermodynamic properties of n-dodecane," *Energy & Fuels* 18, 960-967 (2004).
42. Watkinson, A.P., and Wilson, D.I., "Chemical reaction fouling: A review," *Experimental Thermal and Fluid Science* 14, 361-374 (1997).
43. Widegren, J.A., and Bruno, T.J., "Thermal Decomposition Kinetics of Propylcyclohexane," *Industrial & Engineering Chemistry Research* 48, 654-659 (2008).
44. Bruno, T.J., and Svoronos, P.D.N., *CRC Handbook of Basic Tables for Chemical Analysis*, 2nd ed., CRC Press, Boca Raton (2003).
45. McNair, H.M., and Bonelli, E.J., *Basic Gas Chromatography*, Varian, Palo Alto (1968).
46. Bruno, T.J., Wolk, A., and Naydich, A., "Stabilization of Biodiesel Fuel at Elevated Temperature with Hydrogen Donors: Evaluation with the Advanced Distillation Curve Method," *Energy & Fuels* 23, 1015-1023 (2009).