Thermogravimetric Analysis of Flexible Thermal Protection Systems for Thermal Response Modeling

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A multi-layered, Flexible Thermal Protection System (FTPS) heatshield configuration layup has undergone ground-based testing in an arc-jet facility to simulate heating generated during atmospheric entry. Thermogravimetric Analysis (TGA) was then performed on virgin samples of an aerogel felt insulator from this same FTPS layup configuration to characterize decomposition by obtaining its activation energy. Experiments were performed in an inert environment for Standard TGA and Modulated TGA methods using a TA Instruments Q5000IR experimental apparatus. Limited TGA testing resources in the past have resulted in rough approximations of activation energy of FTPS materials with little knowledge of uncertainty. A rigorous TGA testing campaign is set forth to experimentally determine the activation energy and its corresponding uncertainty for samples of aerogel felt to increase knowledge of the sample's decomposition process. The activation energy and corresponding uncertainty obtained from both Standard TGA and Modulated TGA methods are compared. The activation energy from each method are inserted into an existing thermal response model that simulates heat transfer between layers of a FTPS layup. The resulting temperature traces are compared to thermocouple temperature data recorded during ground-based arc-jet testing to conceptually observe simulation accuracy. Recommendations for future testing and analysis are then summarized.

Nomenclature

β_D	=	Ballistic coefficient
m_D	=	Entry vehicle mass
C_D	=	Drag coefficient
A_D	=	Entry vehicle drag area
k	=	Rate constant
A	=	Arrhenius pre-exponential factor
E_a	=	Arrhenius activation energy
R	=	Gas constant
T	=	Temperature
α	=	Degree of conversion
W_0	=	Initial TGA sample weight
W_t	=	TGA sample weight at time "t"
$\frac{d\alpha}{dt}$	=	Rate of conversion
$k(T)$	=	Rate constant at temperature "T"
$f(\alpha)$	=	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 E1641-15
b	=	Table lookup value from ASTM E1641-15

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A_{MP} = Temperature half-amplitude for modulated TGA testing
L = Amplitude of the natural log of the rate of weight change
$\bar{x}$ = 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 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 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. Previous missions laid the ground work for rigid aeroshells [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 device that produces a large drag area, and as a result, reduces the entry ballistic coefficient shown in Equation 1 below.

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

Ballistic coefficient is a function of the vehicle mass, drag coefficient, and reference area. HIADs reduce the vehicle's ballistic coefficient with a substantial increase in drag area while adding minimal mass. A lower ballistic coefficient allows the vehicle to decelerate higher in the atmosphere, decreasing the peak heat rate experienced by the HIAD TPS. Unlike rigid Thermal Protection Systems (TPS), HIAD TPS must remain flexible to allow for packaging within the confines of a launch vehicle shroud prior to withstanding aerothermal loading. HIAD TPS is referred to as Flexible TPS, or FTPS, from here forward. With the advancement of fabric and thin-film materials, FTPS material development for HIADs may result in a means to increase mission capabilities. 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.

The flight readiness of FTPS materials has been increased through several development efforts. The material that is the focus of this paper is an aerogel felt called Pyrogel 2250 created by Aspen Aerogels. This material serves as an insulator for a wide variety of applications. With a low thermal conductivity, this aerogel felt has proven to be a viable candidate insulator for the HIAD FTPS [3].

In order to choose an optimum FTPS configuration, it is desirable to create a simulation of the temperature profiles that the FTPS will experience upon entry. One way to replicate the high temperatures of reentry is to test samples in an arc-jet facility, which has been completed several times. From these arc-jet tests, one can measure the temperatures within each layer of FTPS to gain a deeper understanding of its internal physical processes. To simulate these physical processes, Dr. Roy Sullivan and Eric Baker at NASA Glenn Research Center have developed a detailed thermal model using COMOSL Multi-Physics software.

Creating a thermal model that accurately predicts temperatures within an FTPS layup requires detailed understanding of the physical processes and thermal properties associated with each material layer. The first stage in developing a thermal model is to ensure all the pertinent physical processes are included and all thermal properties have been verified through property testing over the appropriate temperature and pressure range of interest. Next, the model must be validated by comparing arc-jet test temperature data to the one-dimensional (1D) thermal response of the FTPS COMSOL model. Finally, the performance of the COMSOL model is evaluated based on how closely the 1D model temperature predictions match the arc-jet thermocouple temperature data for each thermocouple.

The objective of this research is to continue thermal model development by characterizing the decomposition behavior of an aerogel felt insulator. The Arrhenius equation has been chosen to model the decomposition behavior, which is shown in Equation 2 below [4].

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

The Arrhenius equation defines the approximate relationship between the rate constant, "k", and the activation energy, "E_a", for a material. It also defines "A" as the pre-exponential factor, "R" as the universal gas constant, and "T" as the temperature for each TGA run. In order to fully define the Arrhenius equation for a material, one needs to first obtain the rate constants for several TGA runs and then extract the activation energy from an Arrhenius plot. This calculation process is described in great detail below. The specific type of TGA test methods performed in this study are dynamic methods, and each aerogel felt sample is being tested in Helium to capture decomposition behavior. The following study assumes that decomposition can be accurately modeled using the Arrhenius equation and calculates the resulting activation energy of the aerogel felt.

