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Material Analysis for a Fire Assessment

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Abstract

This report consolidates technical information on several materials and material classes for a fire assessment. The materials include three polymeric materials, wood, and hydraulic oil. The polymers are polystyrene, polyurethane, and melamine-formaldehyde foams. Samples of two of the specific materials were tested for their behavior in a fire-like environment. Test data and the methods used to test the materials are presented. Much of the remaining data are taken from a literature survey. This report serves as a reference source of properties necessary to predict the behavior of these materials in a fire.

ACKNOWLEDGMENTS

Prof. Richard Hull from the University of Central Lancashire kindly contributed the references on combustion product toxicity. Reviews by Randy Watkins and Roy Hogan are appreciated.

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ACRONYMS

ANSI	American National Standards Institute
ARA	Applied Research Associates
ASTM	American Society for Testing and Materials
CFD	Computational Fluid Dynamics
DOE	Department of Energy
DTG	Derivative Thermogravimetry
ISO	International Organization for Standardization
MSDS	Material Safety Data Sheet
PS	Polystyrene
SFPE	Society of Fire Protection Engineers
SONEX	Sonex brand melamine-formaldehyde soundproofing foam
TGA	Thermogravimetric analysis

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1. INTRODUCTION

As part of the 2013-2014 fire hazard analysis of the US Air Force’s Kirtland Underground Munitions Maintenance and Storage Center (KUMMSC), there is a need to evaluate the fire behavior of several relevant materials that could be involved in a fire scenario. The particular properties of interest are those thermal and chemical properties that are required to simulate the behavior of the materials in a three-dimensional CFD fire combustion model. Heat transfer properties, quantitative pyrolysis reaction mechanisms, and thermal behavior are all needed. This is a companion report to a fire hazard analysis report. This report is intended to reduce the need to present technical data in the other report by providing an adequate single reference for such information. It is also hoped to be useful for future fire analyses of a similar nature.

The materials in question are all standard commercial materials. This means that there are historical data that can be accessed and used. However, it is risky to use historical data on a representative material because construction materials often include impurities, fire retardants, or other features that are specific to the process used to create the materials. Trace materials can have a pronounced effect on fire behavior. For this reason, it is sensible to perform some confirmatory work to verify that the fire analysis uses the best approximations possible.

Another motivation for this report is to consolidate the information on the behavior of these materials in a fire. Much can be inferred on common materials in the literature; however, this information is not normally all found in a single report. This paper will present the analysis of the relevant materials and attempt to consolidate the relevant information. A disproportionate focus is placed on the assessments for some of the materials compared to others. The amount of focus placed on the materials was related to the importance of the material to the project requirements and the perceived adequacy of existing data.

There are five materials of interest to the present effort, each being a potential component to a fire scenario. These materials are listed below:

1. Dow High Load 100 polystyrene foam blocks (PS)
2. Sonex melamine-formaldehyde soundproofing foam (SONEX)
3. Polyurethane foam packing material
4. Wood (generic), mostly present as furniture, pallets, boxes, or structural material
5. Hydraulic oil

Once a fire scenario has been postulated, it is necessary to have appropriate physical properties of relevant materials with which to populate a computational model. To predict fire behavior, it is important to know heat transfer properties including density, specific heat, and conductivity. It is also important to understand the thermal reaction behavior, which includes charring propensity, kinetic reaction rates, heats of reaction, and phase transition information. Reaction products are important to the gas phase combustion behavior, as well as the toxicity of the fire products. These parameters can all be used as properties in fire modeling tools that predict the outcome of fire events. The accuracy of the properties contributes to the accuracy of the predictions.

Because materials all vary in their properties, behavior, and complexity, it is necessary to qualify whatever assumptions are made with respect to material behavior. When selecting material property data for a model, it is helpful to be able to compare the behavior of known materials with reference or sample materials to assess the accuracy of the property data. Characterization testing can be useful in this regard. If a material property exists, it can be verified by back-comparison to the subsequently derived data. In some cases (like for this case the proprietary SONEX material), the exact nature of the materials in question is not known. Reference data from the general classification of material type might or might not be applicable to the real materials. Materials testing can help ascertain the adequacy of data.

Some fire scenario modeling is planned involving the above-listed materials. The objective of this report is to provide comprehensive information on the fire materials such that their behavior can be modeled with accuracy, fitting the needs of the program. The information in this report is of two types. First, some information is gleaned from searching reports and open literature. The use of literature data relies on the accuracy and applicability of the data, as well as the credibility of the group that produced the report. Second, there was information that was incomplete, lacking, or less certain. Limited experimental testing has been performed to either confirm critical assumptions, or to generate data where data were lacking.

