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Burning Behavior at High Applied Heat Flux Levels: Implications for Determination of Material Properties

by

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Abstract

A challenge related to characterizing the fire performance of material systems and how to measure true (scaleable) fire properties of these systems is currently faced by the composites industry as well as the fire engineering industry. The growth in the use of fire models to simulate actual scenarios necessitates that fire engineers have material “property” information that is valid. Understanding materials’ performance at high heat fluxes allows for insight into determination of scaleable properties as well as providing an opportunity for the composites industry to clearly demonstrate superior performance of its materials. This paper presents results from a recent study conducted in the Advanced Flammability Measurements Apparatus (AFM), which is an enhanced bench scale apparatus similar to Fire Propagation Apparatus ASTM E 2058 and Cone Calorimeter ASTM E 1354, to provide more insight into phenomena associated with horizontal ignition and burning. It builds upon previous work presented at Composites 2004 where burning results were preliminary and not yet distilled. This new work builds upon that and presents significant conclusions for burning behavior and its key “property” heat of gasification. This “property” is found to vary with heat flux level (heating rate) and to be different as compared to the value obtained from differential scanning calorimetry. These results will be detailed and discussed in the context of proper use of these values for indexing of materials as well as in fire modeling.

Introduction

A recent study was conducted in FM Global’s Advanced Flammability Measurements[1,2,3] Apparatus (AFM) to provide more insight into phenomena associated with horizontal ignition and burning. The key aspect of this study was the use of real-scale heating rates from 21 to 236 ºC/min (applied heat flux from 10 to 200 kW/m^2) which is well beyond that typically considered in current testing. An unexpected non-linear trend is observed in the typical engineering analysis plots currently used in fire protection engineering for ignition and mass loss flux data for several materials tested in the AFM. Review of literature data also shows the same non-linear trend although not as clearly due to the limited heating rate range used.

The study[4] presented at Composites 2004 took a simple approach to investigating the unexpected non-linear results of the ignition data. This approach was to investigate the measured temperature profile by comparing it to a predicted profile during heat up to ignition. The temperature profile predicted by the analytical solid, 1D conduction solution for an inert material with semi-infinite behavior and constant applied heat flux and constant thermal properties gives a good match, within the uncertainty, to the experimental profile for alumina silicate, which is truly inert, and black PMMA with inert behavior. Using this approach to investigate decomposing material behavior shows that viewing ignition as an inert material process is inaccurate at predicting the surface temperature at higher heat fluxes. This analysis of thermal effects suggests that decomposition kinetics at the surface and possibly even in-depth may need to be included in an analysis of the temperature profile and the process of ignition. The current study looks more closely at the steady burning data.

Mass Loss Flux Results

Figure 1 shows the steady state mass loss flux vs. applied heat flux for tests done in the AFM and Cone Calorimeter well as some results from Tewarson[5] and Hopkins and Quintiere[6] for 25 mm thick black PMMA. The typical plotting method currently used in fire protection engineering for mass loss data is used to plot the mass loss flux vs. applied heat flux. This typical plotting method is based on an ablative material assumption.

The general comparability, shown in Figure 1, between the AFM, Cone and literature results of Hopkins and Quintiere show that the AFM is operating properly and giving results as expected for applied heat flux ranges reachable by the Cone. This provides support for the accuracy of higher heat fluxes in the AFM given that the same calibration procedures were used for the entire applied heat flux range. Close inspection of the data, however, shows a slight variation of the literature results of Tewarson in that it appears to have a slightly different slope than the current study data and the data of Hopkins and Quintiere. This information will become important later.

Note the unexpected non-linear trend starting at around 60 kW/m^2. Various checks were conducted to confirm that the unexpected non-linear trend in the plot is not an artifact of the apparatus. The non-linearity appears to be a true material response and is investigated by examining the measured temperature profile during steady burning and comparing it to a predicted profile (using the viewpoint of an assumed ablative material).

Burning Temperature Profile

Before investigating the non-linearity of the mass loss flux data using the typical plotting technique, some thought needs to be given as to the basis for this technique. This technique evolved from the classic ablation problem[7] which views burning strictly as a surface process where the only energy related to the decomposition process is the heat of vaporization plus the heat up to temperature. The assumed temperature profile in the solid comes from applying a constant temperature boundary condition at the surface. As such, the actual temperature profile in the solid during burning as well as information about any decomposition occurring in-depth would be helpful in investigating the mass loss flux results.

