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)* 31 July 2016	2. REPORT TYPE Technical Note	3. DATES COVERED *(From - To)* 04 January 2016 - 31 July 2016
4. TITLE AND SUBTITLE Hydrocarbon Fuel Thermal Performance Modeling based on Systematic Measurement and Comprehensive Chromatographic Analysis		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Billingsley, M., Keim, N., Hill-Lam, B., and Synovec, R.		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER Q0A4
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRC 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680		8. PERFORMING ORGANIZATION REPORT NO.
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB, CA 93524-7048		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) **AFRL-RQ-ED-TN-2016-001**

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. PA Clearance Number: 16004 Clearance Date: 1/11/2016

13. SUPPLEMENTARY NOTES
For presentation at AIAA Joint Propulsion Conference; Salt Lake City, UT; July 2016

14. ABSTRACT

In a typical hydrocarbon-fueled liquid rocket engine, enthalpy is removed from the combustion chamber by a regenerative cooling system comprising a series of passages through which fuel flows at high pressure and velocity, thereby maintaining the thrust chamber surface at acceptably low temperature. Ensuring reliable and predictable fuel thermal performance and material compatibility in cooling passages is crucial, particularly as engine operating conditions and lifecycle requirements extend beyond the domestic experience base.[1,2] In addition to the extreme thermal-material environments accompanying advanced propulsion cooling systems and the multifaceted physicochemical processes of fuel degradation and surface fouling, clear understanding of fuel thermal behavior is inhibited by chemical complexity and compositional variability, which can occur as a result of fuel production method, refining conditions, treatment processes, and blending.

15. SUBJECT TERMS
N/A

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON M. Billingsley
a. REPORT **Unclassified**	b. ABSTRACT **Unclassified**	c. THIS PAGE **Unclassified**	SAR	7	19b. TELEPHONE NO *(include area code)* N/A

Standard Form 298 (Rev. 8-98) **Prescribed by ANSI Std. 239.18**

Hydrocarbon Fuel Thermal Performance Modeling based on Systematic Measurement and Comprehensive Chromatographic Analysis

Matthew Billingsley
Air Force Research Laboratory (AFRL/RQRC), Edwards AFB, CA
matthew.billingsley.1@us.af.mil

Nicholas Keim and Benjamin Hill-Lam
The Johns Hopkins University, Baltimore, MD

Robert Synovec
The University of Washington, Seattle, WA

ABSTRACT

In a typical hydrocarbon-fueled liquid rocket engine, enthalpy is removed from the combustion chamber by a regenerative cooling system comprising a series of passages through which fuel flows at high pressure and velocity, thereby maintaining the thrust chamber surface at acceptably low temperature. Ensuring reliable and predictable fuel thermal performance and material compatibility in cooling passages is crucial, particularly as engine operating conditions and lifecycle requirements extend beyond the domestic experience base.[1,2] In addition to the extreme thermal-material environments accompanying advanced propulsion cooling systems and the multifaceted physicochemical processes of fuel degradation and surface fouling, clear understanding of fuel thermal behavior is inhibited by chemical complexity and compositional variability, which can occur as a result of fuel production method, refining conditions, treatment processes, and blending.

Full scale testing can assess fuel suitability but is expensive and time consuming. Furthermore, verification of fuel performance and applicability is typically required early in the development cycle. Instead, predictive approaches that couple physical measurements with advanced compositional analyses of fuel chemistry spanning the potential trade space are being matured. Recently, chemometric methods were applied in the unprecedented correlation of comprehensive two-dimensional gas chromatographic (GC×GC) rocket fuel data with physical and thermochemical properties, resulting in corresponding partial least squares (PLS) models based solely on chemical information; the quality of model predictions was encouraging.[3] A similar approach was subsequently used in the context of temperature-dependent fuel volatility modeling and was met with an equal degree of success.[4] Herein, these analytical methodologies are applied for the first time to a formidable application-specific behavior inherent to and of vital importance for hydrocarbon-fueled propulsion systems: fuel thermal performance as indicated by physical and chemical effects of cooling passage deposit formation. Thermal integrity encompasses the

---

[1] Billingsley, AIAA Paper 2008-5126, *44th Joint Propulsion Conference*, Hartford, CT, 2008.