2. METHODS

Proximate and Ultimate Analysis

To characterize physical properties of some of the materials, standard lab analysis was employed to measure the constituencies and behavior. These analyses can help confirm the nature of the materials of present interest, and affirm that they are close enough to use parameters from other materials whose characteristics are detailed in documents and reports on the thermal/fire behavior.

Samples were sent to ALS Environmental (Tucson, AZ) for analysis. ALS processed the materials according to standard instrument analyses, including a proximate and ultimate analysis, heating value analysis, and inorganic analysis.

The tests performed conformed to various ANSI or ASTM standard tests. The test standards are listed in Table 1.

Table 1. Tests and associated standards employed for material analysis

Standard	Test	Yield
D5373 D5373 mod D4239	Ultimate Analysis	CHN O S
D7582	Proximate Analysis	Moisture, volatile matter, fixed carbon, and ash
5050 9056	Halogen	F, Cl, Br
D5865	Heating Value	Specific heating value of the material
D6349	Metals	Ash metal content

Thermogravimetric Analysis

A common method for analyzing thermal decomposition of materials is with a thermogravimetric analyzer (TGA). It is a standard instrument that actively weighs a small sample in a gas environment at well-controlled temperatures. It is standard practice to use both air and an inert gas while heating samples at fixed heating rates to be able to distinguish the effects of the presence of oxygen (oxidative reactions in air) from that of pure pyrolysis.

For this study, TGA runs were performed using a Netzsch STA 449F3 instrument with a type-S thermocouple, using Al_2O_3 crucibles, with sample masses between 3 and −5 mg for each run. Runs were conducted in ultra-high-purity nitrogen (Matheson Tri-gas) and in air (Parker Balston lab air generator, model 74-5041NA). In all cases, a continuous flow of 170 mL of nitrogen was used as a purge gas flow. For nitrogen runs, an additional 50 ml/min of N_2 was introduced to the flow. For air runs, 50 ml/min of air was introduced to formulate an air surrogate gas flow; although the oxygen content is diluted in this way, as will be shown, the runs were generally consistent with the literature for air TGA reactions. A post-calibration check of the thermocouple, as illustrated in Figure 1, was performed to ensure accurate temperatures were recorded. System measured temperatures are within 2% of the calibration source, as plotted.

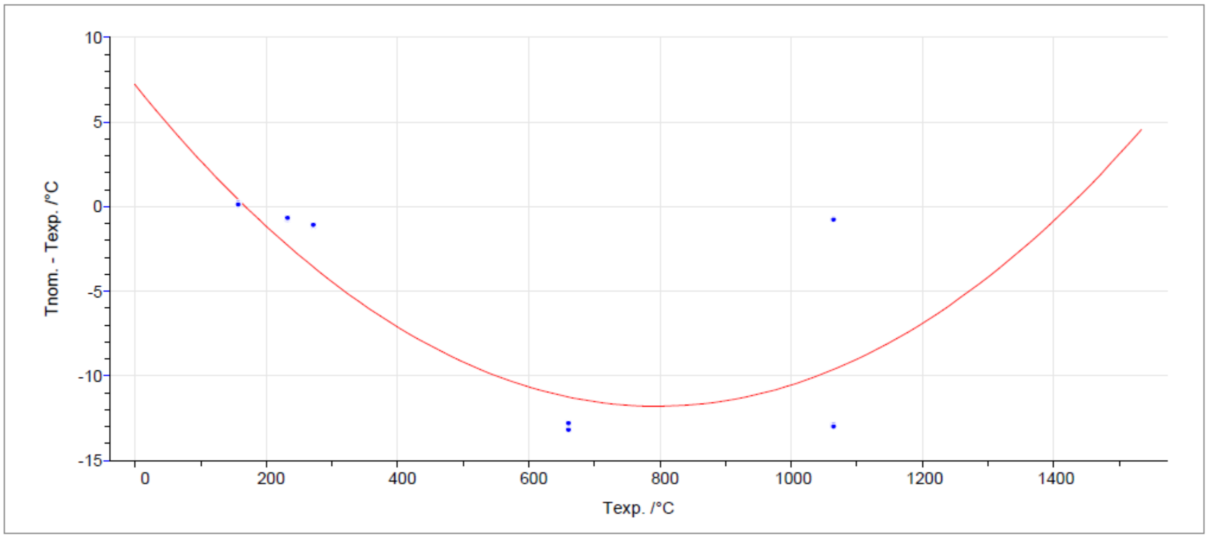

Figure 1. Post-calibration check of TGA thermocouple. Recorded temperatures are within a few perfect of actual temp.