Generally, the primary objective of a TGA test campaign is to gain a deeper understanding of a material's decomposition so it can be more accurately simulated in a thermal response model. TGA testing has been used in the past to obtain a decomposing material's activation energy, which is the minimum amount of energy to be present for a mass decomposition process to occur. The activation energy of decomposing FTPS insulators will be determined using two different methods: the Standard TGA test method (Ozawa-Flynn-Wall) and a recently developed Modulated TGA test method. A material testing methodology will obtain the approximate probability distribution of activation energy using both TGA test methods. The probability distribution of activation energy will provide additional knowledge used to investigate decomposition sensitivities during thermal response model Monte Carlo simulations.

A TGA test 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. To obtain the activation energy of a TPS material using TGA testing, previous work follows the Ozawa-Flynn-Wall method, initially developed in 1966[5]. In this work, the Arrhenius relation is used to model insulator mass decomposition[6, 7, 8]. The first objective is to find the activation energy of decomposing FTPS insulators using TGA testing. This activation energy is inserted into a thermal 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 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[9, 10]. In this investigation, this method 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 normally distributed activation energies, as described by the Distributed Activation Energy Model (DAEM)[11, 12, 13]. If the analyst makes this common assumption, he may approximate the activation energy with a 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 an aerogel felt insulator called Pyrogel 2250 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.

II. Motivation for TGA Testing of FTPS Materials to Improve Current Thermal Model Predictions

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 Generation 1 Layup 1

(Gen 1 L1), containing Nextel BF-20 as the outer fabric, Aspen Aerogel's Pyrogel 2250 as the aerogel felt insulator, and Aluminized Kapton laminated to Kevlar (AKK) as the gas barrier. Additionally, a thermocouple (TC) temperature measurement device is placed between each FTPS layer to obtain experimental temperature measurements at multiple depths during arc-jet testing.

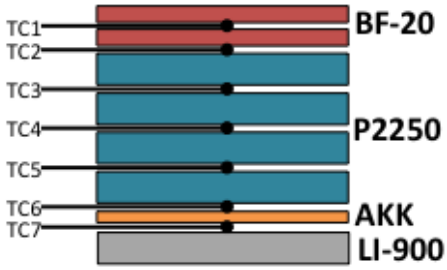

Figure 1. Generation 1 Layup 1 (Gen 1 L1 - BF-20, Pyrogel 2250, AKK) [14]

Using the COMSOL Multi-Physics software framework, the many physical processes experienced during arc-jet testing have been combined within the cohesive thermal model mentioned above, which includes the governing equations for conservation of mass, momentum, and energy. Southern Research Institute (SRI) successfully performed various experiments on FTPS material samples to obtain measured values of the thermophysical properties. The material property databases for virgin and charred FTPS layers are input into the model in tabular form. Additionally, these properties are input as a function of temperature and pressure. Performing FTPS testing in the Boeing LCAT facility helps analysts gain a deeper understanding of the complex thermal response of these materials and obtain thermocouple measurements from which the mathematical model can be compared.

After performing experimental testing, it was shown that as Pyrogel materials are heated to the region between 375℃ and 600℃, they begin to shrink in size while decomposing and emitting gases as a result of pyrolysis. The decomposition and pyrolysis gas flow are energy absorbing mechanisms that potentially lower the temperatures through a FTPS layup [15]. Pyrogel 2250 exhibits similar decomposition and pyrolysis behavior, which must be accounted for in the thermal model before accurate temperature predictions can be made. Complex phenomena such as the potential for boundary layer flow through the porous outer fabric and insulation layers and pyrolysis gas flow to the surface through these layers have been added to the model for higher fidelity. Understanding the decomposition of Pyrogel 2250 as a function of temperature, pressure, and time is crucial to obtaining successful temperature predictions. The thermal model has successfully modeled convection, surface radiation, and solid/gas conduction through FTPS layers. The current model includes the physics to properly describe insulator mass decomposition using the Arrhenius Equation [4].

Preliminary results indicate that the thermal model consistently predicts thermocouple temperatures with discrepancies when compared with measured arc-jet thermocouple data. Temperature predictions for the bondline interface, which sits between the bottom insulator layer and the gas barrier, are consistently higher than temperature measurements. While this conservative estimate leads to a "safer" FTPS design, these predictions could produce an FTPS mass beyond requirements, which adds unnecessary to mass and ultimately decreases usable payload mass. Once the thermal model can be validated with accurate thermocouple temperature predictions, the model can be integrated into a probabilistic heat shield sizing process to avoid unnecessarily "over-margining" heat shield thickness. In order to minimize the thermal model's temperature prediction gap and progress towards model validation, a TGA testing campaign has been performed to gain a deeper understanding of the mass decomposition process and gather more data to accurately calculate Arrhenius weight loss constants for thermal modeling.