Figure 2 shows the temperature profile normalized to the regressing surface for applied heat fluxes of 28, 60 and 90 kW/m^2 as well as a 0 kW/m^2 free burn run. Note that the profiles are different from the predicted profiles and can be considered invariant with applied heat flux due to the positional uncertainty of the thermocouples of 1 mm. This comparison suggests that the ablation viewpoint of applying a constant temperature boundary condition to the solid to obtain an assumed temperature profile is inaccurate.

Experimental observations, also seen by others,[8,9,10,11,12] during burning show surface "bubbling" occurring as well as some flame "jetting" which is presumably related to the bursting "bubbles". The sample was inspected after burning to obtain the depth that bubbles were formed. The size of the bubbles and the depth of the "bubbling layer" during burning change with applied heat flux. At lower fluxes the bubbles are "large" and the depth of the bubble layer "thick." These observations indicate that in-depth decomposition is occurring, especially at the lower applied heat fluxes. As the applied heat flux increases, the bubbles get smaller (i.e., decrease in diameter) and the bubble layer gets thinner until at the highest applied heat flux in this study, the bubble size and layer depth appear to be of the same magnitude.

It can be seen from Figure 2 that the ablation problem temperature profile more accurately predicts the measured profile at the higher applied heat fluxes. This makes sense since the bubbling layer depth is getting very thin at the higher applied heat flux levels so that it is reasonable to consider the decomposition a surface event. However, this has interesting implications for the mass loss flux plot given in Figure 1. It was assumed that the linear curve fit of the data at the lower applied heat fluxes indicated that the ablation viewpoint was representing the physics accurately and that the higher heat flux results were a divergence. The temperature profiles and experimental observations of bubbling layers indicate the opposite in that the simplified ablation solution should work better at the higher applied heat fluxes and not the lower. Since the lower applied heat flux results of the mass loss flux plot are used to obtain the apparent heat of gasification, a closer look was taken at this parameter.

Heat of Gasification

The apparent heat of gasification can be obtained from the typical plotting technique currently used in the fire protection engineering field. This plot is a representation of the surface energy balance (using the assumption of a constant temperature boundary condition)

$$\dot{q}''_{\text{flame}} = \dot{q}''_{\text{radloss}} - a\dot{q}''_{\text{applied}} + \dot{m}''h_g$$

where $\dot{q}''$ is heat flux, a is the surface absorptivity, usually assumed to be unity, $\dot{m}''$ is the mass loss flux and h_g is the apparent heat of gasification. The implied simplification is that the apparent heat of gasification includes only the change in the sensible and latent heat of the material. This equation can be put into a "y=mx+b" form given as

$$\dot{m}'' = \frac{a\dot{q}''_{\text{applied}}}{h_g} + \frac{\dot{q}''_{\text{flame}} - \varepsilon\sigma T^4_{\text{surface}}}{h_g}$$

where the slope "m" is contained in the first term and the intercept "b" is the second term on the right. Note that this plot gives two pieces of information, the slope and the intercept. This is the same technique used by Hopkins and Quintiere, Tewarson and the SFPE Handbook.[13]

The mass loss flux data as a function of applied heat flux is plotted[14] (representing the "y=mx+b" form of the equation) and a linear curve fit is made to the data. The inverse of the slope is interpreted as the apparent heat of gasification, h_g. This calculation of apparent heat of gasification assumes that the mass loss flux data plotted as a function of applied heat flux follows a linear curve fit for all levels of applied heat flux.

As was seen in Figure 1, the mass loss flux data for black PMMA does not follow the expected linear trend at the higher applied heat fluxes. This presents a complication in fitting a linear curve to the data in order to find the heat of gasification. Forcing a line that fits all the data is not reasonable since the non linearity represents a true material response. Fitting a linear curve through only either the lower or higher applied heat flux levels would imply that either (i) the heat of gasification is changing with applied heat flux (rate of heating) which would only be possible if the products of decomposition change with heating rate or (ii) the ablation "surface only decomposition" viewpoint energy balance does not accurately represent the physics occurring for the entire applied heat flux range.

