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Thermogravimetric Analysis of Carbon Felt Insulation for Flexible Thermal Protection System Thermal Response Modeling

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A multi-layered, Flexible Thermal Protection System (FTPS) heatshield configuration layup has previously undergone ground-based testing in an arc-jet facility to simulate atmospheric entry heat exposure. An existing thermal response model has been developed at NASA to simulate heat transfer through an FTPS layup during an arc-jet experiment by predicting measured temperatures between layers. A carbon felt insulator, located in the middle of this FTPS layup, decomposes when exposed to high heating in an atmosphere that contains significant amounts of oxygen. The current module in the FTPS thermal response model that simulates insulator decomposition has not yet leveraged experimentally determined quantities. In an effort to achieve better temperature predictions in the thermal model, a Thermogravimetric Analysis (TGA) experimental campaign was performed on virgin samples of a carbon felt insulator to rigorously characterize decomposition by obtaining its activation energy. Experiments were performed in a zero-moisture air environment using Standard TGA and Modulated TGA methods with a TA Instruments Q5000IR apparatus to obtain estimates of activation energy. The mean activation energy for carbon felt was determined to be 131.56 kJ/mol and 121.16 kJ/mol for Standard and Modulated TGA methods, respectively. Limited TGA testing resources in the past have resulted in rough approximations FTPS insulator activation energy with little knowledge of uncertainty. This TGA experimental campaign also determined the corresponding activation energy uncertainty for carbon felt samples using a t-distribution. The activation energy standard deviation was determined to be 5.79 kJ/mol and 8.66 kJ/mol for Standard and Modulated TGA methods, respectively. The activation energy obtained from the Standard TGA method was inserted into the FTPS thermal response model to compare resulting temperature profile predictions with measured thermocouple temperature data recorded during ground-based arc-jet testing. Preliminary results show significant improvement in thermal response model temperature predictions using this experimentally-determined value for activation energy. This investigation shows promise for a newly developed decomposition module within the FTPS thermal response model based on rigorous experimentation and enables future probabilistic analysis to include activation energy as an uncertain parameter.

Nomenclature

β_D	=	Ballistic coefficient of entry vehicle
m_D	=	Mass of entry vehicle
C_D	=	Drag coefficient of entry vehicle
A_D	=	Drag area of entry vehicle
k	=	Rate constant
A	=	Arrhenius pre-exponential factor
E_a	=	Arrhenius activation energy
R	=	Gas constant
T	=	Temperature

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α = Degree of conversion
W_0 = Initial TGA sample weight
W_t = TGA sample weight at time "t"
$\frac{d\propto}{dt}$ = Rate of conversion
$k(T)$ = Rate constant at temperature "T"
$f(\propto)$ = Kinetic expression
n = Reaction order for nth order kinetics
β = Constant heating rate of TGA test
m = Slope of Arrhenius plot
E_{it} = Iterative activation energy estimate
a = Table lookup value from ASTM E1641-16
b = Table lookup value from ASTM E1641-16
A_{MP} = Temperature half-amplitude for modulated TGA testing
$\frac{d\propto_p}{dt}$ = Maximum value of $\frac{d\propto}{dt}$ curve at conversion $\propto$
$\frac{d\propto_v}{dt}$ = Minimum value of $\frac{d\propto}{dt}$ curve at conversion $\propto$
L = Difference between max and min $\frac{d\propto}{dt}$ curve at conversion $\propto$
$\bar{x}$ = Sample mean of activation energy calculations for each TGA method
N = Number of experiments performed for each TGA method
x_i = Sample calculation of activation energy
s^2 = Sample variance of activation energy calculations for each TGA method
s = Sample standard deviation of activation energy calculations for each TGA method

I. Introduction

THERMOGRAVIMETRIC Analysis (TGA) describes the process of studying the decomposition behavior of a variety of materials as a function of temperature and time in a controlled testing environment. TGA experimentation is commonly used to characterize the decomposition behavior of heatshield materials for atmospheric entry spacecraft. Atmospheric entry vehicles traveling to Mars have used vehicle geometry designs derived from heritage Viking missions. Each follow-on mission has incrementally improved landing mass capability. It is believed that the Mars Science Laboratory (MSL) mission that landed in 2012 maximized current state of the art landing capacity for entry vehicles on Mars[1]. Additionally, rigid ablators like the Super Lightweight Ablator (SLA-561V) and Phenolic Impregnated Carbon Ablator (PICA) have been used on every Mars mission to date. Landing additional mass beyond the MSL capability has been shown to be difficult with present technology, motivating the advancement of technologies to enable future missions. One such technology is a Hypersonic Inflatable Aerodynamic Decelerator (HIAD) [2].

A HIAD is an inflatable aeroshell that reduces the entry ballistic coefficient when compared with atmospheric entry vehicles fitted with traditional rigid aeroshells. Ballistic coefficient is a function of the vehicle mass (m_D), drag coefficient (C_D), and drag reference area (A_D) shown in Equation 1. HIADs reduce the vehicle's ballistic coefficient by substantially increasing the vehicle's drag area while adding minimal mass.

$$\beta_D = \frac{m_D}{C_D A_D} \tag{1}$$

A lower ballistic coefficient allows the vehicle to decelerate higher in the atmosphere and decrease the peak heat rate experienced by the HIAD TPS. Unlike rigid Thermal Protection Systems (TPS), HIAD TPS must remain flexible to enable inflation before entry. The HIAD must also allow for compact packaging within the confines of a launch vehicle shroud for extended periods prior to withstanding entry aerothermal loading. With the advancement of fabrics, insulation, and thin-film materials, HIADs may result in a means to increase mission capabilities. Additionally, by making improvements in FTPS material characterization and thermal modeling, designers can obtain more accurate and more reliable FTPS mass estimations for future Earth and Mars entry missions.

In order to choose an optimum FTPS configuration, it is desirable to create a thermal response model to simulate entry aerothermal loads applied to the FTPS surface. One way to test FTPS response to high reentry heating is to expose FTPS layups to heated flow generated by an arc-jet facility. An extensive experimental campaign performed by the HIAD team at NASA Langley Research Center has been underway for the past decade exposing various FTPS stackup configurations to arc-jet heated flow. During each arc-jet test, the HIAD team measured temperatures between each layer of FTPS to gain a deeper understanding of its thermal response. To simulate these physical processes, Dr. Roy Sullivan and Eric Baker at NASA Glenn Research Center have developed a one-dimensional (1D) thermal response model using COMOSL Multiphysics software. A significant amount of additional thermal model development was carried out by Steven Tobin and members of the HIAD team at NASA Langley Research Center.

Creating a thermal model that accurately predicts temperatures within an FTPS layup requires detailed understanding of the physical processes and thermal-material properties associated with each layer. The first stage in developing a thermal model is verification that all pertinent physical processes are included and all thermal-material properties have been obtained through testing or expert-opinion over the appropriate temperature and pressure range of interest. Next, the model must be validated by comparing recorded arc-jet test temperature data between FTPS layers to corresponding temperature predictions in the thermal response model. Finally, the performance of the thermal model is evaluated based on how closely the temperature predictions as a function of time match the arc-jet temperature data measured at each thermocouple location.