Other Analysis

An ARES rheometer was used to detect the presence of a fluid phase in the decomposition of the melamine-formaldehyde material. The rheometer imposes an oscillatory stress in contact with the material. The presence of the liquid phase is deduced from the change in the mechanical stress-strain relationships as a function of temperature. The stress-strain relationship is indicative of an intermediate phase during decomposition, and is used to determine pyrolysis behavior.

3. POLYSTYRENE FOAM BLOCKS

The polystyrene material considered in this analysis is a DOW highload foam that has a compressive strength of 100 kPa. This specific material was one of the samples of focus for a ARFL/ARA analysis of polystyrene foams (Kalberer et al, 2005) to characterize the fire risk of the material. These authors report on a performance-based fire analysis of the material. A sample was provided by the Kirtland Air Force base fire protection staff for analysis. Said sample presumably has a pedigree that does not involve any environmental factors that would result in the material not being representative of all such material. The sample did not appear to be weathered or worn. Furthermore, it is believed to be representative of materials of interest to a fire study being jointly performed with this effort. This is mentioned because Kalberer et al. (2005) mention that there were manufacturing changes to the material depending on the date of manufacturing. The date of manufacture is not obvious (i.e., printed or labeled as such) with relation to the sample provided, or with any other materials in question. Therefore, we proceed with an analysis to help determine the nature of the provided material.

Figure 2. Picture of a small piece of the Dow Styrofoam^{TM} Highload polystyrene foam before TGA analysis.

Polystyrene in general is a fairly simple material. It is a polymer of the styrene monomer, which has a fundamental molecular formula of C_8H_8. Being a very common polymer, there is a lot of information in the literature on polystyrene, and peer-reviewed scientific studies of polystyrene reaction and properties are not difficult to find. However, the fact that the polystyrene of present interest is an expanded foam block (as opposed to solid polystyrene) means that not all literature properties are applicable. Many of the studies involving polystyrene properties were performed with nonexpanded polystyrene. While it is probably safe to use certain information (like reaction kinetics) from studies on nonexpanded polystyrene for an expanded block, there are other parameters that cannot be used, such as density and conductivity.

A review of the recent scientific literature uncovered some good information on polystyrene. Kannan et al. (2007) present a detailed review of past work on polystyrene degradation models, with the aim of understanding the decomposition of polystyrene foam molds. They highlight other efforts for other applications of polystyrene decomposition, proposing that the styrene monomer is the primary product of decomposition, with some minor polymer production and fragments depending on the conditions of pyrolysis. This is corroborated by the high-resolution mass spectrometry work of Brown et al. (2001). Several research groups present similar models for polystyrene behavior in a fire. These are Kannan et al. (2007), Kruse et al. (2002), Faravelli et al. (2001), and Bockhorn et al. (2000). These researchers model the polymer as a long chain of monomers, and use bond scission kinetics to determine the break-down of the primary polymer chains. This allows the model to make a determination of the inception of a liquid phase and to employ multiphase evaporation models to predict the evolution of the liquid. This type of modeling is high-fidelity, and represents the most advanced in current methods. The presence of a liquid phase is consistent with the findings of Kalberer et al (2005). This feature complicates modeling efforts, since the flow of the polymer melt constitutes a liquid phase contribution to modeling efforts that generally only consider flow of gases.

It is more common to represent the reactions with a simpler model that is based on thermogravimetric analysis. Recent examples of this type of effort include that of Lyon et al. (2012) and Snegirev et al. (2012). The reaction data are not thought to be as broadly applicable to varying environments, but the simplicity of the models is compelling for rapid modeling.

A large amount of data are found in Babrauskas (2003) and the Society of Fire Protection Engineers handbook (SFPE Handbook, 2002). From Babruskas (2003), we learn that polystyrene dust has a propensity for explosions, which has been studied in past work. It has a minimum ignition energy of 40 mJ, with the likelihood for detonation being heavily related to the concentration in the environment. This suggests that, in a degraded state, there is a risk of rapid reaction if the right conditions are attained. We also find additional confirmation of the liquid transitional phase that occurs with the polystyrene material.

Thermal Properties

Thermal properties are widely available for many common materials. When they are not available, they can often be easily measured. Thermal properties can be important to heat-transfer calculations, which in turn are a component of a fire model calculation.

The polystyrene material in question was evaluated for certain properties. Other properties were extracted from the literature. For thermal analysis, one must know density, heat capacity, and conductivity. For reacting materials, the kinetic rates are important, as is the heat of pyrolysis. Because kinetics will be discussed in subsequent sections, kinetics are omitted in this section. Since appropriate data were mostly available, no effort was made to take additional measurements for parameters that were well described. Because the material provided is an expanded foam, the density is obviously dependent on the manufacturing process; this needs to be evaluated for the specific material, and may have a range of values depending on the manufacturing process. Conductivity will also be dependent on the degree to which the material is expanded. Other properties such as absorptivity and pyrolysis rate are not thought to be as sensitive to the expansion. Because the chemical analysis of the material suggests a fairly pure polystyrene with minimal impurities, the use of data from the literature for other properties is thought to be acceptable.