Thermocouples were placed between each FTPS layer during arc-jet testing to obtain temperature vs. time profile measurements 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 profile predictions at the same arc-jet testing depths. 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 accepting arc-jet measured heat flux as the driving boundary condition on the top surface of Gen 1 L1 and solving for temperature predictions 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, albeit with some uncertainty, using traditional methods. Generally, material property testing is limited in range in both temperature and pressure and is also obtained

at discrete points. Moreover, the arc-jet test conditions have the potential of producing temperatures that exceed the bounds of collected data. In these cases, the data in the thermal model is extrapolated to provide a contiguous set of data. The capability does exist to make property measurements in high temperature regions around 2000 °C. In general, the uncertainty in the measurement grows as temperature increases. Therefore, the primary motivation to perform TGA testing is to minimize COMSOL thermal model temperature prediction discrepancies by providing a more accurate portrayal of insulator decomposition. Testing objectives include obtaining the Arrhenius kinetic parameters to describe Pyrogel 2250 decomposition, along with many repeated testing to fully characterize uncertainty in these measured properties.

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

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 the Georgia Tech Research Institute's (GTRI) Material Analysis Center (MAC), run by Dr. Lisa Detter-Hoskin and Erin Prowett. An image of the TA Q5000IR is shown below in Figure 2.

Figure 2. TA Instruments TGA Model Q5000IR [16]

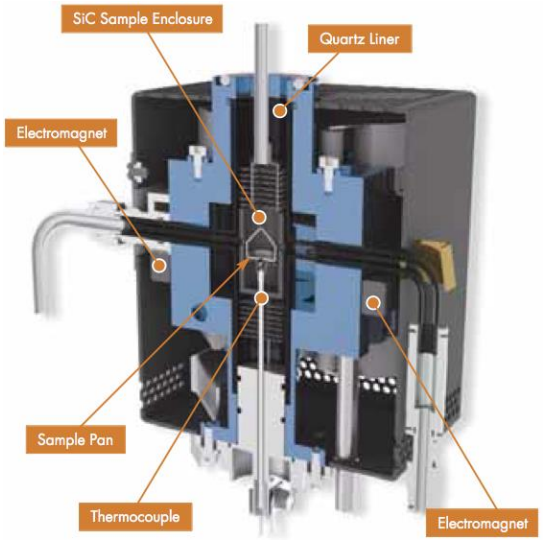

Figure 3. TA Q5000IR Furnace Cross Section [16]

The TA Q5000IR is a relatively new TGA instrument that has many advanced capabilities. The "IR" in its name stands for infrared, which refers to the method at which the furnace is heated. 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 automatically. For each TGA run, the user is able to specify a detailed series of events that is carried out in the 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, which eliminates the need to run a "blank" run to correct for buoyancy.

The focus of this study is on the mass decomposition response of an aerogel felt, Pyrogel 2250, exposed to Helium at during dynamic TGA runs at various temperatures. This section will briefly outline the experimental procedure used to complete each TGA run, followed by an initial discussion of the TGA curves. Referring to Figure Set 4 below, the reader can see a snapshot of the series of events that transported each sample into the TA Q5000IR furnace.

The order of succession in Figure Set 4 starts in the top left and continues from left to right, row by row, until the final image in the bottom right corner. Each aerogel felt sample was taken directly from the same, larger disk of aerogel 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. A convenient comparison between pre-test and post-test samples is shown in the bottom-right corner of Figure Set 4. Notice that the post-test sample on the right experienced radial shrinkage during the test when compared with a virgin sample on the left.

Figure Set 5 gives the reader insight into maintenance tasks performed between rounds of testing. The image on the far left shows an example of TGA calibration at a specific heating rate with an aluminum alloy, a nickel alloy, and powdered cobalt. 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 4. Visual Representation of Sample Loading Procedure into TA Q5000IR

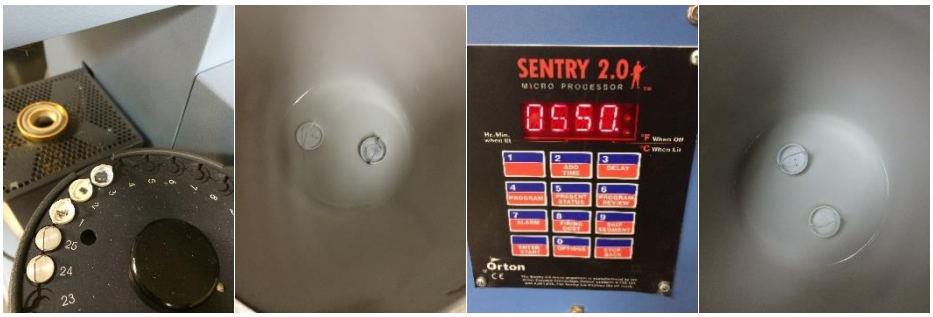

Figure Set 5. Visual Representation of TA Q5000IR Maintenance Tasks

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 Helium 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 40 °C. The dynamic stage, followed directly after, consisted of a linear ramp to a final temperature of 1100 °C for Standard TGA or sinusoidal ramp to a final temperature of 1000 °C for Modulated TGA.