This investigation focuses on a carbon felt called KFA5 created by Sigratherm, which serves as an insulator for a wide variety of applications. With a low thermal conductivity, this carbon felt has proven to be a viable candidate insulator for the HIAD FTPS. The objective of this study is to continue thermal response model development by characterizing the decomposition behavior of a carbon felt insulator at high temperatures in an oxidative environment. The Arrhenius equation has been chosen to model the carbon-oxidation decomposition behavior, which is shown in Equation 2 [3].

$$k = A\, e^{\left(-\frac{E_a}{RT}\right)} \tag{2}$$

This fundamental form of the Arrhenius equation defines the approximate relationship between the rate constant (k) and the activation energy (E_a) for a material. This expression is a function of the pre-exponential factor (A), the universal gas constant (R), and the temperature (T) of the sample material. In order to fully define the Arrhenius equation for a material, one needs to expose the sample to a controlled thermal event by selecting the gaseous environment composition, pressure, and varied temperature profiles. Exposure of samples to a controlled environment is achieved by performing a series of careful TGA experiments. The activation energy can be calculated from prescribed data reduction procedures set forth by the American Society for Testing and Materials (ASTM) according to the type of TGA method. The types of TGA methods performed in this study feature near-constant heating rate profiles with respect to time, and each carbon felt sample is being tested in zero-moisture air to capture the resulting carbon-oxidation decomposition behavior. The following study assumes that the carbon-oxidation decomposition can be accurately modeled using the Arrhenius equation and calculates the resulting activation energy of the carbon felt.

As mentioned, the primary objective of a TGA experimental campaign is to gain a deeper understanding of a material's decomposition in a controlled environment. In this case, the deeper understanding gleaned from TGA of carbon felt is applied to obtain more temperature predictions within the FTPS thermal response model. This is performed by obtaining the candidate insulator's activation energy, which is the minimum amount of thermal energy required for the carbon-oxidation decomposition process to occur. The activation energy of decomposing FTPS insulators in this study is determined using two different methods: the Standard TGA test method (Ozawa-Flynn-Wall) and a recently-developed Modulated TGA test method. The following TGA test campaign contains an embedded material testing methodology that approximates the probability distribution of activation energy using both TGA test methods. These probability distributions of activation energy provide experimentally-determined ranges used to investigate decomposition sensitivities during thermal response model Monte Carlo simulations.

II. Motivation for Thermal Response Model Improvement with Experiment-Based Decomposition Module

While many different layup configurations have been tested in the Boeing Large Core Arc Tunnel (LCAT) facility, only one configuration will be investigated in this analysis. Figure 1 below is referred to as a Pure KFA5 Layup because the insulation region is composed of only KFA5 carbon felt. The layup contains two layers of COI Ceramics' Nicalon Silicon-Carbide (SiC) for the outer fabric, four layers of Sigratherm's KFA5 carbon felt for the insulation, and Aluminized Kapton laminated to Kevlar (AKK) for the gas barrier.

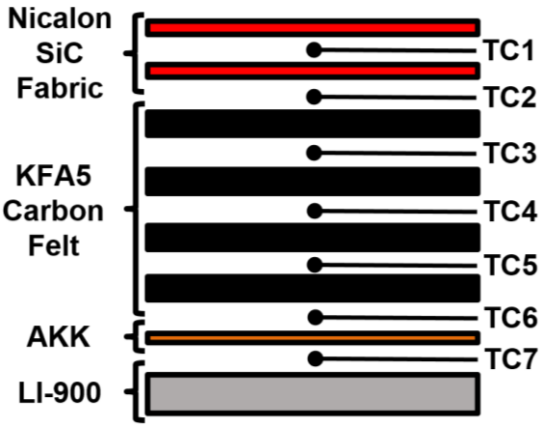

Figure 1. Pure KFA5 Layup (SiC, KFA5, AKK) [4]

During arc-jet testing, thermocouple (TC) sensors are placed between FTPS layers to obtain experimental temperature measurements with time at various depths (TC1, TC2, TC3, TC4, TC5, TC6, and TC7 from Figure 1). The COMSOL thermal response model mentioned previously is used to generate corresponding thermocouple temperature vs. time predictions at the same thermocouple depths within the FTPS layup. The goal of the modeling effort is to produce thermocouple predictions within an acceptable closeness to thermocouple measurements. The thermal model initially solves the direct heat transfer problem by applying an arc-jet measured temperature profile at TC2 of the Pure KFA5 Layup as the driving boundary condition and predicting temperature at the appropriate depths. Discrepancies produced by the model itself and by uncertain knowledge of the boundary condition are expected to cause initial predictions to deviate from measurements.

Thermophysical properties can be measured with confidence using traditional methods, but characterization of the uncertainty of these properties is particularly challenging. A methodology described later in this study attempts to characterize material property uncertainty in a probabilistic manner to enable future probabilistic analysis methods. Generally, material property testing is performed over discrete temperature and pressure ranges. In limited instances, arc-jet test conditions can potentially produce temperatures that exceed the bounds of collected thermophysical data, forcing the analyst to extrapolate to provide continuity. In other cases, experimentally determined thermophysical property data is not available, and properties must be estimated. The current insulator decomposition module within the FTPS thermal response model uses estimates for activation energy that are not rigorously determined from traditional experimentation. For a carbon insulator that experiences significant oxidation in the presence of a high-temperature, oxygen-rich environment, it is particularly important to accurately determine decomposition parameters from physical experiments. Therefore, the primary motivation of the following TGA test campaign is to rigorously obtain the KFA5 carbon felt activation energy along with its uncertainty. A decomposition module grounded in experimental data enables the minimization of thermal model temperature prediction discrepancies.

The COMSOL thermal response model simulates thermophysical processes experienced by the FTPS layup during arc-jet testing by defining governing equations for conservation of mass, momentum, and energy. Over the past decade, many research laboratories have collaborated to perform material property characterization on FTPS layers as a function of temperature and pressure to improve the thermal simulation accuracy. Performing arc-jet testing on FTPS layups in the Boeing LCAT facility helps analysts gain a deeper understanding of FTPS performance by collecting temperature measurements from thermocouples between layers and comparing them to temperature predictions at depth from the physics-based model.

Experimental testing has shown that KFA5 samples heated above 300℃ in zero moisture air begin to experience significant decomposition due to carbon oxidation. The decomposition process is an energy absorbing mechanism that can potentially lower temperatures throughout an FTPS layup, which must be accounted for in the thermal model before accurate temperature predictions can be made [5]. Complex phenomena have been recently added to the model increase fidelity, including boundary layer flow through the porous FTPS layers and pyrolysis gas flow from insulators to the surface. In addition, the thermal model has successfully modeled heat transfer processes such as convection, surface radiation, and solid/gas conduction through FTPS layers. Finally, the current thermal model includes the physics to properly describe insulator mass decomposition using the Arrhenius Equation [3].

Preliminary results indicate the thermal model consistently under-predicts measured arc-jet thermocouple data. Temperature predictions for the bondline interface, which sits between the fourth layer of insulation and the gas

barrier, are consistently lower than thermocouple measurements. While this conservative estimate leads to a "safer" FTPS design, these predictions could produce an FTPS mass beyond heatshield requirements for an atmospheric entry mission, which ultimately decreases landed payload mass capability. However, as thermal model temperature predictions at depth become more accurate, heatshield thickness and mass margins become more exact, leading to significant mass savings. Minimizing the gap between thermal model temperature predictions and arc-jet temperature measurements facilitates progress towards model validation. The TGA testing campaign in this study has been performed to gain a deeper understanding of the KFA5 carbon felt mass decomposition process by obtaining an experimentally activation energy from experimentation.

As previously mentioned, the overall objective of conducting further material property testing is to provide the FTPS thermal model with a more detailed, accurate material database to produce temperature profile predictions with reduced discrepancies. The goal is to reduce the discrepancies between in-depth thermocouple predictions and thermocouple measurements.

