

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 01-07-2008		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Decomposition Rate Measurements of RP-1, RP-2, n-Dodecane, and RP-1 with Fuel Stabilizers (Preprint)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Megan E. MacDonald, David F. Davidson, Ronald K. Hanson (Stanford University)				5d. PROJECT NUMBER	
				5e. TASK NUMBER 48470244	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSA 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RZ-ED-TP-2008-290	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-TP-2008-290	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (PA #08276A).					
13. SUPPLEMENTARY NOTES For presentation at the 44 th AIAA Joint Propulsion Conference, Hartford, CT, 20-23 July 2008.					
14. ABSTRACT Decomposition rates of gas-phase kerosene-based fuels and surrogates with and without the addition of a thermal stabilizer additive were measured at high temperatures in an aerosol shock tube. Fuels studied include RP-1, RP-2, and n-dodecane, and the thermal stabilizer studied was 1,2,3,4-tetrahydroquinoline. Decomposition rates were measured in approximately 0.5% fuel/argon mixtures for temperatures of 1100 to 1300 K and pressures of 3 to 8 atm. Fuel concentration was measured using infrared laser absorption at 3.39 micrometers. The decomposition rates for neat RP-1 and RP-2 were found to be very similar and were found to be slower than that of a simple kerosene surrogate, n-dodecane.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON Mr. Matthew Billingsley
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A

Decomposition Rate Measurements of RP-1, RP-2, n-Dodecane, and RP-1 with Fuel Stabilizers (Preprint)

Megan E. MacDonald¹, David F. Davidson² and Ronald K. Hanson³
Stanford University, Stanford, CA, 94305

Decomposition rates of gas-phase kerosene-based fuels and surrogates with and without the addition of a thermal stabilizer additive were measured at high temperatures in an aerosol shock tube. Fuels studied include RP-1, RP-2, and n-dodecane, and the thermal stabilizer studied was 1,2,3,4-tetrahydroquinoline. Decomposition rates were measured in approximately 0.5% fuel/argon mixtures for temperatures of 1100 to 1300 K and pressures of 3 to 8 atm. Fuel concentration was measured using infrared laser absorption at 3.39 micrometers. The decomposition rates for neat RP-1 and RP-2 were found to be very similar and were found to be slower than that of a simple kerosene surrogate, n-dodecane.

Nomenclature

C	=	fuel concentration
I	=	detected laser signal
I_o	=	detected reference laser signal
k	=	decomposition rate
L	=	path length through the shock tube
P	=	pressure
R	=	universal gas constant
t	=	time
T	=	temperature
THQ	=	1,2,3,4-tetrahydroquinoline
X	=	fuel mole fraction
α	=	absorbance
σ	=	absorption cross section

I. Introduction

HIGH-performance regeneratively cooled engines require fuel that not only performs well as a propellant, but also acts as a coolant for the engine. These fuels are exposed to high temperatures in cooling passages and are designed to “crack” into smaller fuel fragments, thereby absorbing both sensible and chemical energy from the engine. However, operating temperatures of the engines in these high-performance vehicles is often high enough that fragments of cracked fuel form coke in the cooling channels, restricting the flow and hindering the heat transfer process. Three main mechanisms of coke formation have been described in the literature: oxidative, catalytic, and condensation.¹⁻³ This study deals with the prevention of condensation coke, which is predominant at temperatures above 825 K and occurs when the fuel is heated enough to decompose into smaller fuel fragments.³ Many groups have proposed additives to act as thermal stabilizers for existing fuels⁴⁻¹² and Ref. 5 even reports decomposition rates for n-dodecane with the additives benzyl alcohol and 1,2,3,4-tetrahydroquinoline (THQ). Here we seek to determine decomposition rates for RP-1, RP-2, and a common surrogate, n-dodecane, and to study the effect of THQ on the decomposition rate of RP-1. If we assume that faster decomposition leads to faster deposit formation, and that an additive which decreases fuel decomposition rate also decreases deposit formation, then studying decomposition rate gives a measure of how useful an additive may be in preventing deposit formation. RP-1 was studied because of its use in high-temperature engines where coking is a major concern. RP-2 is a slightly different

¹ Graduate Research Assistant, Mechanical Engineering, Stanford University, AIAA Student Member.