[2] Billingsley, et al., AIAA Paper 2010-6824, *46th Joint Propulsion Conference*, Nashville, TN, 2010.

[3] Kehimkar, et al., *Journal of Chromatography A*, Vol. 1327, 2014, pp. 132-140.

[4] Kehimkar, et al., *Analytical and Bioanalytical Chemistry*, Vol. 407, 2015, pp. 321-330.

processes of homogeneous (bulk fuel reactions) and heterogeneous (reactions at the cooling channel surface) chemistry as well as local fluid dynamics and thermal fields. To achieve progress toward reliable prediction of the outcome of these intertwined phenomena, three key elements are required: a set of fuels comprising adequate compositional diversity, particularly with regard to those compounds and hydrocarbon classes of importance for cooling passage reactivity; a qualified experimental method capable of systematically quantifying physical and chemical behavior indicative of thermal integrity (and the application of this method to the full referee fuel set); and the combination of a robust and sensitive chromatographic-detection platform with appropriately developed chemometric strategies, both of which accommodate the multivariate datasets generated by thermal integrity testing and test article analysis.

The selection and acquisition of a set of chemically diverse fuels is pivotal for a successful outcome since test method validation and model development both rely on fuel compositional variability. (Additionally, a concern from an operational standpoint is precisely how allowable variations in specification fuels will impact system behavior and performance.) A referee fuel set comprising nineteen fuels [eight (8) RP-2 samples, seven (7) RP-1 samples, JP-7, and JP-900] was procured based on established criteria such as safety and handling, hydrocarbon type diversity, availability, cost, and so on. Physical and chemical property data were acquired for many of these samples. In some cases, reported values in fuel conformance documents were available. Figure 1 presents ASTM D86 distillation data for the nineteen fuels, along with JP-8 for comparison. Several of these fuels are the subject of previous efforts,[5,6] and thus a reasonably established database was available.

A test metrology capable of rapidly assessing thermal integrity at conditions relevant to rocket cooling systems but using small fuel volumes was developed and applied to the acquired referee fuel set. In this versatile convective heat transfer and material compatibility experiment, referred to as Compact Rapid Assessment of Fuel Thermal Integrity (CRAFTI), fuel is pressurized by a positive displacement pump and flows through an ohmically heated test article. Electrical current is maintained via automated control of the dual power supplies, resulting in constant power during the test. Backpressure is held constant by an electropneumatically controlled backpressure regulator. Serial downstream heat exchangers cool the fuel to safe levels prior to sampling and collection. The experiment is conducted in vacuum to reduce heat loss to surroundings, minimize oxidation of test article surfaces, and isolate the operator from potential hazards. Combined control of fuel flowrate, test article geometry, and supply power defines surface temperature profile, which in turn determines fuel exit bulk temperature. Figure 2 shows details of the experimental assembly.

Qualifying the CRAFTI experiment as a capable test method required demonstrating its ability to: (1) produce meaningful data in a short timeframe with small fuel quantities; (2) operate at conditions relevant to the intended application; (3) acquire thermal performance data with good repeatability; (4) discriminate between fuels that are otherwise indistinguishable in terms of

[5] Lovestead, et al., *Energy & Fuels*, Vol. 24 (10), 2010, pp. 5611 – 5623.