III. TGA Testing Procedure

A TGA experiment exposes a material sample to a specified temperature profile, pressure, and surrounding gas composition to measure sample mass loss as a function of temperature and time. The traditional way of obtaining the activation energy of a TPS material with TGA follows the Ozawa-Flynn-Wall method, initially developed in 1966[6]. In this work, the Arrhenius relation is used to model insulator mass decomposition[7, 8, 9]. The first objective is to find the activation energy of decomposing FTPS insulators using TGA testing. Later on, this activation energy is inserted into the FTPS thermal response model to accurately simulate heat transfer through FTPS layups exposed to flight-relevant heating conditions in an arc-jet.

Finding the activation energy of a material using the Standard (Ozawa-Flynn-Wall) method is time consuming because it requires TGA tests at four different heating rates. This requires many re-calibrations of the TGA instrument and many sample runs. Recently, a new method called Modulated TGA has been developed to find the activation energy of a material using a single test at a single heating rate[10, 11]. In this investigation, Modulated TGA will be used to find the activation energy of decomposing FTPS insulators for the first time. The activation energy obtained from the Standard (Ozawa-Flynn-Wall) TGA method and the new Modulated TGA method will be compared to potentially show that Modulated TGA is a viable option for future use. Due to scarcity of experimental resources, TGA testing is performed sparingly. For example, to find the activation energy of one material, an experimentalist may perform one repeated test (2 tests) at three different heating rates (6 tests total) before estimating its activation energy. This challenge is exacerbated if one seeks the associated activation energy uncertainty.

Many materials are assumed to have an activation energy that follows a normal probability distribution function, as described by the Distributed Activation Energy Model (DAEM)[12, 13, 14]. If the analyst makes this common assumption, he may approximate the activation energy with an experiment-based t-distribution. The more experiments that are performed, the closer the t-distribution approaches a normal distribution. The present work defines a methodology to obtain an approximate probability distribution of activation energy by completing repeated tests. Obtaining the probability distribution of activation energy provides a straightforward method to obtain its uncertainty. While this method will be demonstrated by finding the distribution of activation energy, it can be extended to other material properties as well.

This investigation presents the procedures used to obtain the activation energy of a carbon felt insulator, called KFA5, along with a conceptual evaluation of the FTPS thermal response model with new activation energy values substituted in. Inserting experimentally-derived values for activation energy into the COMSOL thermal response model is expected to help correlate FTPS thermal model temperature predictions to measured temperatures from arc-jet experimental data by providing another degree-of-freedom for adjustment.

TGA testing was performed on carbon felt samples using a TA Instruments TGA Model Q5000IR, referred to as the TA Q5000IR from here forward. This highly capable testing apparatus is owned by Dr. Lisa Detter-Hoskin's Materials Analysis Center (MAC) in Georgia Institute of Technology's School of Materials Science and Engineering. An image of the TA Q5000IR is shown below in Figure 2.

Figure 2. TA Instruments TGA Model Q5000IR [15]

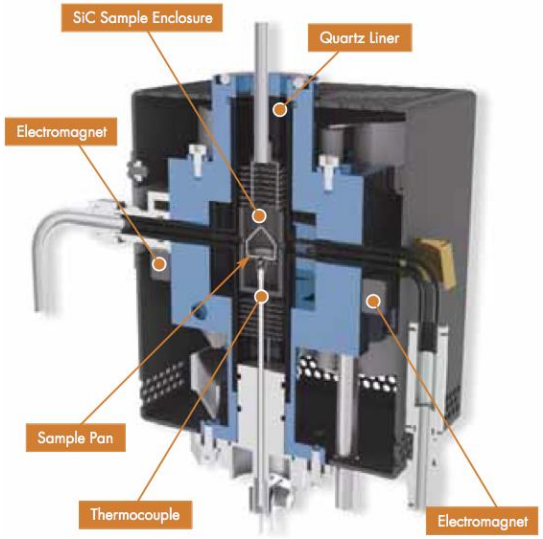

Figure 3. TA Q5000IR Furnace Cross Section [15]

The TA Q5000IR is a relatively new instrument that has many advanced capabilities. The "IR" refers to infrared furnace heating provided by internal lamps. Using infrared heating allows for high precision of temperature profiles and near instantaneous equilibration to specified temperatures for isothermal testing. In addition to having a high precision balance to measure weight loss as a function of time, the TA Q5000IR also has the ability to run a pre-defined sequence automatically. For each TGA run, the user is able to specify a detailed series of events that is carried out in a prescribed order. Also, the instrument has the capability to transfer samples automatically using a rotating carousel. These capabilities were utilized and appreciated by the analyst in the following tests. Figure 3 above shows a cross sectional diagram of the furnace itself. It is important to note that the gas flows across the sample in the direction parallel to the ground. This eliminates the need to run a "blank" run to correct for buoyancy as one might have to do for a furnace with a vertical sample gas flow.

The focus of this study is on the mass decomposition response of a carbon felt, KFA5, exposed to zero-moisture Air for many Standard and Modulated TGA experiments. This section will briefly outline the experimental procedure used to complete each TGA run, followed by an initial discussion of the resulting weight-loss curves. Figure Set 4 provides the reader with a detailed account of sample preparation and loading procedures into the TA Q5000IR furnace.

The order of succession in Figure Set 4 starts in the upper left corner and continues from left to right, row by row, until the final image in the bottom right corner. Each carbon felt sample was cored directly from a larger disk of carbon felt material from the manufacturer. Using the brass, T-shaped "coring" device, cylindrical cores of samples were sliced out of the larger piece, shown in the top-left corner. Once the samples were cut, they were placed into Alumina pans on the sample carousel and loaded into the TA Q5000IR furnace. Once closed, the furnace is heated to a temperature of 600˚C at a specified heating rate, shown in the bottom-right corner.

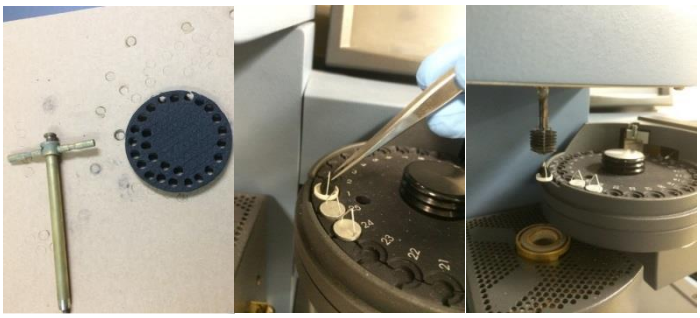

Figure Set 4. Sample Loading Procedure of KFA5 Samples into TA Q5000IR

Figure Set 5 gives the reader insight into maintenance tasks performed between rounds of testing. The following three images show how debris was routinely cleaned from the alumina pans through a prescribed bake out procedure in a muffle furnace.

Figure Set 5. TA Q5000IR Alumina Pan Cleaning Procedure

Before each TGA run, the analyst turned to the TA software to create a run program for the TA Q5000IR. The flow rates of gas through the instrument were programmed first, sending a flow rate of 10 ml/min of Argon to the balance and a flow rate of 25 ml/min of zero-moisture Air to the sample. Each TGA run shown in this study followed identical run sequences. Each run sequence contained two distinct stages, which will be referred to as the moisture removal stage and the dynamic stage. The objective of the moisture removal stage was to drive all excess moisture out of the furnace and the sample before ramping up to the specified dynamic run sequence. The moisture removal stage took approximately 40 minutes, resulting in a dry sample and a dry environment inside the furnace at a temperature of approximately 30°C. The dynamic stage, followed directly after, consisted of a linear ramp to a final temperature of 600°C for Standard TGA or sinusoidal ramp to a final temperature of 600°C for Modulated TGA.