² Senior Research Scientist, Mechanical Engineering, Stanford University, AIAA Member.

³ Professor, Mechanical Engineering, Stanford University, AIAA Fellow.

hydrocarbon mixture than RP-1, with tighter restrictions on sulfur and lower olefin content intended to give it better thermal stability than RP-1.¹³ Dodecane is a common single-component surrogate for many kerosenes.¹⁴

II. Experimental Setup

The experiments were performed in the Aerosol Shock Tube (AST) facility in the High Temperature Gasdynamics Laboratory at Stanford University described in detail in Refs. 15 and 16. For many shock tube studies, the concentration of heavy fuels is limited by the low vapor pressure of the fuel. The AST is unique in its fuel introduction method in that the fuel is nebulized into aerosol form, which then flows through the tube in a carrier bath gas. With this method, much higher fuel concentrations can be obtained than by conventional vapor pressure methods. Two lasers were used in these experiments, both transmitting through a window located 5 cm from the end wall of the tube. A non-resonant wavelength (670 or 1335 nm) generated using a diode laser was located away from any absorption features of the fuels, intermediate species, and products. It therefore was only sensitive to scattering of the aerosol droplets. The second laser was a mid-infrared HeNe emitting at 3.39 μm (2947.909 cm^{-1}) which was located on an absorption feature characteristic to hydrocarbon fuels and is therefore sensitive to both aerosol scattering and vapor absorption. Figure 1 shows the laser layout for these experiments.

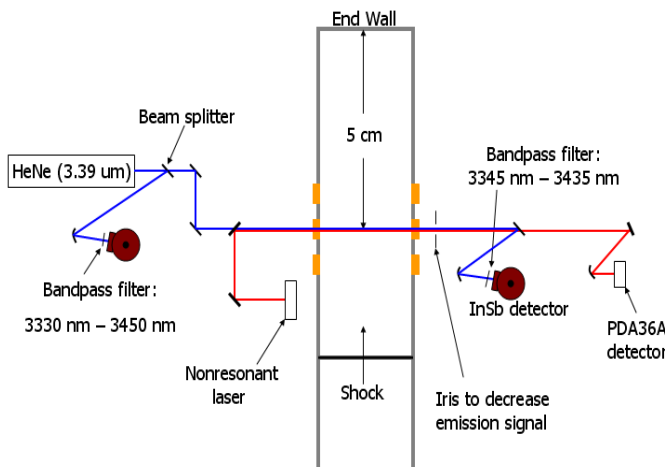


Figure 1. 3.39 μm and non-resonant (670 or 1335 nm) laser setup.

III. Theory

The amount of RP-1 in each shock tube experiment is determined using a Beer's law absorption method, which relates fuel concentration to the amount of light that is absorbed when the laser light passes through the test gas mixture. Each fuel has a unique absorption band, or wavelength region in which it absorbs light. The strength of the absorption is characterized by its absorption cross section.

To determine decomposition rates from our shock tube measurements, we employ two key concepts. The first is Beer's law, given in Eq. (1).

$$\frac{I}{I_0} = \exp(-\sigma CL) \quad (1)$$

The cross section, σ , is a measure (per mole) of how much light the RP-1 vapor absorbs. C is the fuel concentration in the test mixture, and L is the path length through the shock tube. The cross section is a function of the laser wavelength and of the temperature of the fuel vapor. For these high molecular weight fuels the cross section is independent of pressure. The absorption cross sections of the fuels in gaseous form were measured in a Nicolet 6700 FTIR for many wavelengths and at various temperatures. Reference 17 describes the test procedure for gaseous measurements of liquid fuel blends. The temperature-dependent cross sections at the wavelength of interest (3.39 μm) are shown in Fig. 2a for the fuels tested. With knowledge of the cross section as a function of temperature, the transmission (I/I_0) through the test gas mixture, and the path length through the tube, we can make quantitative measurements of fuel concentration in the shock tube.