IV. Calculation of Activation Energy with the Arrhenius Equation

As mentioned above, a series of dynamic TGA tests were performed at various heating rates for an aerogel 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 Arrhenius kinetic parameters; activation energy and pre-exponential coefficient. The first type of TGA test exposes the sample to constant heat rates of 2 °C/min, 5 °C/min, 8 °C/min, and 10 °C/min in a Helium environment. This method is referred to as a Standard TGA and one must perform experiments at 4 different heating rates to obtain the kinetic parameters. The second TGA test profile is referred to as a Modulated TGA, which exposes the sample to a sinusoidal variation about a constant heat rate profile in a Helium environment. The heat rate chosen for this study is 2 °C/min, the modulation period was chosen to be 200 seconds, and amplitude was chosen to be ± 5 °C. The advantage of this advanced TGA procedure is the obtainment of the activation energy and pre-exponential factor of a sample after only one experiment. The following discussion will introduce the reader to the basic Arrhenius relation framework while listing the governing equations each method uses to calculate the Arrhenius parameters.

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 below in Equation 3.

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

To create an accurate simulation of decomposition in the future, one must obtain the activation energy of the tested aerogel 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 below 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 Ramp TGA Test Method

Decomposition kinetics for the Standard Ramp method are modeled using the Ozawa/Flynn/Wall method outlined in the ASTM Standard Test Method E1641-15 [4]. The following equations show the majority of the accepted Ozawa/Flynn/Wall method of calculating activation energy and pre-exponential 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 Ramp TGA data.

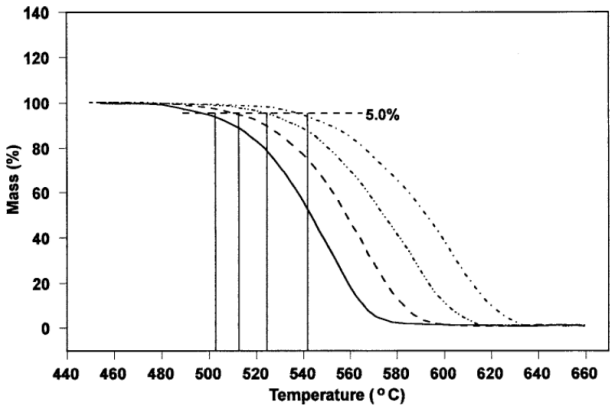

Figure 6. Sample Dynamic TGA Curves [4]

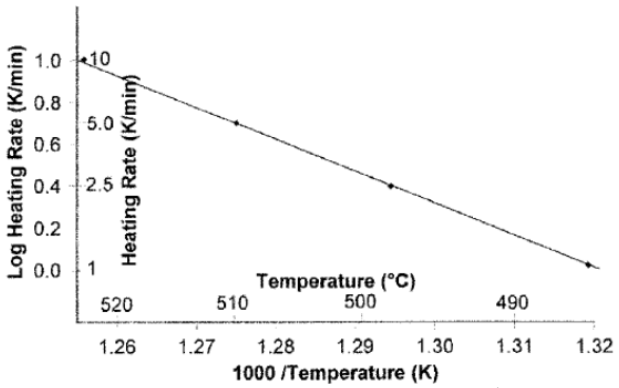

Figure 7. Sample Arrhenius Plot [4]

The slope of the Arrhenius plot is a key quantity used to obtain the kinetic parameters. 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 developed by 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) [17]." Figure 8 below shows an example of a modulated temperature profile, represented by the green line, which oscillates about the average temperature of its constant heat rate temperature ramp profile.

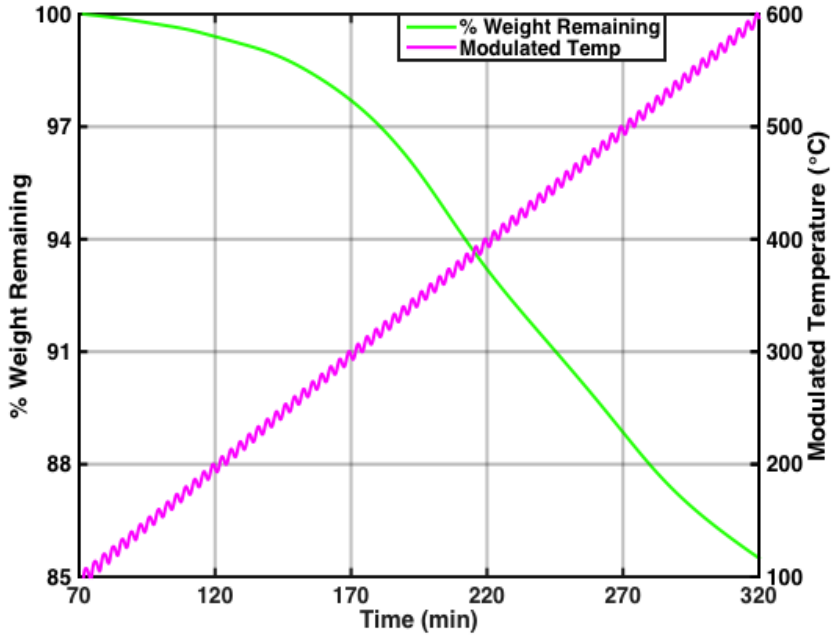

Figure 8. Sample Modulated TGA Test of Pyrogel 2250 in Helium at 2 ° C/min

ASTM Standard Test Method E2958 – 14 outlines the proper testing procedure for a modulated ramp TGA test, which is followed very 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 [9,10].