IV. Calculation of Activation Energy Using the Arrhenius Equation

As mentioned above, a series of dynamic TGA experiments were performed at various heating rates for a carbon felt sample. The goal of these tests was to further characterize its decomposition process to be simulated with a finite-element thermal model. Two different types of TGA tests were performed to obtain the activation energy. The first type of TGA experiment, referred to as a Standard TGA, and requires exposing the sample to 4 different heating rates to obtain the activation energy. In this study, the analyst chose to subject samples of KFA5 carbon felt to heating rates of 2°C/min, 5 °C/min, 8 °C/min, and 10 °C/min in a zero-moisture Air environment. The second TGA test profile, referred to as a Modulated TGA, exposes the sample to a sinusoidal variation about a constant heat rate profile. The heat rate chosen for this study was 2°C/min, the modulation period was chosen to be 200 seconds, and amplitude was chosen to be ± 5 °C in a zero-moisture Air environment. The advantage of Modulated TGA is the obtainment of the activation energy of a sample after only one experiment. The following discussion will introduce the reader to the basic Arrhenius relation framework and show the governing equations used in Standard and Modulated TGA to calculate the sample activation energy.

A. General Arrhenius Formulation for TGA Testing

To model weight loss in a material as a function of temperature, the Arrhenius equation is commonly used, as shown in Equation 3.

$$k = A\, e^{\left(-\frac{E_a}{RT}\right)} \tag{3}$$

To create an accurate simulation of decomposition, one must obtain the activation energy of the tested carbon felt. The following step-by-step procedure will show how Equation 3 is used to obtain a general expression for the rate of conversion as a function of kinetic parameters. Equation 4 relates the degree of conversion, "α", to standard quantities obtained through TGA testing, such as initial sample weight, "W_o", and sample weight as a function of time, "W_t". Equation 5 shows a general expression for the reaction rate, "$\frac{d\propto}{dt}$", in terms of the rate constant, "k(T)", and the kinetic expression, "f(α)". Equation 6 is the familiar Arrhenius equation as a function of temperature. Equation 7 shows that an nth order kinetic expression was chosen for this study. For simplicity, the reactions discussed in this study are considered first-order reactions, where n = 1. Finally, Equation 8 displays the reaction rate in terms of kinetic parameters.

$$\propto = \frac{W_0 - W_t}{W_0} \tag{4}$$

$$\frac{d\propto}{dt} = k(T)\, f(\propto) \tag{5}$$

$$k(T) = A\, exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

$$f(\propto) = (1-\propto)^n \tag{7}$$

$$\frac{d\propto}{dt} = A\, exp\left(-\frac{E_a}{RT}\right)(1-\propto)^n \tag{8}$$

B. Standard TGA Method Summary

Decomposition kinetics for the Standard Ramp method are modeled using the Ozawa/Flynn/Wall method outlined in the ASTM Standard Test Method E1641-15 [3]. The following equations show the majority of the accepted Ozawa/Flynn/Wall method of calculating activation energy factor from dynamic TGA data at four different heating rates for first order reactions. Please refer to the ASTM method for more details about the calculation method. Figure 6 shows four sample TGA curves at different heating rates, while Figure 7 shows the resulting Arrhenius plot one can create from Standard TGA data.

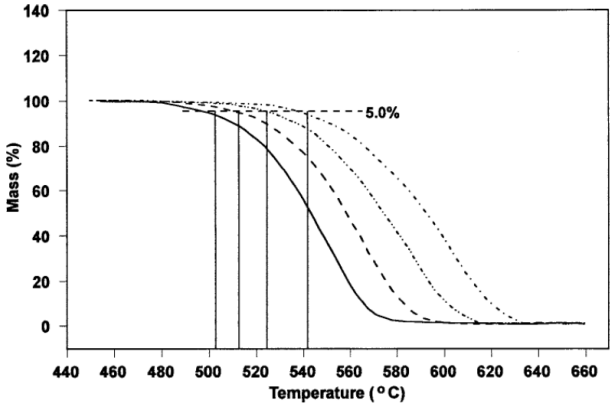

Figure 6. Sample Dynamic TGA Curves [3]

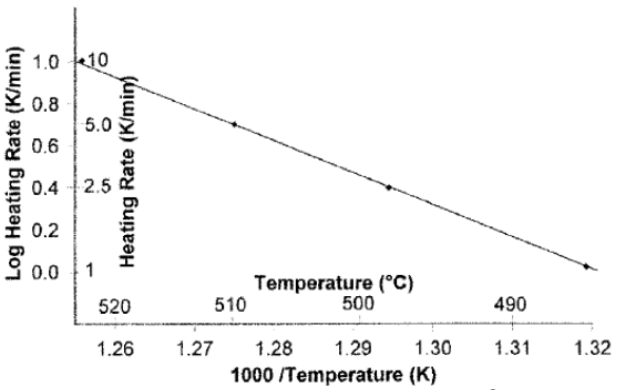

Figure 7. Sample Arrhenius Plot [3]

The slope of the Arrhenius plot is a key quantity used to obtain the activation energy. Equation 9 shows how one can obtain the slope of the Arrhenius plot, referred to as "m". After obtaining this slope, and iterative procedure begins to converge on the activation energy. The Ozawa/Flynn/Wall method outlined in ASTM E1641-15 provides a lookup table to help the analyst complete this iteration procedure by hand. The quantities referred to as "a", "b", and "E/RT" are all values listed in this table. Equation 10 shows how one calculates the initial guess for activation energy using the "b" parameter. Equation 11 shows how another value for activation energy is calculated, referred to as "E_{it}". The

calculations in Equations 10 and 11 are repeated until convergence is achieved. Finally, the converged value for activation energy is used to calculate the pre-exponential factor shown in Equation 12.

$$m = \frac{\Delta(ln\,\beta)}{\Delta\left(\frac{1}{T}\right)} \tag{9}$$

$$E_a = -\left(\frac{R}{b}\right)\frac{\Delta(ln\,\beta)}{\Delta\left(\frac{1}{T}\right)} \tag{10}$$

$$E_{it} = \frac{E_a}{RT} \tag{11}$$

$$A = \frac{\beta\, R\, \ln(1-\propto)\, 10^a}{E_a} \tag{12}$$

C. Modulated Ramp TGA Test Method

The Modulated TGA method was championed by researchers at TA instruments as a way to obtain the decomposition kinetics of a sample with less experimental effort. This method produces an "…oscillatory response in the rate of weight loss. Deconvolution of this response, using real-time discrete Fourier transformation (DFT), leads to the desired kinetic parameters (E and A)" [16]. Figure 8 below shows an example of a modulated temperature profile. The green line represents the weight-loss curve as a function of time while the magenta curve shows the corresponding modulated temperature profile oscillates about a constant heating rate of 2°C/min.