[6] Fortin, *Energy & Fuels*, Vol. 26 (7), 2012, pp. 4383 – 4394.

thermal integrity; (5) produce results that are traceable to existing experiments; and (6) possess qualities characteristic of a standard test method, such as automation, ease of assembly, safe operation, etc. A set of standard test conditions was prescribed for the purpose of systematically assessing experimental reliability and repeatability and enabling side-by-side comparison between different fuels. Run duration was 15 min.; approximate heated test article (C10100 copper) length was 4 in. (10.2 cm); backpressure was maintained at 1000 psi (6.9 MPa), above the apparent critical pressure; the input electrical power was 4500 W; and wall temperature varied from 800 – 1200°F (430 – 650°C). Test method repeatability as indicated by pressure drop and sensitivity evidenced by measured test article surface temperature are shown in Figure 3 and Figure 4, respectively. The ability of the CRAFTI metrology to distinguish between relatively thermally stable fuels is demonstrated by measured carbon deposit as a function of test article axial location for select fuels in Figure 5. Additional data, including evaluation of the traceability of the CRAFTI metrology to existing experiments, will be included in the final manuscript.

Although multidimensional chromatography has recently experienced increased applicability for aerospace fuel analysis, the extent of its utility has heretofore been limited in most cases to qualitative, often visual, comparisons between fuels and in some cases hydrocarbon type classification, owing to the immensity of the datasets offered by GC×GC. The sheer quantity of chemical information obtained from GC×GC coupled with sensitive detection, i.e., time-of-flight mass spectrometry (TOFMS), poses a significant challenge for gleaning useful information from the data. However, use of powerful chemometric techniques can aid in the interpretation of complex data sets and establish important linkages between chemical composition and physical behavior.

In the modeling portion of this project, CRAFTI thermal integrity data, test article carbon deposit data, and comprehensive fuel chemical information, obtained with GC×GC–TOFMS, all obtained for the referee fuel set, were analyzed using a variety of chemometric approaches. Principal component analysis (PCA) mathematically reduced the large multiparametric datasets in order to glean useful information about the fuels. PCA served two primary purposes: (1) Establish groups to distinguish between fuels with observed thermal integrity performance differences, thus serving the purpose of assigning categorical quality, i.e., high performing and low performing, for subsequent Fisher ratio (F-ratio) analysis; and (2) Identify GC×GC–TOFMS chromatographic variations, e.g., hydrocarbon compositional differences between fuels, that correlate with measured performance differences. F-ratio analysis also served dual purposes: (1) Produce a refined set of GC×GC–TOFMS data for the purpose of optimizing subsequent PLS analyses; (2) Identify class distinguishing features, (chemical compounds in the GC×GC–TOFMS data) that contribute to a fuel's group assignment, in this case thermal integrity. Finally, PLS was used to develop models that relate thermal integrity behavior to fuel composition. Predictive models were developed for physical behavior measured during CRAFTI testing (for example, maximum pressure drop – see Figure 6) as well as for test article deposit formation measured during post-test analyses. One important outcome of PLS modeling is the ability to isolate and identify compounds and regions of chromatographic space that are responsible for an observed directional (positive or negative) change in a measured parameter. The final manuscript will provide additional detail on how these relationships were established and will discuss their implications regarding fuel compositional requirements and specification.
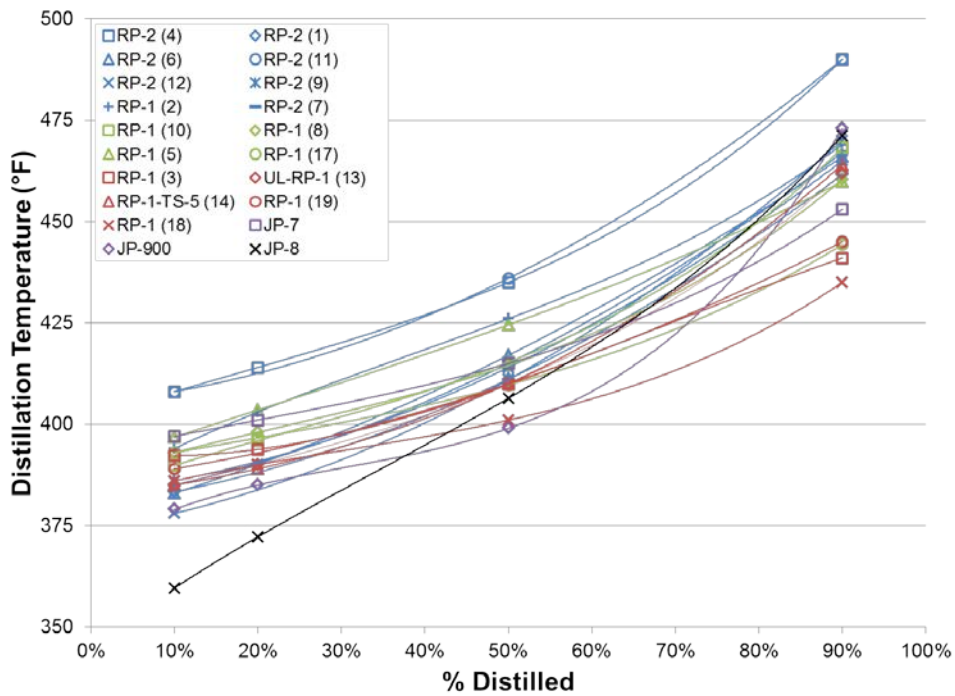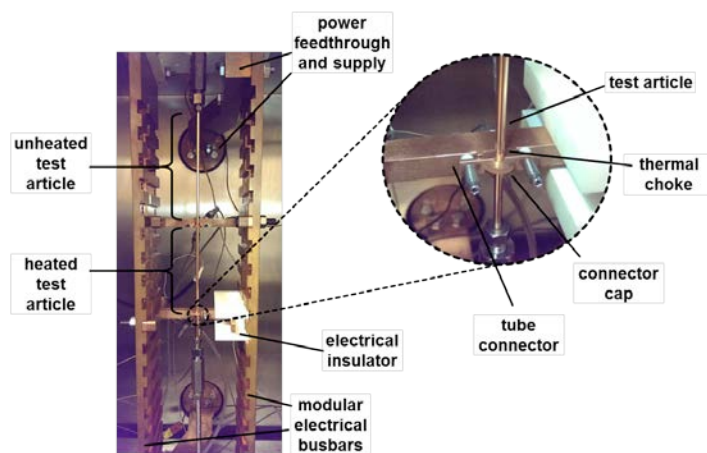
Figure 1. Referee fuel set ASTM D86 distillation.