For the lower range of applied heat flux, the current study obtains an apparent heat of gasification value of 2.4 ± 0.2 kJ/g for black PMMA for 20.9 % ambient oxygen concentration as seen in Figure 3. The uncertainty comes from the variation of the linear curve fit through the experimental data. (The slope can fit differently through the data and is bounded. The uncertainty comes from this variation and not from a regression analysis.) This current value is also found by other literature[6,15,16] sources, however, Tewarson's historical data, using a FPA, gives an apparent heat of gasification of 1.6 ± 0.2 kJ/g for 20.9 % ambient oxygen concentration.

Agrawal and Atreya[17] use a Cone Calorimeter and give a value of 1.6 kJ/g for the apparent heat of gasification but close inspection of their data traces shows that they are using the peak mass loss flux and not the steady state value which is indicative of thermally thick behavior. Using their steady state values for the mass loss flux gives an apparent heat of gasification of 2.2 kJ/g. Magee and Reitz[18] conduct steady burning experiments at applied heat flux levels up to 15 kW/m^2 and obtain an apparent heat of gasification of 1.7 kJ/g.

The typical plotting method currently used in fire protection engineering implicitly assumes that the sample surface absorptivity is equal to 1 by virtue of its abscissa being the applied heat flux and not the absorbed heat flux. For luminous flames where soot is observed to be on the sample surface, this assumption is valid, however, tests were also conducted with a coating of carbon black as a check. The apparent heat of gasification values were unchanged.

The typical plotting method also assumes that the flame heat flux is constant, otherwise the axis would be the applied heat flux plus the flame heat flux. This assumption is found to be true from measurements in the current study, however, an additional look should be taken at the data in a nitrogen atmosphere, where there will be no flame nor oxygen. The results are shown in Figure 4.

It is seen from this plot, that the apparent heat of gasification from pyrolysis data conducted in a nitrogen atmosphere, 1.6 kJ/g, is different than the 2.4 kJ/g obtained for steady burning in an atmosphere containing 20.9 % oxygen shown in Figure 1.18. Interestingly the nitrogen pyrolysis value matches DSC measurements conducted by a third party. They obtain a heat of vaporization value of 0.9 kJ/g for a heating rate of 100 °C/min which leads to a heat of gasification of 1.6 kJ/g (No uncertainty is given by the provider). This heating rate is the average of what is obtained in AFM, FPA and Cone steady burning tests for applied heat flux levels up to 60 kW/m^2. Note that DSC tests are normally conducted in a nitrogen atmosphere but this study also had DSC tests run with a 20.9 % oxygen atmosphere giving 0.9 kJ/g for the heat of vaporization at a 100 °C/min heating rate, which leads to a heat of gasification of 1.6 kJ/g. Vovelle, Akrich and Delfau[19] did pyrolysis experiments with 10 cm samples in both nitrogen and air environments for applied heat fluxes up to 30 kW/m^2. They obtained an apparent heat of gasification of 1.6 kJ/g in both cases.

As seen above, the heat of gasification obtained from steady burning experiments is different than that obtained from pyrolysis experiments. It is likely the presence of the flame and not simply the oxygen that makes the difference. However, the work of Magee and Reitz contradict this. It is debatable if the oxygen presence by itself or the flame is the underlying cause of the difference.

From a more practical angle, the question arises as to which heat of gasification is the proper one to use in models. First, one must decide if (i) there is only one heat of gasification that does not change with heating rate, or (ii) it changes with heating rate. A change in the heat of gasification with heating rate implies that the products of decomposition are changing with heating rate and this would need to be incorporated into the energy balance.

If one adopts the viewpoint that there is to be only one heat of gasification that does not change with heating rate, then a decision needs to be made to use either the value obtained from pyrolysis tests or burning tests. If the value obtained from the DSC, which is usually considered the "correct" and "fundamental" value, is used then the ablation solution energy balance is too simplified to represent the physics occurring for steady burning for any applied heat flux since it does not obtain this value. If one uses the steady burning value, then the energy balance is reasonable to apply at the lower fluxes but would need to be modified to be able to predict the higher applied heat flux results. Related work[20] shows that the apparent heat of gasification obtained from steady burning tests can be a practically useful parameter when used to obtain large scale results of flame heat flux whereas the DSC value could not.