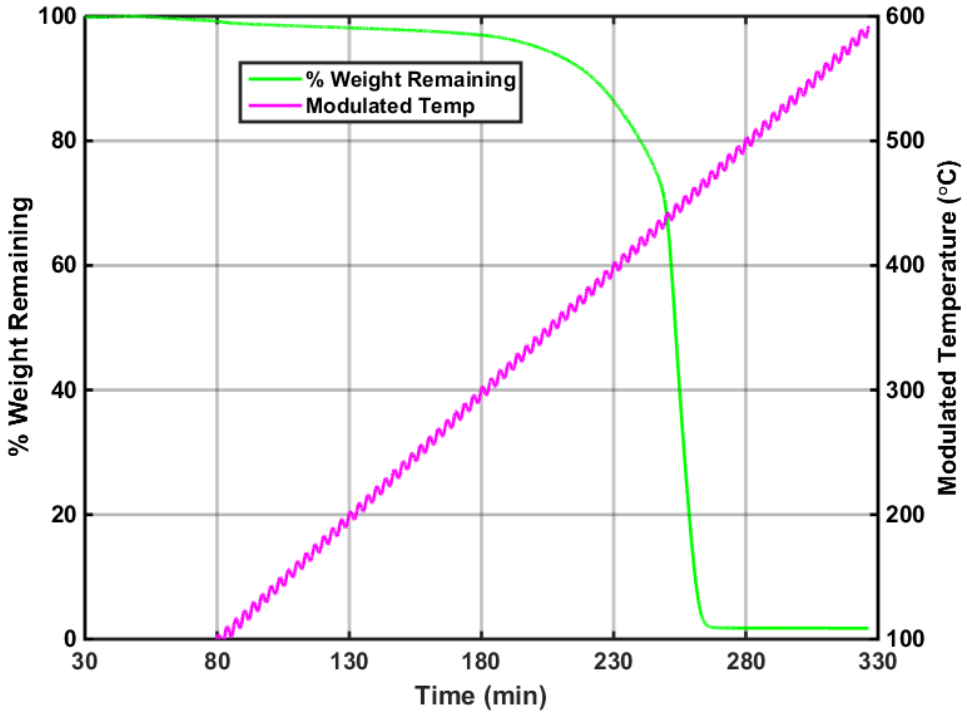

Figure 8. Sample Modulated TGA Test of KFA5 in zero-moisture Air at 2 °C/min

ASTM Standard Test Method E2958 – 14 outlines the accepted testing procedure for a Modulated TGA experiment, which has been adhered to closely in the following analysis. Using slightly different expressions, Equations 13 – 15 briefly show how the calculation is performed to obtain the activation energy and the pre-exponential factor of a sample exposed to a single modulated ramp TGA test. In these equations, "T" represents the average temperature, "A_{MP}" represents the temperature half-amplitude, and "L" represents the amplitude of the natural log of the rate of weight change. Please refer to included references for more information about these equations and related derivations [10,11].

$$E_a = \frac{R(T^2 - A_{MP}{}^2)L}{2A_{MP}} \tag{13}$$

$$\text{where } L = \ln\left(\frac{d\propto_p/dt}{d\propto_v/dt}\right) \tag{14}$$

$$\ln A = \ln\left(\frac{d\propto}{1-\propto}\right) + \frac{E_a}{RT} \tag{15}$$

D. Number of TGA Tests Required to Obtain Adequate Activation Energy Distribution

As mentioned previously, thermophysical properties can be measured with confidence using traditional experimental methods, but characterization of property uncertainties is particularly challenging. The following methodology uses experimental repetition to establish the ± 3σ uncertainty bounds for a specific material property to enable future probabilistic analysis methods.

In this investigation, the probability distribution of activation energy is approximated using two types of TGA testing. The confidence level describes the percentage of a distribution that fits between a specified confidence interval. As the number of total TGA experiments increases (including repetitions), the percentage of the t-distribution within the ± 3σ uncertainty bounds, or confidence level, increases. The left portion of Figure 9 compares a normal distribution to two t-distributions with varying degrees of freedom. Degrees of Freedom (DoF) were varied between 1 and 10 for t-distributions to find the minimum degrees of freedom required to exceed the 95% confidence level between ± 3σ uncertainty bounds. As shown in the right portion of Figure 9, a minimum of 4 DoF's, or 5 experiments, are required to exceed a confidence level of 95%.

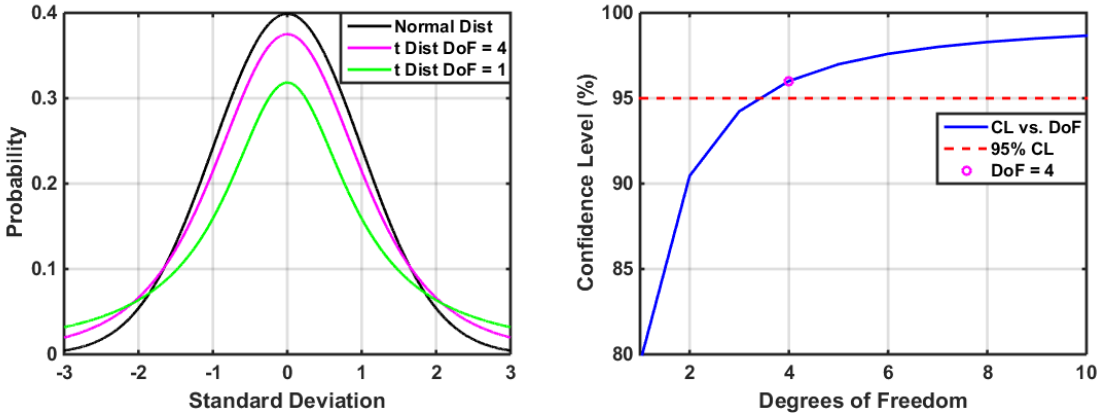

Figure 9: Sample t-Distributions vs. Normal Distribution (Left) and Degrees of Freedom Required for a t-Distribution to Exceed a Confidence Level of 95% Between ± 3σ (Right)

These results suggest two important conclusions: a t-distribution with a 95% confidence level between ± 3σ closely approximates a normal distribution and 5 experiments are required at each TGA testing condition to obtain this t-distribution for activation energy. After completing 5 TGA tests at each condition for Standard and Modulated TGA, the analyst is able to obtain 5 independent determinations of activation energy for each method. The sample mean and sample variance for activation energy can be calculated using Equation 16 and Equation 17.

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{16}$$

$$s^2 = \frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2 \tag{17}$$

The accompanying distributions of activation energy for Standard and Modulated TGA methods are shown in the following section along with other pertinent results.

V. Results

After calibrating the TGA instrument to run at a heating rates of 2, 5, 8, and 10 °C/min, the analyst was able to complete a rigorous testing TGA experimental campaign using Standard and Modulated TGA methods. As described

above, a total of 5 tests were completed at each TGA test condition so an adequate t-distribution of activation energy can be obtained with each method. The following figures show sample results for both TGA methods for KFA5 carbon felt in zero-moisture air to help the reader understand each step in the analysis process.