Figure 2. Compact Rapid Assessment of Fuel Thermal Integrity (CRAFTI) test article assembly showing and electrical connection details.
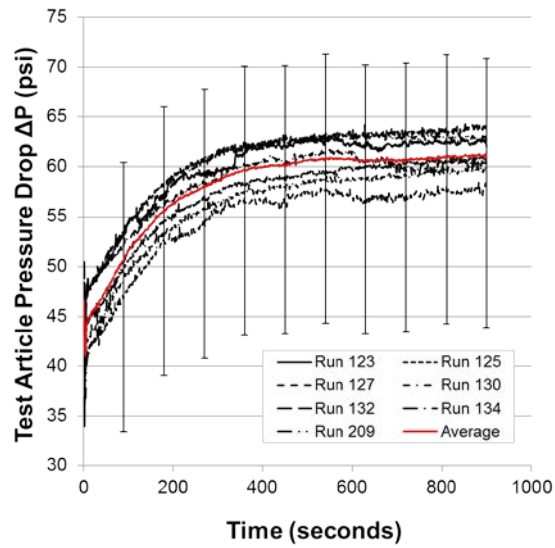
Figure 3. Repeatability of CRAFTI test method is indicated by pressure drop as a function of run duration at standard test conditions using RP-2 fuel (Sample 1).
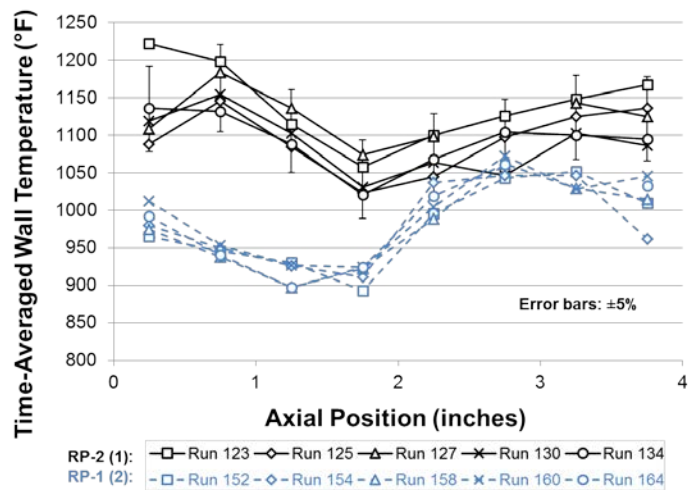