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

$$\text{where } L = \ln\left(\frac{d\alpha_1}{d\alpha_2}\right) \tag{14}$$

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

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

The objective of this study is to find the ± 3σ uncertainty bounds for the activation energy 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 TGA runs increases, 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 below, a minimum of 4 DoF's, or 5 experiments, are required to exceed a confidence level of 95%.

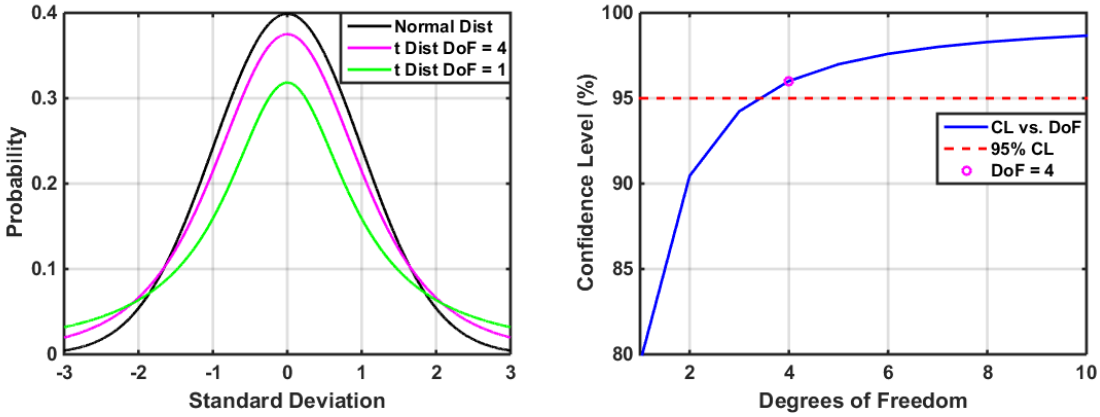

Figure 9: Sample t-Distributions vs. Normal Distribution (Left) and Degrees of Freedom Required for a t-Distribution to Exceed a Confidence Level of 95% Between ± 3σ (Right)

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 required by Standard and Modulated TGA methods, 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 following results section presents the resulting distributions of activation energy obtained through Standard TGA testing and Modulated TGA testing.

V. Results

After calibrating the TGA instrument to run at a heating rates of 2, 5, 8, and 10 ℃/min, the analyst was able to complete a rigorous testing TGA 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 types of TGA tests for Pyrogel 2250 in Helium to help the reader understand each step in the analysis process.

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 1100℃ 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 ℃/min as a function of temperature. While the test was performed up to 1100℃, the figure below only shows data up to 400℃ because this investigation focuses on finding the activation energy for the first mass decomposition event that occurs at approximately 375℃.

After completing 5 sets of Standard TGA runs at heating rates of 2, 5, 8, and 10 ℃/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 data set 2. The linear fit is fairly accurate, showing that the Arrhenius relation can accurately capture decomposition for this material.

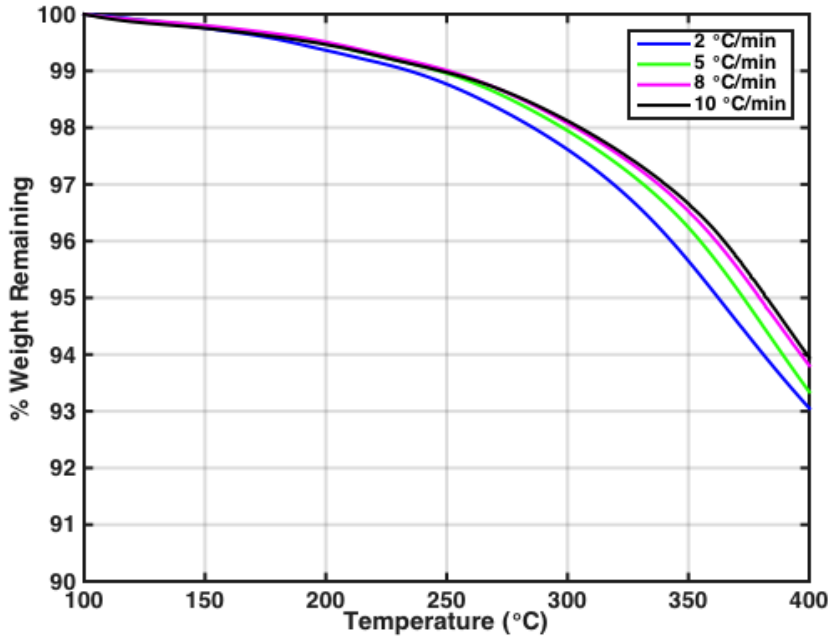

Figure 10. Sample Set of 4 Standard TGA Tests of Pyrogel 2250 in Helium at 2, 5, 8, and 10 °C/min