The measured FTIR cross sections were limited to temperatures below approximately 800 K because the fuel begins to decompose in the cell faster than the measurement can be completed. To obtain high temperature cross sections, we once again employ Beer's law to calculate cross sections from shock data. Rearranging Beer's law gives the definition of absorbance, α , a useful quantity for describing the data given in Figs. 3a and 3b. Equation (2) gives this definition and a form of the absorbance that includes the mole fraction (this form requires the assumption that the test mixture is an ideal gas).

$$\alpha \equiv -\ln\left(\frac{I}{I_o}\right) = \frac{XP}{RT}\sigma L \quad (2)$$

In Eq. (2), X is the mole fraction of fuel, P is the test mixture pressure, R is the universal gas constant, and T is the test mixture temperature. Since the fuel mole fraction is constant across a shock wave, solving Eq. (2) for the mole fraction in region 2 (the region after the incident shock and before the reflected shock) and equating to the mole fraction in region 5 (the post-reflected shock region) gives Eq. (3). This relationship between the cross sections in regions 2 and 5 holds for a single wavelength. (Regions 2 and 5 are labeled in Fig. 3a.)

$$\sigma_5 = \frac{\alpha_5 T_5 P_2}{\alpha_2 T_2 P_5} \sigma_2 \quad (3)$$

With Eq. (3), for each shock we can calculate a high-temperature cross section in region 5 based on application of the FTIR-determined cross sections in region 2. This results in the cross section plot shown in Fig. 2b.

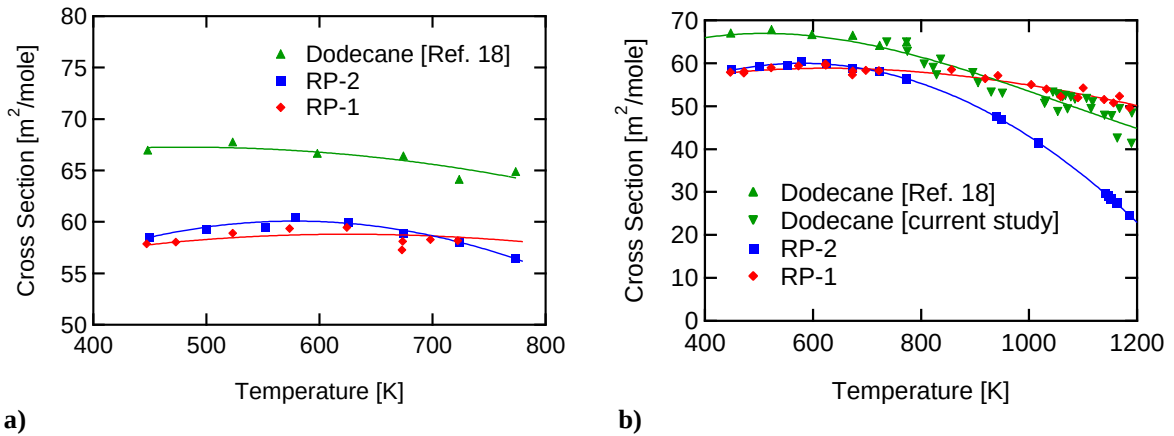


Figure 2. a) FTIR-based absorption cross-sections at 3.39 μm. b) FTIR- and shock-based absorption cross-sections.

The second main concept required for determination of the overall decomposition rate is the assumption that the decomposition reactions of these fuels follow the form of pseudo-first-order reactions as shown in Eq. (4) where k is the reaction rate of this decomposition reaction.



For a pseudo-first-order reaction at the high-pressure limit, the decomposition rate does not vary with pressure. Since fuels such as dodecane, RP-1, and RP-2 consist of large molecules, this high-pressure limit occurs at relatively low pressures and we have assumed that the pressures of the current experiments, $P_5 = 3$ to 8 atm, are near the high-pressure limit. The equation describing pseudo-first-order kinetics is given as Eq. (5) where C is the fuel concentration and t is time.

$$\frac{dC}{dt} = -kC \quad (5)$$

Solving Eq. (5) for the time varying concentration gives Eq. (6).

$$\frac{C(t)}{C_0} = \exp(-kt) \quad (6)$$

Equation (2) gives the normalized fuel concentration from the measured absorbance and Eq. (6) is the means by which we determine decomposition rates, k , from the time histories of fuel concentration.