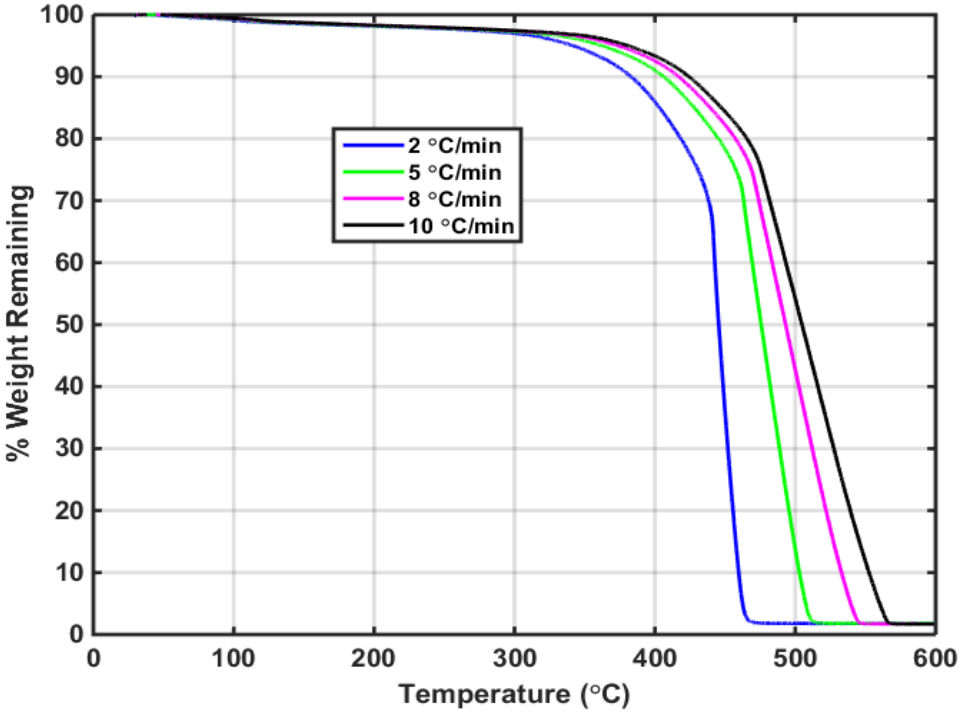

Figure 10. Sample Set of 4 Standard TGA Tests of KFA5 in zero-moisture Air at 2, 5, 8, and 10 °C/min

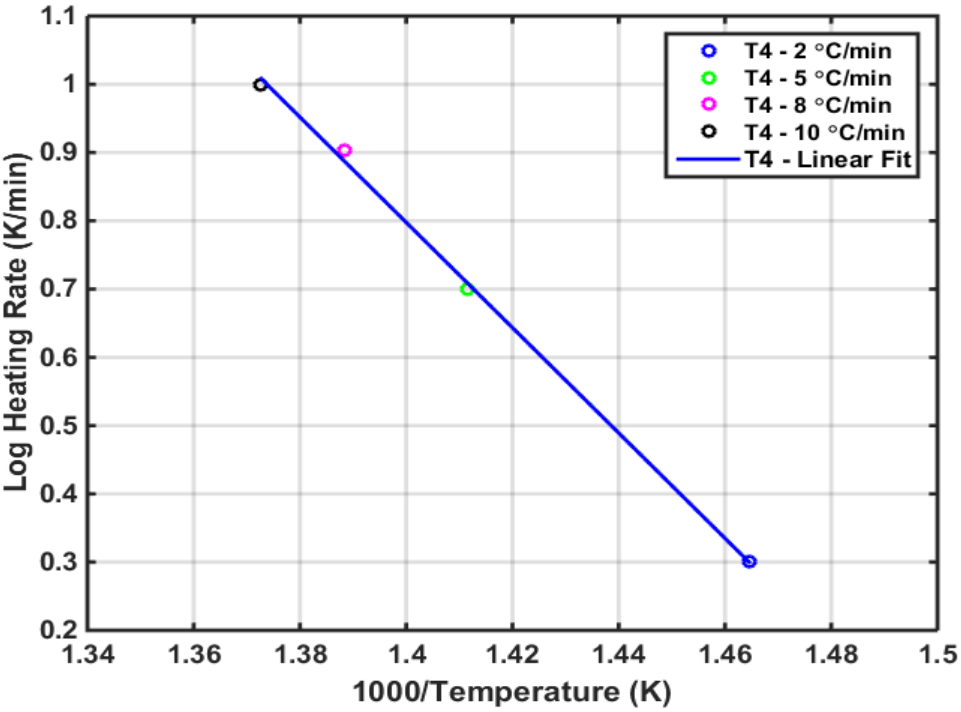

Figure 11. Sample Arrhenius Plot for a Set of 4 Standard TGA Tests of KFA5 in zero-moisture Air at 2, 5, 8, and 10 °C/min with a Linear Fit

Limited portions of the entire data set are shown for brevity but can be obtained upon request. In this study, a Standard TGA test increases the temperature of the sample's environment from ambient to 600°C at a constant heating rate, creating a linear temperature "ramp" profile. Figure 10 shows the weight loss profile for a family of 4 Standard TGA tests at heating rates of 2, 5, 8, and 10°C/min as a function of temperature. While the test was performed up to 600°C, this investigation focuses on finding the activation energy for the region of constant conversion of the decomposition event occurs at a weight remaining percentage of 83% and a temperature of approximately 408°C.

After completing 5 sets of Standard TGA runs at heating rates of 2, 5, 8, and 10°C/min, the analyst had gathered enough data to measure activation energy with 5 independent measurements according to the ASTM E1641-15 standard. Accordingly, 5 Arrhenius plots were created. One of these plots is shown in Figure 11 below for the KFA5 disk referred to as "T4". The linear fit is fairly accurate, showing that the Arrhenius relation can accurately capture decomposition for this material.

As mentioned, a Modulated TGA test creates a sinusoidal temperature modulation about a standard linear temperature ramp. The precise controllability of the TA Q5000IR TGA furnace allows for this complex heating profile to be programmed with ease. Figure 8 shows a typical modulated TGA sinusoidal temperature profile. Figure 12 shows weight loss curves as a function of temperature, along with their corresponding activation energy signals, for the set of 5 Modulated TGA tests performed in zero-moisture Air. Resulting activation energy was obtained using the calculations in the previous section as prescribed by ASTM E2958 – 14. A first order reaction is assumed at the region of constant conversion of the decomposition event occurring at a weight remaining percentage of 83% and a temperature of approximately 408°C.

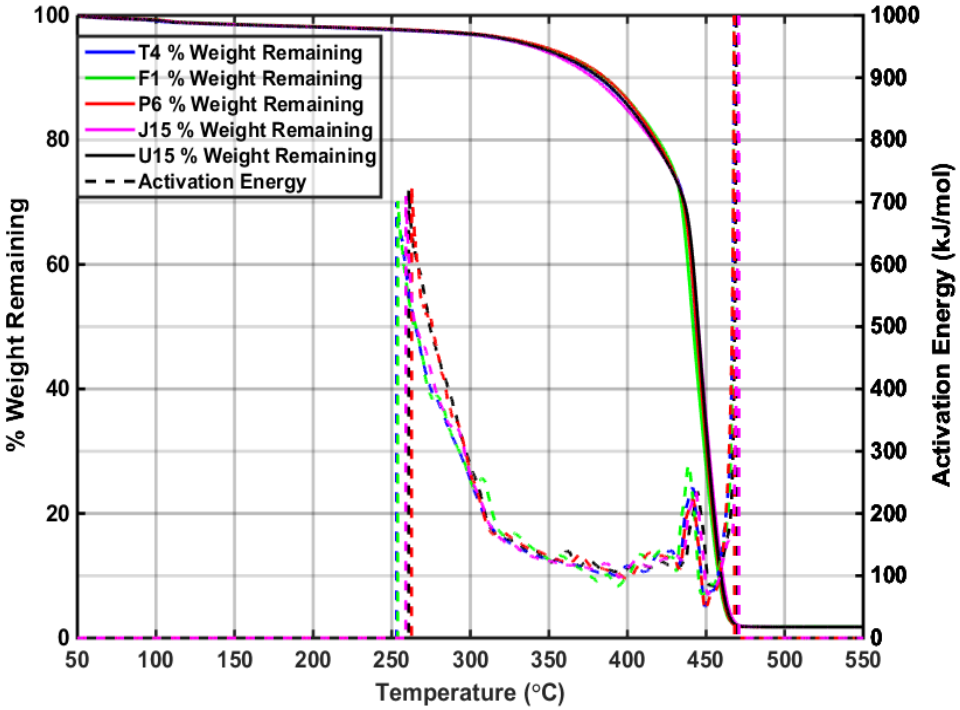

Figure 12. 5 Sample Modulated TGA Tests of KFA5 in zero-moisture Air at 2 °C/min

After completing the required TGA experimentation and activation energy calculations for both methods, the final t-distributions could be obtained. Figure 13 below shows both distributions in the same plot to show scale. Figure 14 shows the corresponding ± 3 standard deviation bounds for each t-distribution. The mean and standard deviation of the Standard TGA t-distribution is approximately 131.56 kJ/mol and 5.79 kJ/mol, respectively. The mean and standard deviation of the Modulated TGA t-distribution is approximately 121.16 kJ/mol and 8.66 kJ/mol, respectively.