Use of Heat of Gasification

The apparent heat of gasification obtained in small scale tests is used to predict the flame heat flux of large scale fires. From the plot, the intercept is used with the apparent heat of gasification to obtain the flame heat flux.

Figure 5 shows the measured total flame heat flux values for several sample sizes tested in a related study.. Also shown is the total flame heat flux calculated from the mass loss flux and the apparent heat of gasification.

Observe from Figure 5 that the total flame heat flux calculated from the mass loss flux data using Tewarson's DSC heat of gasification value of 1.6 kJ/g does not match the measured value. Use of the apparent heat of gasification value of 2.4 kJ/g gives a calculated total flame heat flux value that reasonably matches the measured value. This is thought to be due to the "applicability" of the small scale apparent heat of gasification to the large scale test due to the correspondence of the large scale flame heat flux with the initial linear region of the mass loss flux vs. applied heat flux plot. In other words, the "heat of gasification" was obtained for material response to a flame heat flux less than 50 kW/m^2 and the average large scale flame heat flux is about this value. Apparently, whatever physics or chemical processes that are buried in the apparent heat of gasification term is the same for both small scale, 10.2 cm, and large scale, 122 cm, sample sizes.

Delrin

Another material was also tested to insure that PMMA was not a fluke. The mass loss flux data was used to calculate the heat of gasification using the same technique presented for black PMMA. The heat of gasification from the linear portion of the data is 4.8 ± 0.5 kJ/g as seen in Figure 6. Hirsch, Beeson and Friedman[21] obtain a value of 4.0 kJ/g in a 22.0 % oxygen atmosphere. Tewarson's historical data gives a value of 2.4 ± 0.5 kJ/g.

For the non luminous flame produced by Delrin, which essentially has no soot, the assumption of surface absorptivity equal to 1 is not strictly valid. The solid sample absorptivity is most likely not the right choice either since the surface is actually a "bubbling layer" consisting of translucent bubbles and liquid "melt." As such, the actual absorptivity is not known. A solution to this is to put a coating of carbon black on the surface to force its absorptivity to 1. Interestingly, no difference was seen in the mass loss flux data for Delrin using a carbon black coating, hence the apparent heat of gasification is unchanged. Nitrogen atmosphere tests were also conducted for Delrin and the results are shown in Figure 7.

It is seen from Figure 7, that the apparent heat of gasification from pyrolysis data conducted in a nitrogen atmosphere, 2.4 kJ/g, is different than the 4.8 kJ/g obtained for steady burning in an atmosphere containing 20.9 % oxygen shown in Figure x. Similarly as raised for black PMMA, it is debatable if the presence of the oxygen by itself or the flame is the underlying cause.

Moving Forward

It has been shown that the testing conditions are not the cause for the non linearity of the ignition data. Viewing ignition as an inert material process is inaccurate at predicting the condensed phase temperature profiles at higher applied heat fluxes. The investigation of thermal effects suggests that decomposition kinetics at the surface and possibly even in-depth may need to be included in an analysis of the process of ignition, especially at higher heat fluxes.

It appears that the "typical technique" energy balance, which evolved from the classic ablation problem, is too simplified to represent the physics occurring for all range of applied heat flux. Hence, a new energy balance needs to be developed and two items provide insight into a possible direction, (i) the measured temperature profile and (ii) the observations of the surface and in-depth bubbling behavior. As such, the control volume given by Figure 8 is presented that includes an energy term for this process.

Further work is needed to determine what the $\dot{q}''_{\text{unknown}}$ term should be. This term, for polymers, could be related to (1) transport limitations of the in-depth bubbles or (2) effect of bubbling/melting layer on aborptivity and conduction, (3) an effect of oxygen reacting with the solid sample, (4), a difference in decomposition products due to heating rate (5) presence of flames or (6) some combination of these.

Conclusions

An unexpected non-linear trend is observed in the typical plotting method currently used in fire protection engineering for ignition and mass loss flux data for several materials tested in the AFM. There also exist literature results showing the same non-linear trend as the current study. The non-linearity is not related to the AFM apparatus.