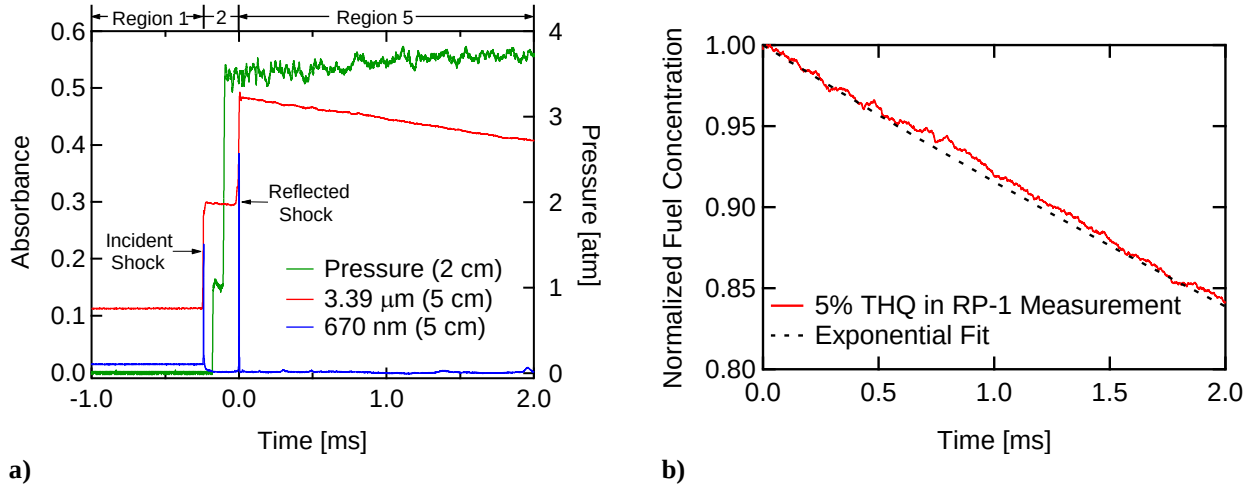


Figure 3. a) Sample data for a 5% THQ in RP-1 shock with 0.3% fuel concentration in argon, $P_5 = 3.5$ atm, $T_5 = 1175$ K, regions 1, 2, and 5 have been labeled. b) Normalized fuel concentration decay for the shock in a), $t = 0$ ms corresponds to the arrival of the reflected shock.

IV. Results and Discussion

Figure 3a shows a sample data trace for a 5% THQ in RP-1 shock. The incident and reflected shocks are clearly visible, as is the decomposition of RP-1 in region 5. Distances listed in Fig. 3a refer to the distance of the laser or pressure transducer from the shock tube end wall.

To convert the HeNe absorbance data of Fig. 3a into concentration, Eq. (2) and the cross section of fuel at T_5 are used. This cross section was obtained by the FTIR/shock method described above and is found in Fig. 2b. Normalizing the time varying concentration to the initial concentration results in the plot shown in Fig. 3b. From Eq. (6), fitting an exponential decay to the normalized fuel concentration in Fig. 3b gives the decomposition rate.

These decomposition rates are plotted in Fig. 4 for the fuels tested.

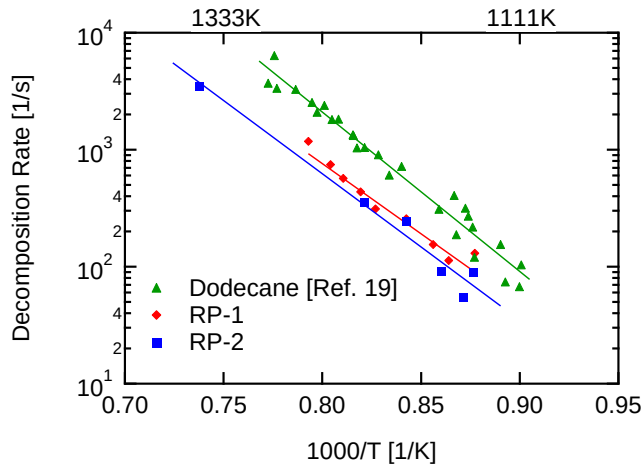


Figure 4. Comparison of decomposition rates for Dodecane, RP-1, and RP-2. Pressure range 3 to 8 atm, 0.2 to 0.5% fuel in argon.