Table 2 summarizes the information assembled for this study on the properties of polystyrene material. The manufacturer-specified density and the measured density from this work are nearly identical, at about 60 kg/m^3. This density can be compared with the density given by Lyon et al. (2012) and Babruskas (2003), which is 1050 kg/m^3, or ~17.5 times greater. This result differs because the latter work was considering unexpanded PS. Heat capacity data was not as easy to find, but the three sources listed in Table 2 suggest that the heat capacity of a liquid is higher than that for a solid composed of styrene. Conductivity was available from multiple sources. A foam tends to conduct like the primary constituent in terms of volume. For a foam such as this, the gas in the voids may be assumed to be air, or a similar gas. From Incropera and DeWitt (1990), air has a conductivity of 0.024 W/mK. Bockhorn et al. (2000) list pure PS as having a conductivity of 0.17. The foams would therefore be expected to tend between those values, and perhaps closer to the air. The three values found vary significantly but are credibly between these two limits. The manufacturer lists the highest conductivity, which may be a conservative value to mitigate against liability. Values in the range of 0.02-0.08 W/mK range might be reasonably assumed based on the data found. Thermal conductivity is often abstracted as a thermal diffusivity (α), which is defined as $\alpha=k/\rho C_{p},$ where k is the thermal conductivity, ρ is the density, and C_p is the specific heat. One can compare parameters on the basis of the thermal diffusivity. Lyon et al. (2012) give thermal diffusivity of their polystyrene, which falls within the range calculated based on the range of thermal conductivities and most appropriate density and heat capacities, as found in Table 2.

Multiple sources for the heat of pyrolysis were found, and are detailed in Table 2. Given the significant figures of the reported data and the range, these values are thought to be only approximate. One normally expects the heat of pyrolysis to be functional with time, and for similar reasons, the extent of decomposition. The data found for the heat of pyrolysis do not reflect this level of fidelity.

Heat of combustion was found in a couple of sources and is fairly uniformly described as 39.8 MJ/kg. This is important because the heat of combustion is a good basis for selecting surrogate behavior. Most hydrocarbon fuels like gasoline and diesel fuel have heats of combustion around 40-42 MJ/kg. Further, their mean molecular weights can be somewhat similar to polystyrene. Thus, they can be used as good surrogates when modeling combustion processes without having to use styrene as the gaseous fuel, which might have more poorly characterized gas-phase thermodynamic data.

The thermal absorptivity is the fraction of thermal radiation that is absorbed when incident on the material. It is normally derived for smooth samples. This parameter can vary depending on the nature of the incident radiative flux and the surface conditions. The values found for polystyrene vary greatly, as indicated in Table 2. Thus, there is a large amount of uncertainty in this parameter. A partially decomposed organic material will normally have an increased absorptivity compared to a pristine sample. Thus, for a material in a fire, the absorptivity would be expected to tend towards the larger values in the table after a short exposure to a fire.

Assuming the applicability and conditions for Kirchoff's law exist, one may assume that the absorptivity and emissivity are the same.

Table 2. A summary of property data for polystyrene

Property	Units	Value	Source
Density	kg/m^3	60.0	MFGR Product Sheet
	kg/m^3	58.1	This work
	kg/m^3	1050	Lyon et al. (2012); (bulk PS)
	kg/m^3	1040	Babruskas (2003) (bulk PS)
Heat Capacity	J/kgK	1210	Incorpera and DeWitt (1990)
	J/kgK	1762-2265	Adapted from webbook.nist.gov (liquid styrene)
	J/kgK	1340	Babruskas (2003)
Conductivity	W/mK	0.03	Engineeringtoolbox.com
	W/mK	0.085	MFGR Product Sheet (R-value conversion)
	W/mK	0.17	Bockhorn et al (2000) (bulk PS)
	W/mK	0.027	Incropera and DeWitt
Heat of Pyrolysis	J/kg	1e6	Lyon et al. (2012); endothermic
	J/kg	1.3e6-1.9e6	SFPE (2002)
Thermal Diffusivity	m^2/s	1.04e-7	Lyon et al. (2012)
	m^2/s	2.3e-6-4.1e-7	Using best above values
Heat of Combustion	MJ/kg	39.7	Babrauskas (2003)
	MJ/kg	39.85	SFPE (2002)
Thermal Absorptivity		0.3-0.9	Babrauskas (2003)

Chemical Analysis

Proximate analysis was performed on a sample sent to ALS Environmental laboratories. Table 3 shows the results of the analysis. The material had no detectable moisture, fixed carbon, or ash. This means that the material decomposed much like a very pure substance, and there is little or no other material present. Were this material designed with a fire resistance additive, additional materials would be expected to be evident in this analysis.