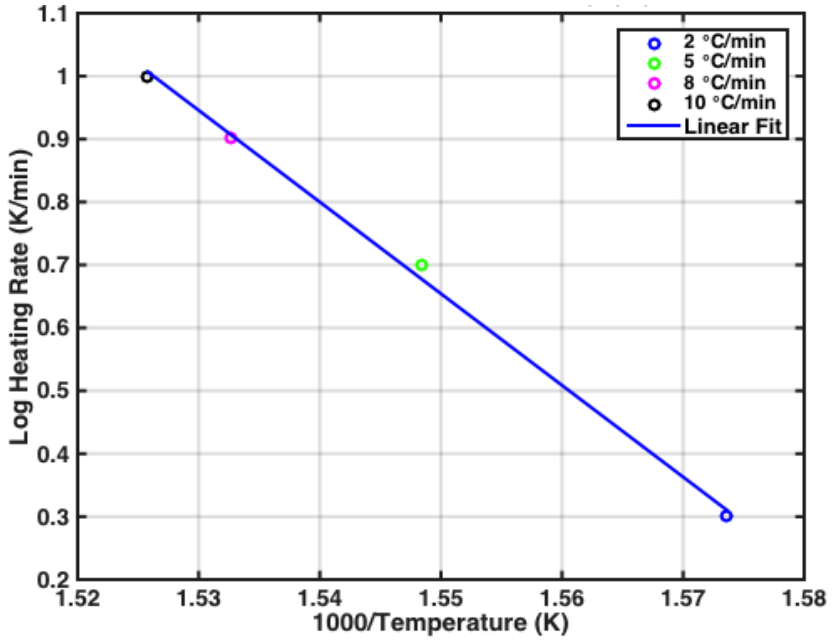

Figure 11. Sample Arrhenius Plot for a Set of 4 Standard TGA Tests of Pyrogel 2250 in Helium at 2, 5, 8, and 10 ° C/min with a Linear Fit

Figure 12 shows the set of 5 Modulated TGA tests performed on Pyrogel 2250 samples. 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 for the set of 5 Modulated TGA tests. Resulting activation energy was obtained using the calculations in the previous section as prescribed by ASTM E2958 – 14. A first order reaction is assumed for the initial reaction occurring at approximately 375 °C. The activation energy was estimated at the point of peak derivative weight loss with respect to temperature, which occurred at approximately 95% weight remaining.

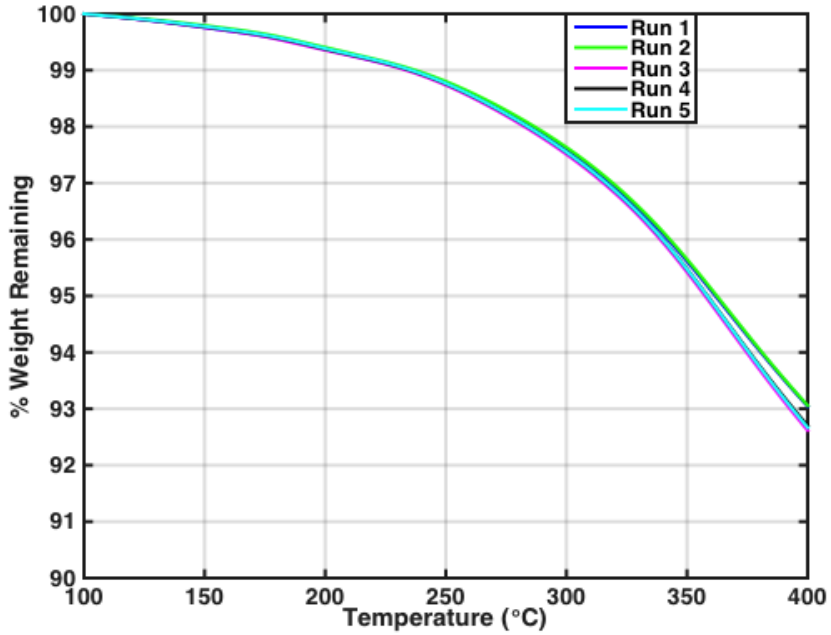

Figure 12. 5 Sample Modulated TGA Tests of Pyrogel 2250 in Helium at 2 °C/min

After completing the required TGA experimentation and activation energy calculations for both methods, the final t-distributions could be obtained. Figure 13 below shows the resulting t-distributions obtained from Standard and Modulated TGA test methods. 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 257 kJ/mol and 17 kJ/mol, respectively. The mean and standard deviation of the Modulated TGA t-distribution is approximately 181 kJ/mol and 1.5 kJ/mol, respectively.