As seen in Fig. 4, RP-2 has a lower decomposition rate than RP-1 in the 1100 K to 1300 K temperature range, as was intended when the RP-2 specifications were set, whereas dodecane has slightly higher decomposition rates.

The wavelength used for the absorption measurements (3.39 μm) corresponds to the C-H stretch vibration mode. Since RP-1 and RP-2 are mixtures containing large hydrocarbons, which have many of these C-H bonds, 3.39 μm is strongly absorbed by both of these fuels and also by dodecane. The intermediate species of the decomposition reactions of RP-1, RP-2, and dodecane are smaller hydrocarbons. For the case of

dodecane, these intermediate hydrocarbons are species such as ethylene, propylene, butane, hexane, methane, pentene, and methane. The concentrations and identities of these species were determined by simulations using existing kinetic mechanisms as explained in Ref. 19. These intermediates also absorb at 3.39 μm and can therefore interfere with an experiment intended to measure only absorption of the parent fuel. By using a kinetic mechanism to predict the amount of each intermediate species as the decomposition progresses, and with knowledge of the absorption cross section of each of the intermediates, a shock tube absorption measurement can be corrected to exclude interference from these species. For dodecane, it has been determined that the absorption interference from intermediates can result in an underestimation of the decomposition rate by 25 to 30%.¹⁹ However, since RP-1 and RP-2 are hydrocarbon mixtures, no accepted kinetic mechanism has been developed, which prohibits the prediction of the identities and concentrations of intermediate species. Therefore, it is noted that accounting for intermediates is likely to increase the decomposition rates of both RP-1 and RP-2, but no correction has been made here because of the current lack of a kinetic mechanism.

Figure 5 shows RP-1 decomposition data from the current study along with lower temperature decomposition rates for RP-1.²¹ It should be noted that the rates from Ref. 21 were obtained by thermally stressing liquid RP-1, while the current study presents decomposition rates of RP-1 in the vapor phase. Even so, these rates match well, despite a temperature separation of nearly 400 K.

Once the decomposition rates of these fuels were characterized, we began studies on how additives would affect the decomposition of RP-1. Several additives have been proposed to slow the decomposition rates of rocket propellants.⁴⁻¹² Presented in Fig. 6 are decomposition rates of RP-1 with the additive 1,2,3,4 - tetrahydroquinoline. THQ has been tested with dodecane and successfully lowered decomposition rates in the 675 K to 725 K temperature range.⁵ In the present study THQ was tested with RP-1 at 5% by volume. The addition of 5% THQ to RP-1 tends to lower the decomposition rate even at high temperatures. As observed in Ref. 5, the effects of additives decrease with increasing temperature, so it of interest to note that THQ lowers the decomposition rate up to temperatures of approximately 1250 K.

V. Conclusion

The AST has proven to be a useful tool in determining the effects of additives on decomposition rates of fuels. From the current data, it can be concluded that in the temperature range 1100 K to 1300 K, dodecane decomposes faster than RP-1, while RP-2 tends to decompose slightly slower than RP-1. The addition of 5% by volume THQ to RP-1 decreases the decomposition rate. These results suggest that THQ would be a good candidate for decreasing deposit formation even up to temperatures of 1250 K.