Table 3. Proximate analysis results for the polystyrene

Sample	Moisture *wt%*	Volatile Matter *wt%*	Fixed Carbon *wt%*	Ash *wt%*
Polystyrene	<0.01	100.90	<0.01	<0.01

The ultimate analysis likewise suggests this is a simple material, with a composition that is very close to that of the monomer (just the trace amount of nitrogen). These results are found in Table 4. The experimental results in the table include the pure theoretical weight fraction that was calculated based on the styrene monomer. The nitrogen found could be due to either impurities in the original materials, or due to nitrogen gas being the blowing agent or a component of the blowing agent used for forming the foam. The differences between the theoretical and measured materials are otherwise a small percent of the total. It is therefore believed that the material tested is well representative of pure polystyrene.

Table 4. Ultimate analysis results for the pyolystyrene compared to a theoretical yield

Sample	Carbon *wt%*	Hydrogen *wt%*	Nitrogen *wt%*	Oxygen *wt%*	Sulfur *wt%*
Polystyrene	89.84	7.90	0.22	<0.50	<0.005
Theoretical Polystyrene	92.3	7.69	0.0	0.0	0.0

Kalberer et al. (2005) mentioned that, in 1996, Dow added hexabromocyclododecane as a fire retardant. The chemical analysis included an analysis of halogen species, which should have uncovered bromine if it were present in any significant quantity. There were no halogens detected to within the detection limits of the instrument (0.02 wt%). We therefore surmise that the block polymer tested is a pre-1996 variety, and that it does not contain any retardant.

Because the ash from these tests was negligibly low, there is no corresponding ash analysis for the polystyrene material.

TGA Analysis

Though Kalberer et al. (2005) performed TGA analysis on the foam samples, they neglected to include plots of the experimental results. The authors summarized the results in text form and state that the various types of polystyrene foam that were analyzed all decomposed at the same rate. However, that rate was not compared to any rates that can be extracted from previous studies that would allow an independent reviewer to affirm that results matched others in the literature. They tested materials with various suppressants. It can be inferred that any suppressant materials that were components of the polystyrene materials that they tested have minimal effect on the rate of pyrolysis. Suppressants rather serve to alter the char formation, and intumescence of the material. The mechanism by which they reduce flammability is by slowing the heat transfer to the inner materials, and reducing the total volatile yield.

For analysis herein, the polystyrene samples were tested under inert and air environments.