The steady burning temperature profiles appear to be invariant with applied heat flux. This shows that viewing burning strictly as a surface process where the decomposition kinetics is lumped into the heat of gasification may be inaccurate. (This viewpoint is the basis for the “typical technique” currently used in fire protection engineering for burning.) This possible inaccuracy was investigated by obtaining the heat of gasification via the “typical technique” using the mass loss flux data and comparing it to the commonly considered “fundamental” value obtained from DSC measurements.

The black PMMA apparent heat of gasification value of 2.4 ± 0.2 kJ/g calculated from small scale mass loss flux data does not match the value of 1.6 ± 0.2 kJ/g obtained from DSC measurements, which is commonly considered “correct” and “fundamental.” The Delrin apparent heat of gasification value of 4.8 ± 0.5 kJ/g calculated from mass loss flux data does not match the value of 2.4 ± 0.5 kJ/g obtained from Tewarson and DSC measurements. Small scale pyrolysis tests conducted in a nitrogen atmosphere obtain approximately 1.6 kJ/g and 2.4 kJ/g for black PMMA and Delrin respectively which match DSC measurements from both nitrogen and air atmospheres. This comparison suggests that the “typical technique” energy balance is too simplified to represent the physics occurring for any range of applied heat flux. Hence, a new energy balance needs to be developed and a possible direction would focus on the in-depth bubbling behavior.

Acknowledgements

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Figures

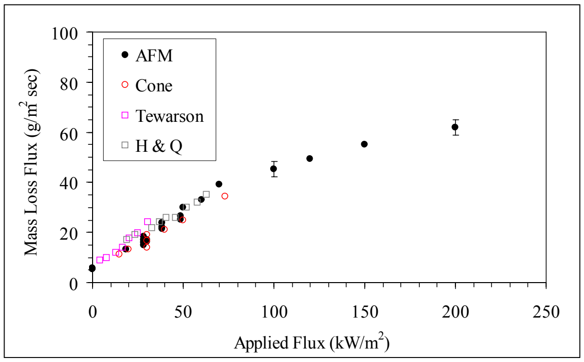


Figure 1. Steady mass loss flux vs. applied heat flux for thermally thick behaving black PMMA. Experimental mass loss flux uncertainty = ± 3 g/m^2 sec.

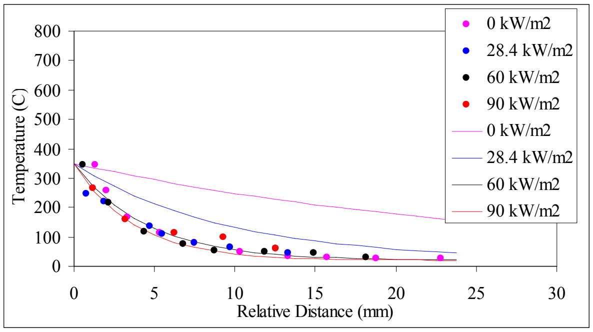


Figure 2 Temperature profile normalized to regressing surface for various applied heat flux for thermally thick behaving PMMA. Symbols: data, Lines: predicted.

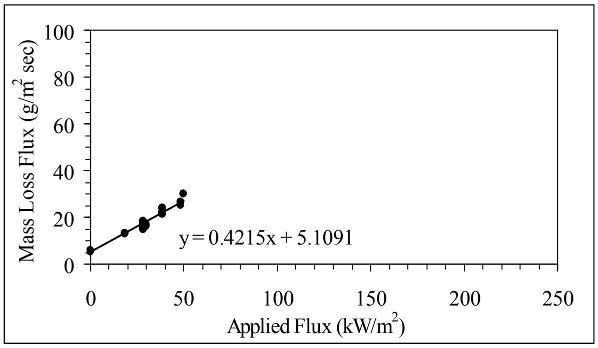


Figure 3 Linear region steady mass loss flux vs. applied heat flux for thermally thick behaving PMMA in a 20.9 % oxygen atmosphere. Experimental mass loss flux uncertainty = ± 3 g/m^2 sec.