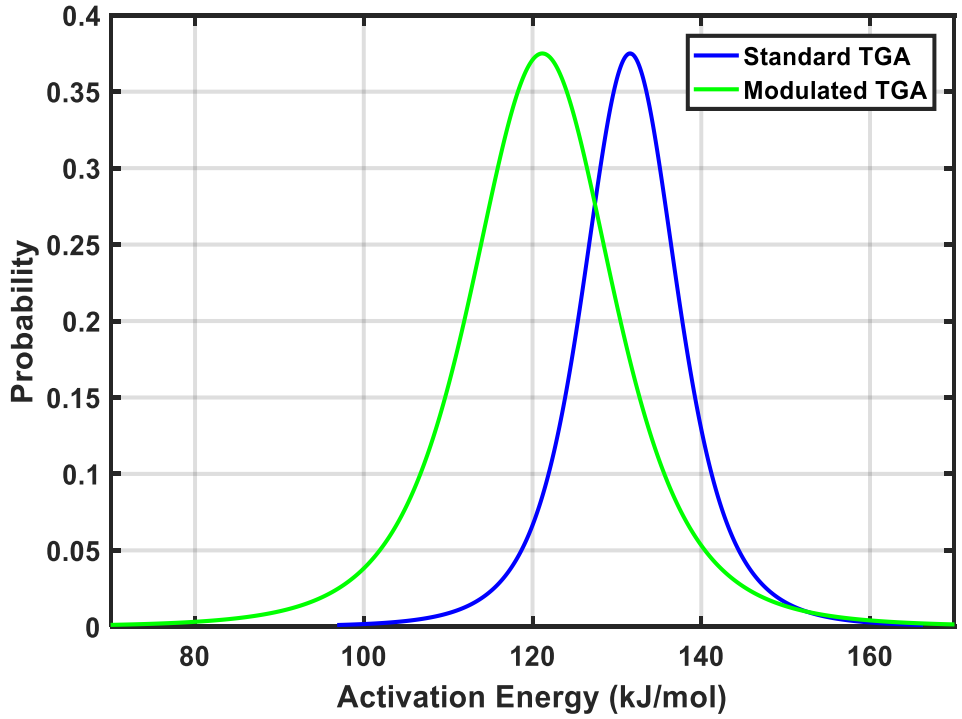

Figure 13. KFA5 Activation Energy t-Distributions Obtained from Standard and Modulated TGA Testing

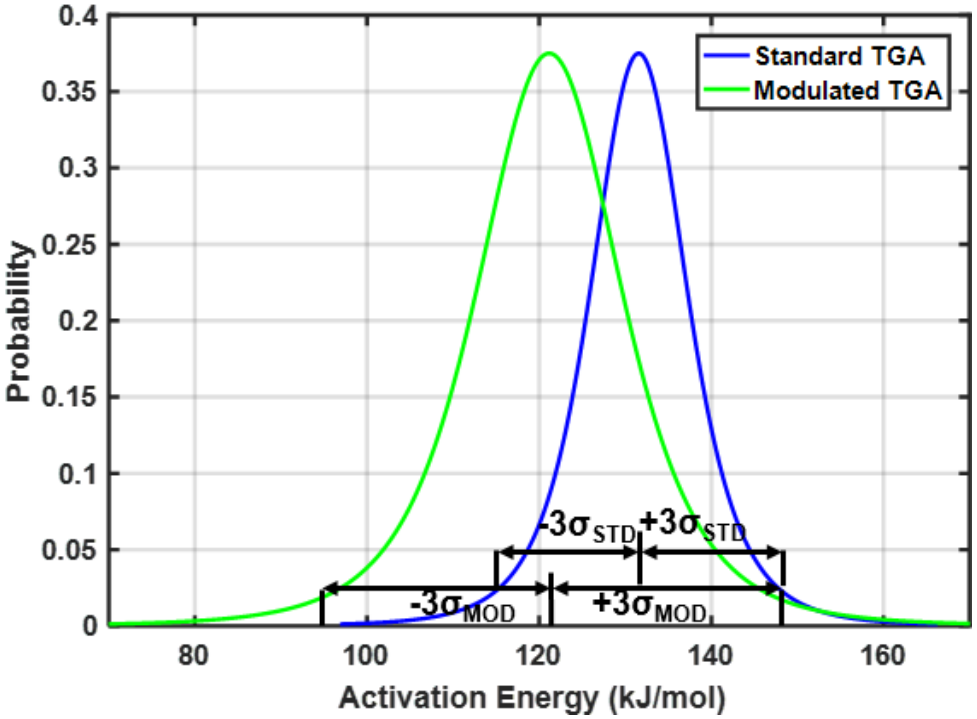

Figure 14. Location of ± 3σ Uncertainty Bounds on KFA5 Activation Energy t-Distributions Obtained from Standard and Modulated TGA Testing

There are a few interesting things to note here. The mean of activation energy for both distributions are fairly close together show excellent agreement. The mean obtained from the Standard TGA method is slightly higher by

approximately 10 kJ/mol, which may be contributed to the calculation procedure averaging results over 4 heating rates (2, 5, 8, and 10 °C/min) that are greater than or equal to the heating rate used for Modulated TGA (2 °C/min).

One can also see that the standard deviation of activation energy is slightly higher for Modulated TGA than that of Standard TGA. Accepted procedure for Modulated TGA instructs the analyst to establish the activation energy in the region of constant conversion, which should be apparent as a "valley" in the activation energy signal, signifying the point where the decomposition event is proceeding at a constant rate. Figure 12 shows the stable "valley" for the activation energy signals obtained from Modulated TGA occurs just above 400 ° C. This finding shows strong agreement with the region of constant conversion obtained from Standard TGA at 408 ° C, and therefore, strong agreement between both methods. It is important to note that the weight loss curves in Figure 12 begin to span a wider range as each sample enters the region of constant conversion, which is likely due to manufacturing variation between samples. This wider range is passed on to the corresponding activation energy signals, which may be the main reason why the standard deviation of Modulated TGA exceeds that of Standard TGA.

The resulting mean activation energies from Standard and Modulated TGA methods, mentioned above, were input into a COMSOL thermal response model simulating Run 2659 in the Boeing LCAT arc-jet facility. The measured temperature profile as a function of time was placed as a boundary condition at TC 2 and the physical processes simulated within the insulation stack of the thermal response model predict temperatures at deeper thermocouple locations (TC 3, TC 4, TC 5, and TC 6). The primary reason for placing this TC Driver boundary condition at TC 2 was to focus on the improvement of temperature predictions between layers of insulation, which are most highly effected by changing the insulator decomposition model.