Future work will include accounting for interference absorption from intermediate species to recover more accurate decomposition rates. Additional work will also be performed to extend the temperature range of these experiments to lower temperatures. This will be accomplished with the installation of a shock tube driver extension,

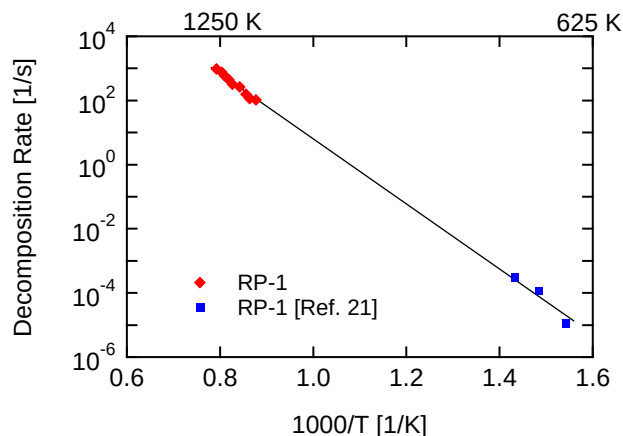


Figure 5. High- and low-temperature decomposition rates for RP-1. Pressure range 3 to 8 atm, 0.2 to 0.5% fuel in argon.

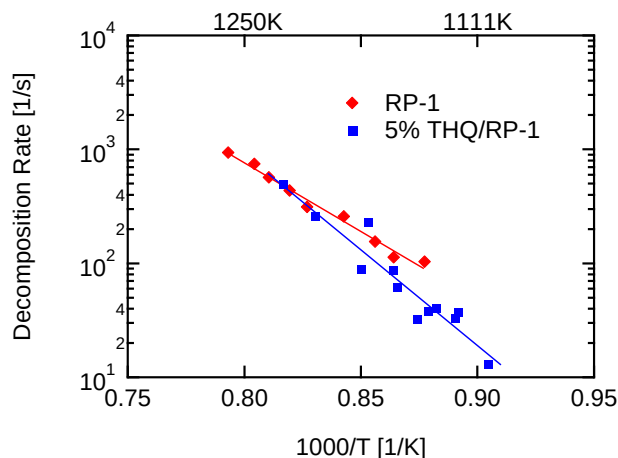


Figure 6. Comparison of RP-1 decomposition rates with and without THQ. Pressure range 3 to 8 atm, 0.2 to 0.5% fuel in argon.

giving longer test times which will allow observations of slower decomposition rates. This larger temperature range may also give a large enough temperature range for an acceptable calculation of the activation energies of these decomposition reactions. Additional additives will also be tested, with focus on benzyl alcohol.

Acknowledgments

The authors thank our sponsor, Dr. David Campbell, program manager for ERC Incorporated at the Air Force Research Laboratory. We would also like to acknowledge the assistance of our contract monitor, Matthew Billingsley, in the Combustion Devices Group at the Air Force Research Laboratory.