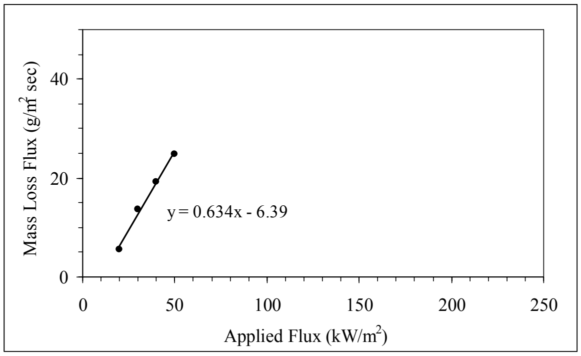


Figure 4 Linear region steady mass loss flux vs. applied heat flux for thermally thick behaving PMMA in a nitrogen atmosphere. Experimental mass loss flux uncertainty = ± 3 g/m^2 sec.

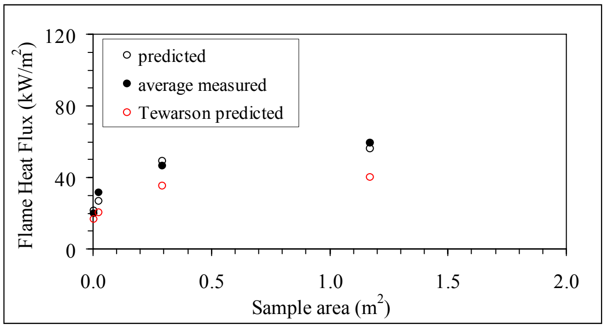


Figure 5 Flame heat flux measurements and calculations for thermally thick behaving black PMMA.

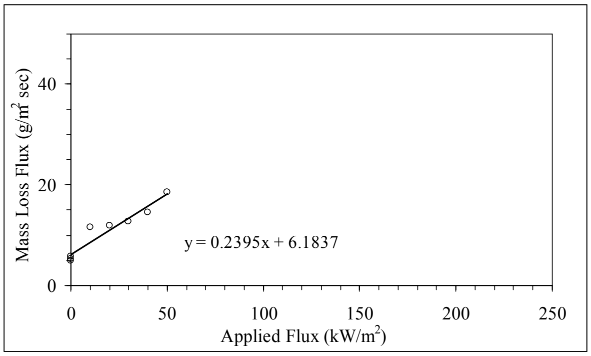


Figure 6 Linear region steady mass loss flux vs. applied heat flux for thermally thick behaving Delrin in a 20.9 % oxygen atmosphere. Experimental mass loss flux uncertainty = ± 3 g/m^2 sec.

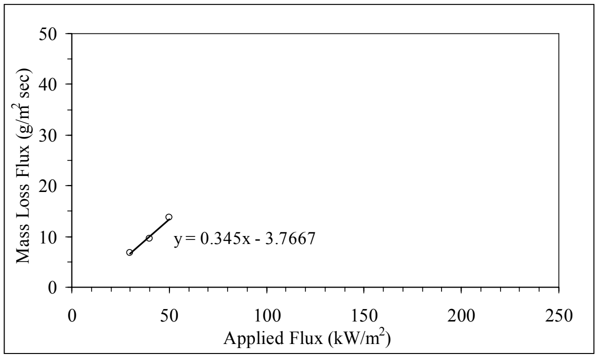
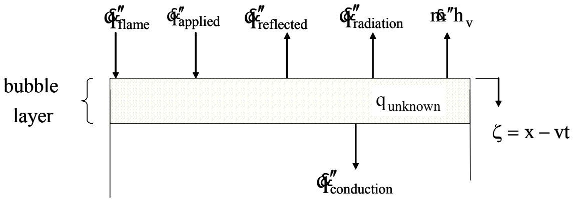


Figure 7 Linear region steady mass loss flux vs. applied heat flux for thermally thick behaving Delrin in a nitrogen atmosphere. Experimental mass loss flux uncertainty = ± 3 g/m^2 sec.



$$\dot{q}''_{flame} = \dot{q}''_{radloss} - a\dot{q}''_{applied} + \dot{m}''h_g + \dot{q}''_{unknown}$$

Figure 8 Bubble zone control volume and energy balance.

Author Biography

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