Figure 4. CRAFTI heated region wall temperature is repeatable (variation within fuels) and sensitive to fuel composition (separation between fuels).
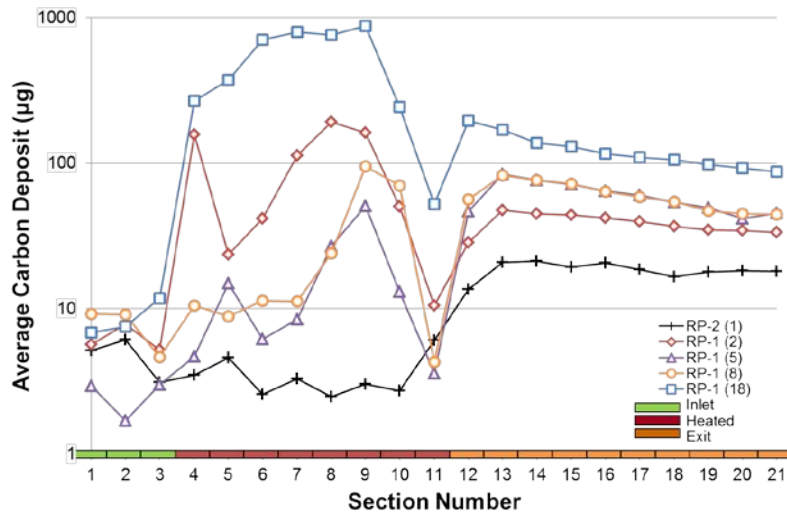
Figure 5. Total carbon deposit as a function of test article location demonstrates sensitivity to fuel composition. Average of multiple runs performed on five fuels shown. Test article condition (unheated inlet, heated region, and unheated outlet) indicated by color band on horizontal axis.
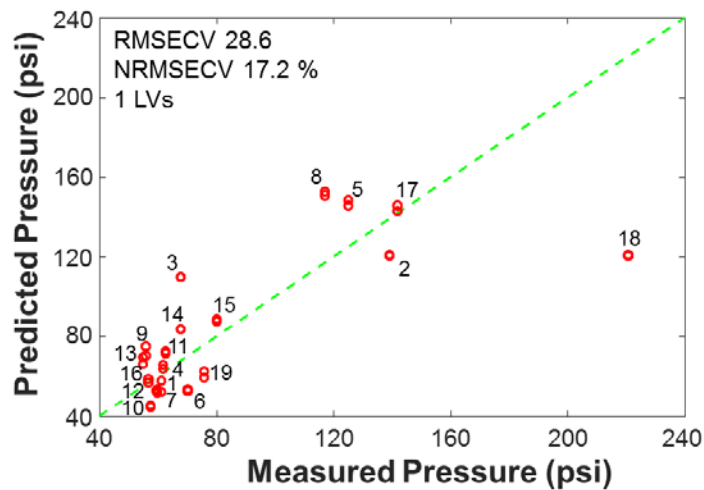

Figure 6. PLS Model of Maximum Test Article Pressure Drop. Non-ideal prediction of fuels with abnormal composition and/or physical behavior (Sample 18) is expected. RMSECV denotes Root Mean Squared Error of Cross Validation; NRMSECV denotes Normalized RMSECV.