References

- ¹Edwards, T., "Cracking and Deposition Behavior of Supercritical Hydrocarbon Aviation Fuels," *Combustion Science and Technology*, Vol. 178, No. 1, 2006, pp. 307-334.
- ²Albright, L.F., and Marek, J.C., "Mechanistic Model for Formation of Coke in Pyrolysis Units Producing Ethylene" *Industrial and Engineering Chemistry Research*, Vol. 27, No. 5, 1988, pp. 755-759.
- ³Wickham, D.T., Atria, J.V., Engel, J.R., Hitch, B.D., Karpuk, M.E., and Striebich, R., "Formation of Carbonaceous Deposits in a Model Jet Fuel under Pyrolysis Conditions" *Symposium on Structure of Jet Fuels V*, Preprints of the ACS, Div. of Petrol. Chem., Vol. 43, 1998, pp. 428-432.
- ⁴Yoon, E.M., Selvaraj, L., Eser, S., and Coleman, M., "High-Temperature Stabilizers for Jet Fuels and Similar Hydrocarbon Mixtures. 1. Comparative Studies of Hydrogen Donors," *Energy & Fuels*, Vol. 10, No. 3, 1996, pp. 806-811.
- ⁵Yoon, E.M., Selvaraj, L., Eser, S., and Coleman, M., "High-Temperature Stabilizers for Jet Fuels and Similar Hydrocarbon Mixtures. 2. Kinetic Studies," *Energy & Fuels*, Vol. 10, No. 3, 1996, pp. 812-815.
- ⁶Coleman, M.M., Selvaraj, M.S., and Yoon, E., "Potential Stabilizers for Jet Fuels Subjected to Thermal Stress above 400°C," *Energy & Fuels*, Vol. 6, No. 5, September/October 1992, pp. 535-539.
- ⁷Corporan, E., and Minus, D.K., "Assessment of Radical Stabilizing Additives for JP-8 Fuel," 34th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, AIAA98-3996, Cleveland, OH, July 1998.
- ⁸Atria, J.V., and Edwards, T., "High Temperature Cracking and Deposition Behavior of an n-Alkane Mixture," *Symposium on Structure of Jet Fuels IV*, Preprints of the ACS, Div. of Petrol. Chem., Vol. 41, 1996, pp. 498-501.
- ⁹Minus, D.K., and Corporan, E., "Deposition Effects of Radical Stabilizing Additives in JP-8 Fuel," *Symposium on Structure of Jet Fuels V*, Preprints of the ACS, Div. of Petrol. Chem., Vol. 43, 1998, pp. 360-363.
- ¹⁰Yoon, E.M., Selvaraj, L., Song, C., Stallman, J., Eser, S., and Coleman, M., "High Temperature Jet Fuel Stabilizers," *Symposium on Structure of Jet Fuels IV*, Preprints of the ACS, Div. of Petrol. Chem., Vol. 41, 1996, pp. 461-463.
- ¹¹Sobkowiak, M., Burgess Clifford, C.E., Beaver, B., "Evaluation of Additives to Inhibit Oxidative and Pyrolytic Deposition of Jet Fuels," Preprints of the ACS, Div. of Petrol. Chem., Vol. 49, No. 4, 2004, pp. 450-452.
- ¹²Minus, D.K., Corporan, E., "Thermal Stabilizing Tendencies of Hydrogen Donor Compounds in JP-8+100 Fuel," 35th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, AIAA99-2214, Los Angeles, CA, June 1999.
- ¹³"Detail Specification, Propellant, Rocket Grade Kerosene," MIL-DTL-25576D, 20 May 2005.
- ¹⁴Edwards, T., Maurice, L.Q., "Surrogate Mixtures to Represent Complex Aviation and Rocket Fuels," *Journal of Propulsion and Power*, Vol. 17, No. 2, 2001, pp. 461-466.
- ¹⁵Haylett, D.R., Davidson, D.F., and Hanson, R.K., "Development of an Aerosol Shock Tube for Kinetic Studies of Low-Vapor-Pressure Fuels," 43rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference, AIAA2007-5678, Cincinnati, OH, July 2007.
- ¹⁶Davidson, D.F., Haylett, D.R., Hanson, R.K., "Development of an aerosol shock tube for kinetic studies of low-vapor-pressure fuels," *Combustion and Flame*, in press, available online 3 March 2008.
- ¹⁷Klingbeil, A.E., Jeffries, J.B., and Hanson, R.K., "Temperature- and Pressure-Dependent Absorption Cross Sections of Gaseous Hydrocarbons at 3.39 μm ," *Measurement Science and Technology*, Vol. 17, 2006, pp. 1950-1957.
- ¹⁸Klingbeil, A.E., Jeffries, J.B., and Hanson, R.K., "Temperature-dependent mid-IR absorption spectra of gaseous hydrocarbons," *Journal of Quantitative Spectroscopy & Radiative Transfer*, Vol. 107, No. 3, 2007, pp. 407-420.
- ¹⁹Klingbeil, A.E., Jeffries, J.B., Davidson, D.F., Hanson, R.K., "Two-Wavelength Mid-IR Diagnostic for Temperature and n-Dodecane Concentration in an Aerosol Shock Tube," *Applied Physics B*, in press.
- ²⁰Yu, J., and Eser, S., "Thermal Decomposition of n-Alkanes Under Supercritical Conditions," *Symposium on Structure of Jet Fuels IV*, Preprints of the ACS, Div. of Petrol. Chem., Vol. 41, 1996, pp. 488-492.
- ²¹Anderson, P.C., and Bruno, T.J., "Thermal Decomposition Kinetics of RP-1 Rocket Propellant," *Industrial and Engineering Chemistry Research*, Vol. 44, No. 6, 2005, pp. 1670-1676.