There are a few interesting things to note here. The mean of activation energy between the two methods are fairly similar, but the mean of Standard TGA activation energy is decidedly higher. This may be due to the fact that the calculation spanned 4 heating rates, which may have considered a wider range of possible activation energy values at each heating rate. One can also see that the standard deviation of activation energy for Modulated TGA is an order of magnitude lower than that of Standard TGA. Again, this is due to the fact that only 5 samples were tested to determine the t-distribution for Modulated TGA, while 20 samples were tested to determine the t-distribution for Standard TGA. The additional variability from testing 4 times as many samples greatly widened the standard deviation for the t-distribution for Standard TGA.

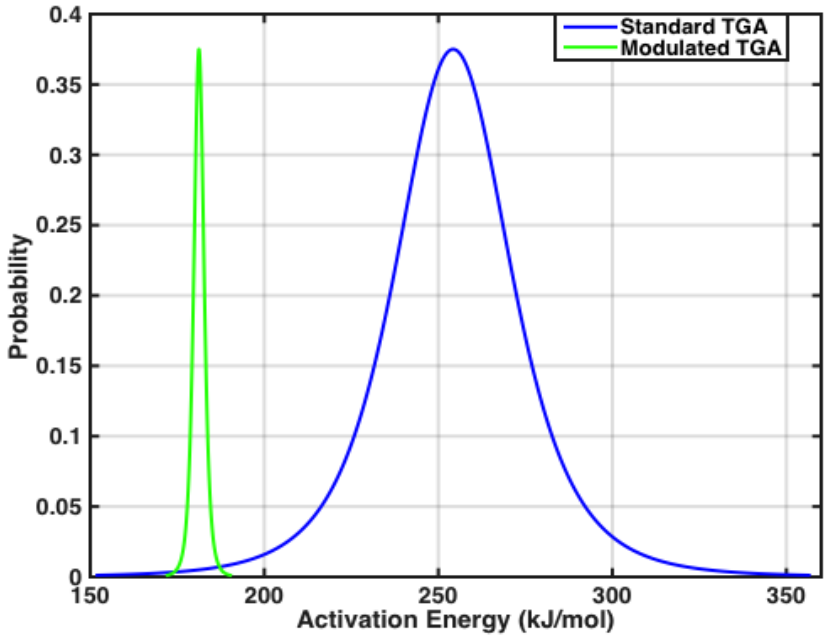

Figure 13. t-Distributions for Activation Energy for Pyrogel 2250 Obtained from Standard and Modulated TGA Testing

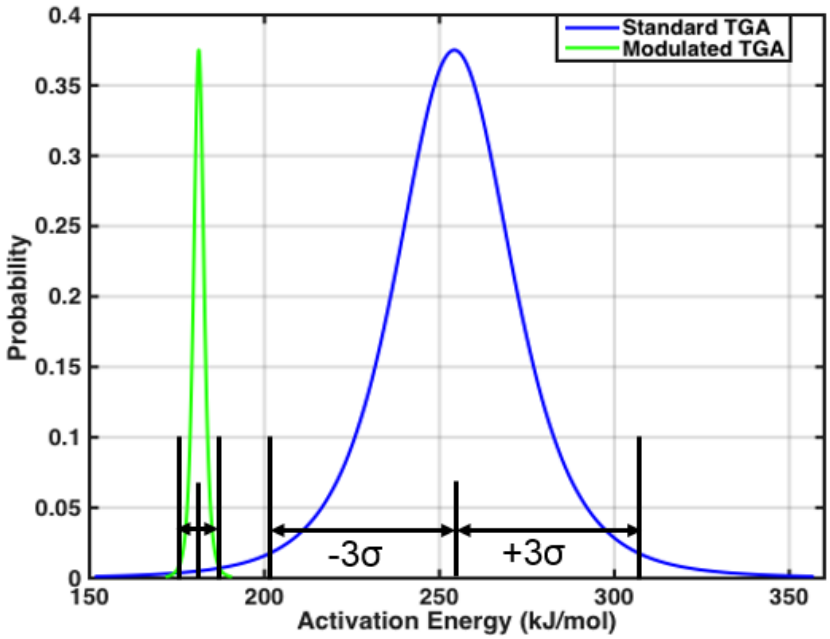

Figure 14. Location of ± 3σ Uncertainty Bounds t-Distributions for Activation Energy for Pyrogel 2250 Obtained from Standard and Modulated TGA Testing

The resulting mean activation energies from Standard and Modulated TGA methods, mentioned above, were input into the COMSOL thermal response model to observe the resulting accuracy of temperature profile predictions at the bondline (TC6). Figure 15 shows the nominal FTPS thermal model predictions with the original two-reaction decomposition model created by Sullivan where prediction lines (dashes) are compared with experimentally measured temperatures in an arc-jet (solid lines). The only changes that were made to this decomposition model were applied to the first reaction. The activation energy was changed according to the data gathered above and the reaction order of the first reaction was changed from 16 to 1 for simplicity.