The resulting accuracy of temperature profile predictions after replacing the old estimated activation energy with a new value determined from experimentation. Figure 15 shows the nominal FTPS thermal model predictions with the original two-reaction decomposition model, created by Sullivan and Baker, where prediction lines (dashes) are compared with experimentally measured temperatures (solid lines) during the arc-jet run. Changes made to this decomposition model feature an updated activation energy and a corresponding updated pre-exponential factor. All other decomposition parameters in the model remained the same, including a reaction order of 1 for simplicity and total weight lost after full decomposition of 97% according to TGA experimental data.

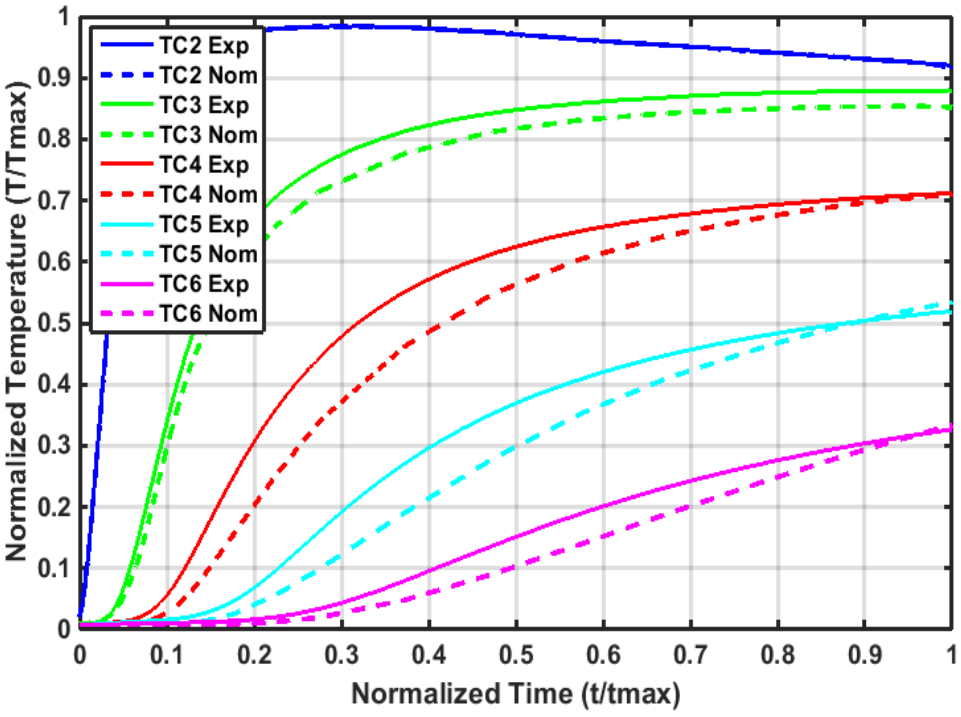

Figure 15. Initial FTPS Thermal Response Model Comparison Between Normalized Arc-Jet Thermocouple Measurements at Depth (Lines) and Nominal Predictions (Dashes) for KFA5 Run 2659

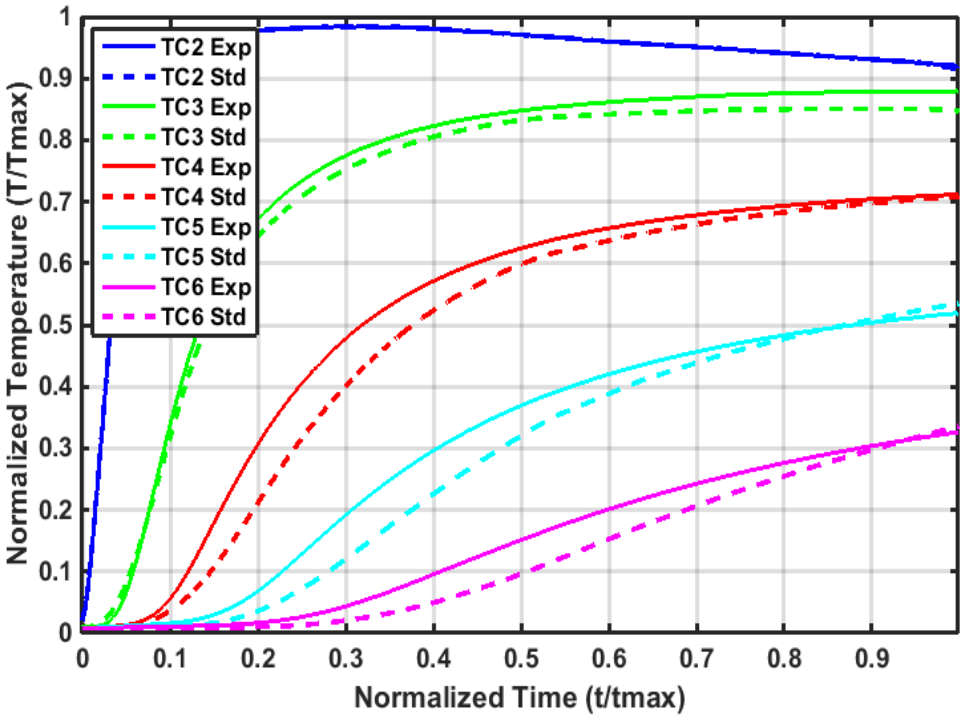

Figure 16. Improved FTPS Thermal Response Model Comparison Between Normalized Arc-Jet Thermocouple Measurements at Depth (Lines) and Improved Predictions (Dashes) Using Activation Energy Determined from Standard TGA for KFA5 Run 2659

After inputting the mean values for activation energy obtained from the Standard TGA method, the resulting bondline predictions were assessed in Figure 16. This plot shows the thermal response model predictions at depth after inputting the mean activation energy value of 131.56 kJ/mol obtained from Standard TGA. Very similar results were obtained if the activation energy was changed to the mean activation energy value of 121.16 kJ/mol from Modulated TGA. Figure 16 shows significantly improved predictions for TC 3, TC 4, and TC 5 and a similar prediction for the bondline (TC 6) temperature. This is an encouraging result, and further probabilistic analysis will leverage the uncertainty distributions for activation energy obtained in this study to investigate the sensitivity of the thermal response model to variations between the determined ±3σ values.

VI. Conclusions and Future Work

Two types of TGA tests were performed on a carbon felt insulator, called KFA5, to obtain its activation energy. After modeling the sample decomposition behavior with the Arrhenius equation, the analyst was able to calculate the mean and uncertainty of activation energy of the carbon felt using the analysis procedures described above. The mean and standard deviation of the activation energy t-distribution obtained from Standard TGA is approximately 131.56 kJ/mol and 5.79 kJ/mol, respectively. The mean and standard deviation of the activation energy t-distribution obtained from Modulated TGA is approximately 121.16 kJ/mol and 8.66 kJ/mol, respectively. Knowledge of these quantities furthers the understanding of how carbon felt behaves at high temperatures in an oxidative environment. The mean and standard deviation values of activation energy t-distributions for both methods show excellent agreement, which suggests that Modulated TGA should be pursued as a technique to obtain similar activation energy measurements as Standard TGA while saving 75% of the experimental effort.

Preliminary thermal model response results with updated values for the activation energy and pre-exponential factor show great promise for the new decomposition model. The analyst was able to input calculated activation energy values to show significant improvement in the thermal response model's temperature predictions at thermocouple locations between layers of FTPS insulation. Future work includes considering other decomposition parameters in order to improve the current decomposition model even further and probabilistic analysis to characterize the sensitivity of thermal model temperature predictions to variation in activation energy. In the future, the thermal model can be validated and integrated into a probabilistic heat shield sizing process to avoid unnecessarily "over-margining" heat shield mass and thickness.

Acknowledgments

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