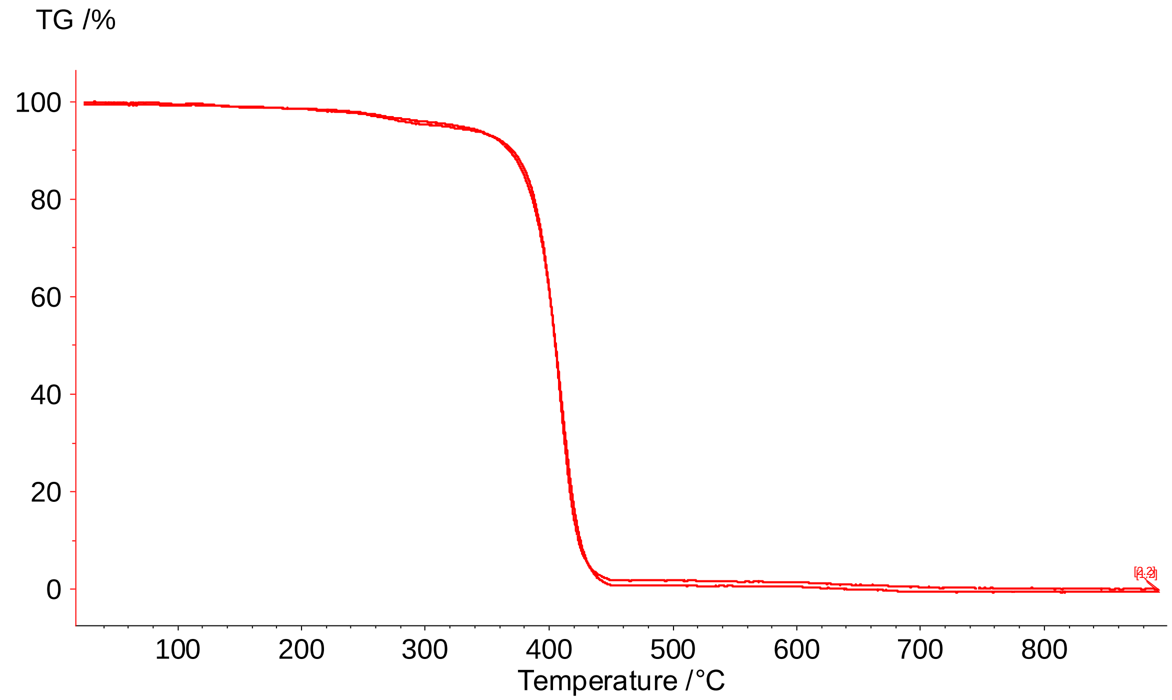

Figure 3. TGA results (two replicates in red) for polystyrene foam heated at 5°C/min nitrogen.

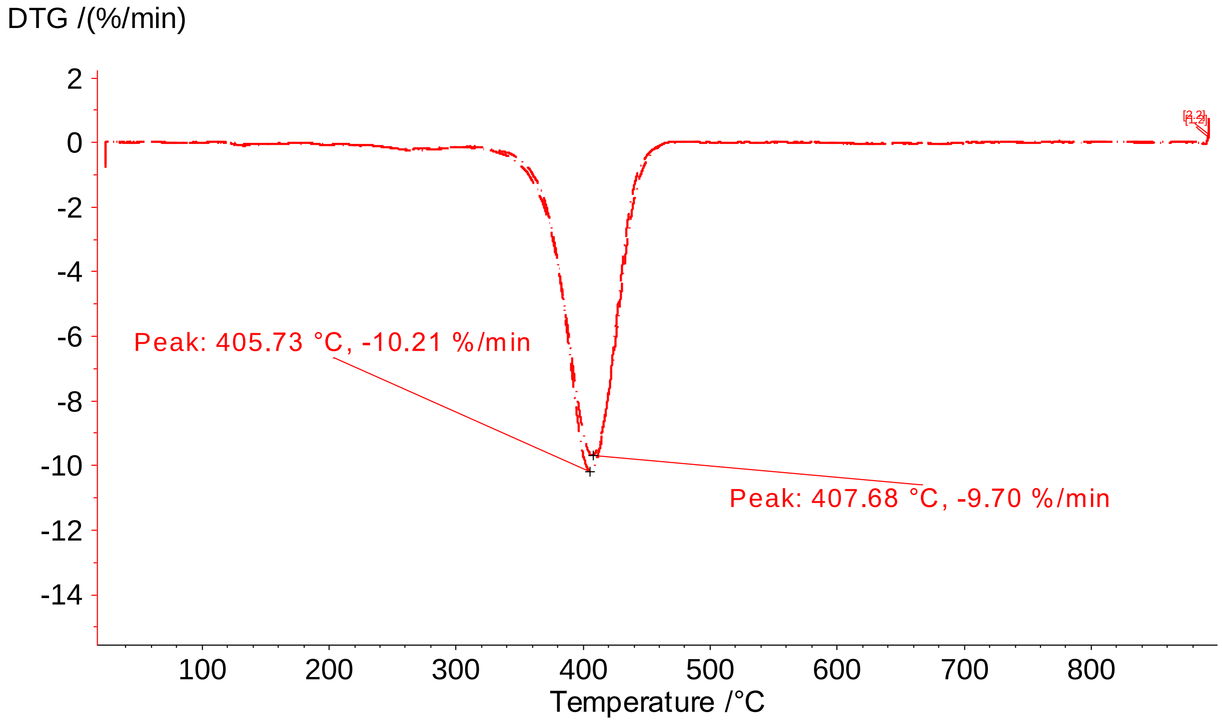

Figure 4. DTG curves (two replicates in red) for polystyrene foam heated at 5°C/min in nitrogen.

Figure 3 shows the TGA results for the polystyrene foam heated at 5°C/min in nitrogen, the first derivative in temperature is shown in Figure 4 for the KUMMSC supplied material. A single reaction step appears to adequately represent the behavior of this material. Peak decomposition rates are within a few degrees of each other for the replicates.