After inputting the mean values for activation energy obtained with Standard and Modulated TGA methods, 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 of 254 kJ/mol obtained from Standard TGA testing and 181 kJ/mol obtained from Modulated TGA testing. Figure 16 shows significantly improved predictions at the bondline (TC6) for both Standard and Modulated TGA methods. Further analysis will be performed in the future to asses temperature prediction results at other thermocouples and to find out which value of activation energy fits the model best.

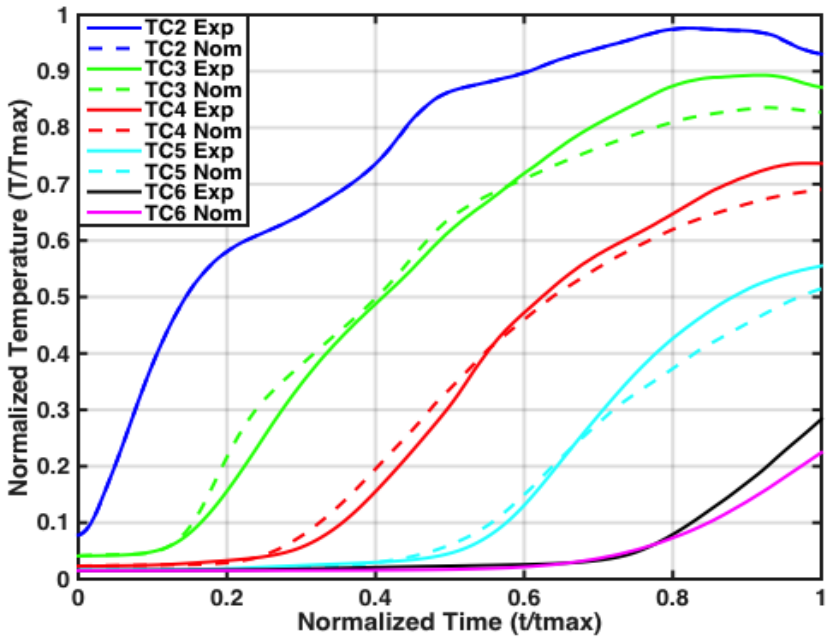

Figure 15. FTPS Thermal Response Model Temperature Prediction Comparison at Depth for Run 2602

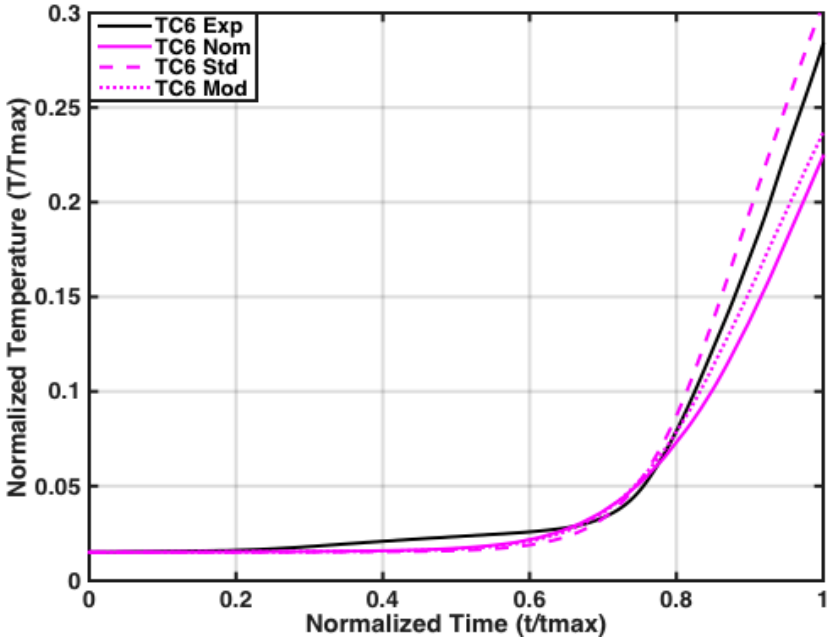

Figure 16. FTPS Thermal Response Model Temperature Prediction Comparison at Depth for Run 2602 Using Activation Energy from Standard TGA Testing

VI. Conclusions and Future Work

Two types of dynamic TGA tests were performed on an aerogel felt insulator called Pyrogel 2250 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 aerogel felt using the analysis procedures described above. The mean and standard deviation of the Standard TGA t-distribution is approximately 257 kJ/mol and 17 kJ/mol, respectively. The mean and standard deviation of the Modulated TGA t-distribution is approximately 181 kJ/mol and 1.5 kJ/mol, respectively. Knowledge of these quantities furthers the understanding of how aerogel felt behaves in an inert environment. The values of activation energy for both methods are comparable, their t-distributions have been obtained, and they both show promise for improving thermal response model predictions.

Preliminary thermal model response results 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 profile predictions at the bondline thermocouple. Future work includes considering other Arrhenius parameters in order to improve the current decomposition model even further and repeating this analysis for a carbon felt insulator.

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