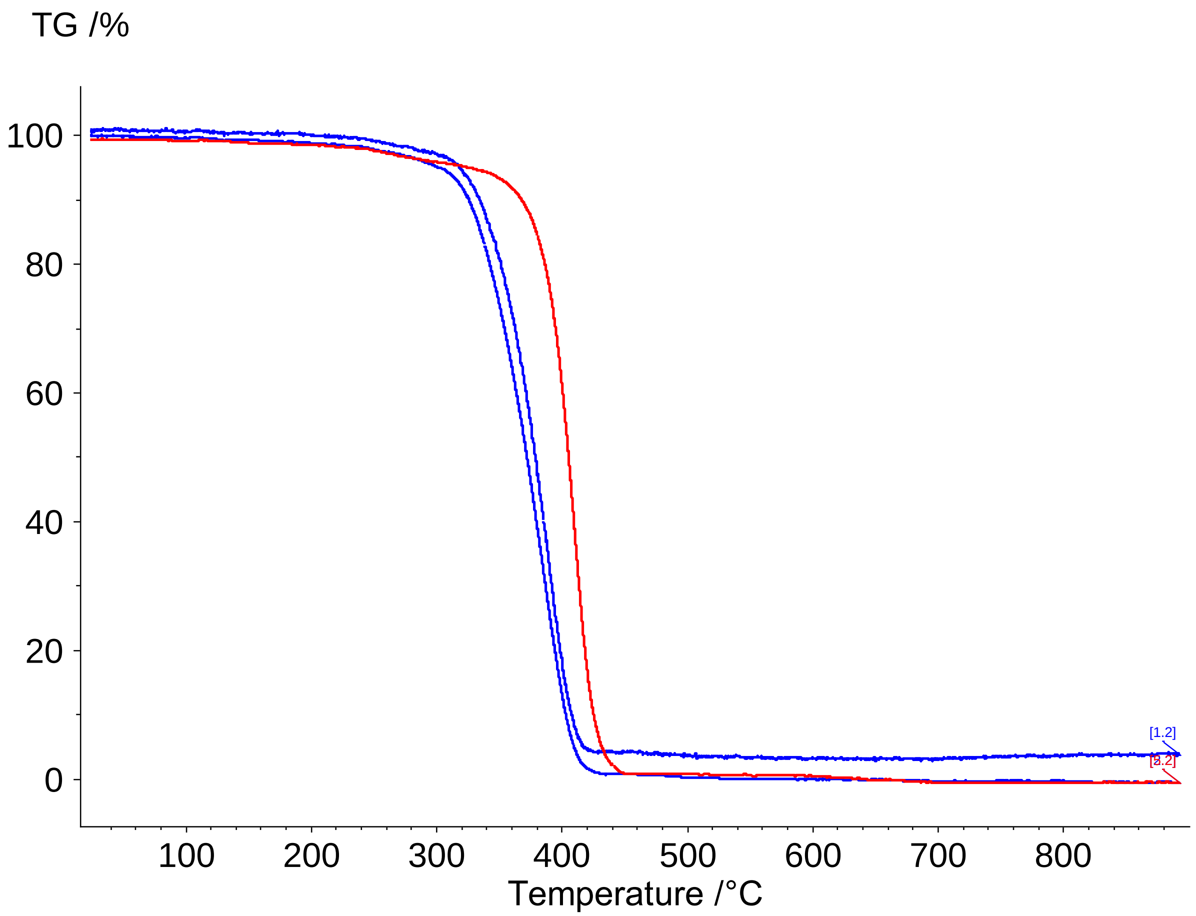

Figure 5. TGA results (two replicates in blue) for polystyrene foam heated at 5°C/min in air, compared to one of the polystyrene runs (in red) heated at 5°C/min in nitrogen.

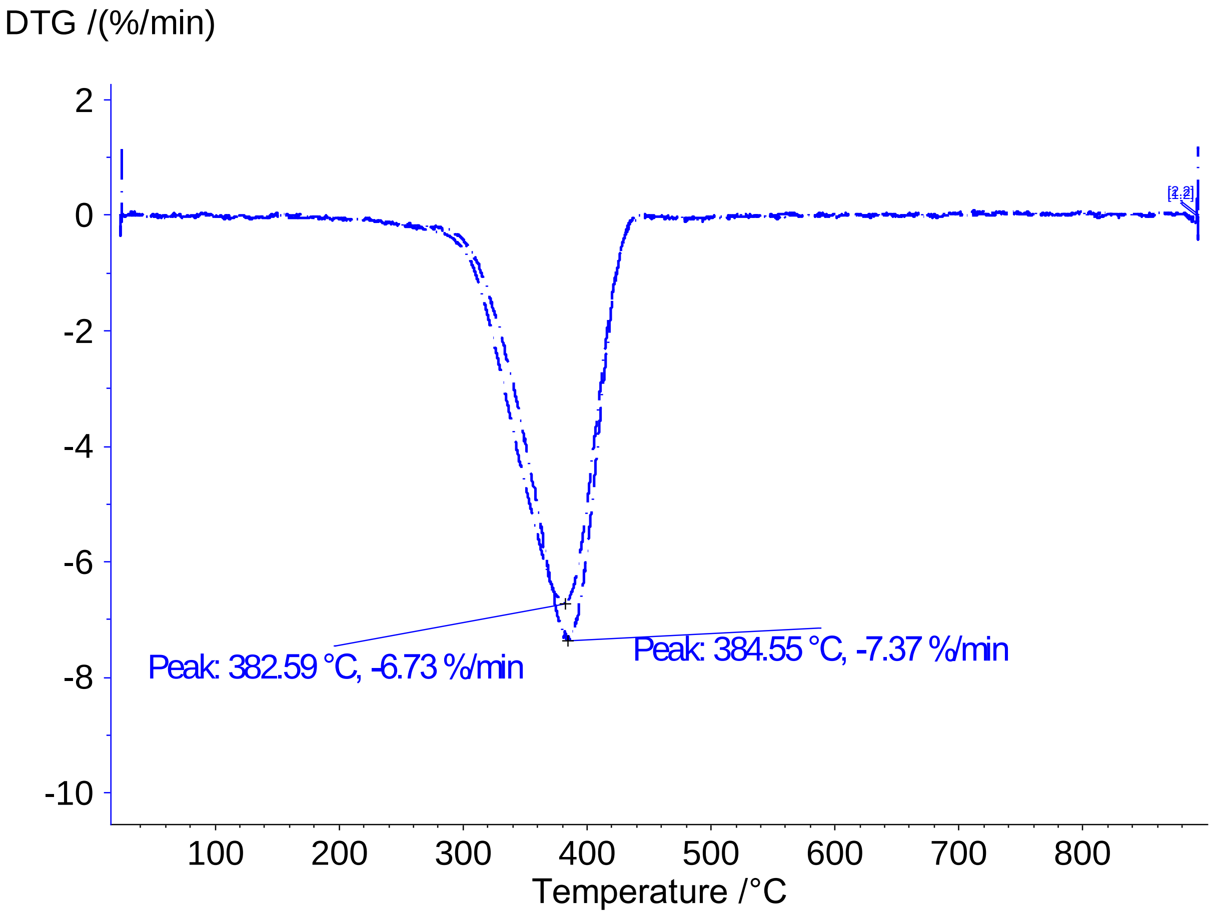

Figure 6. DTG curves (two replicates) for polystyrene foam heated at 5°C/min in air (blue). The peak temperature is ~ 20°C lower in air than in nitrogen (Figure 4).

Figure 5 shows the TGA results for polystyrene foam heated at 5 °C/min in air, the first derivative in temperature is shown in Figure 6. These results are consistent with Kannan et al. (2009) in that they show a fairly simple model of degradation. The replicates were close in agreement, suggesting a high degree of repeatability. The DTG curves are simply an alternate way of representing the TGA results that make the peak decomposition rate more evident.

Kinetics

When modeling the pyrolytic decomposition of solid materials, the parameter that is typically found to be the one with the greatest sensitivity to the results is the rate of pyrolysis, or the kinetics. It can also be the hardest to characterize with accuracy.

Kinetics are often modeled using an Arrhenius form, which involves an activation energy and a pre-exponential as fit parameters. An order of reaction may also be used as a fit parameter. This form of reaction mechanism can be derived from the kinetic theory of gases and is often applied to decomposing solid materials. These are the simplest types of rates and can be easily reproduced in a transport code.

More complex kinetic reaction formulations were described earlier for polystyrene pyrolysis. Fire modeling will often employ simpler one step reaction rates to reduce the complexity of the modeled system. The simple first-order rate (k) presented by Lyon et al. (2012) is the following:

$$k = Aexp(-Ea/RT)$$

In this equation, Ea is the activation energy, R is the ideal gas constant, T is the temperature, and A is the pre-exponential or frequency factor. The other simple model found in the literature is the Snegirev et al. (2012) model. It employs additional coefficients for a non-first-order fit (see the paper for more details). Base constants for both of these are listed below in Table 5.

Table 5. Kinetic parameters for polystyrene decomposition

Model	**Ea**	**A**	**Reference**
Units	*kJ/mol*	s^{-1}	
Arrhenius first-order	210	9.1e13	Lyon et al. (2012)
Arrhenius with coefficients	168	1.18e11	Snegirev et al. (2012)

The Lyon et al. (2012) model, being the simplest, is first evaluated versus the data found for the polystyrene sample. A comparison at the conditions of the TGA instrument is found below in Figure 7. The fit is not exact, but is fairly reasonable. The data suggest reactions occur slightly ahead of the model predictions for most of the decomposition. Most of the modeled reactions occur within about 10 degrees of the data. The model does not capture the early dip from the data, nor the late slow decline at the end of the tests. For the purposes of fire modeling, this should be sufficiently accurate to draw adequate conclusions.

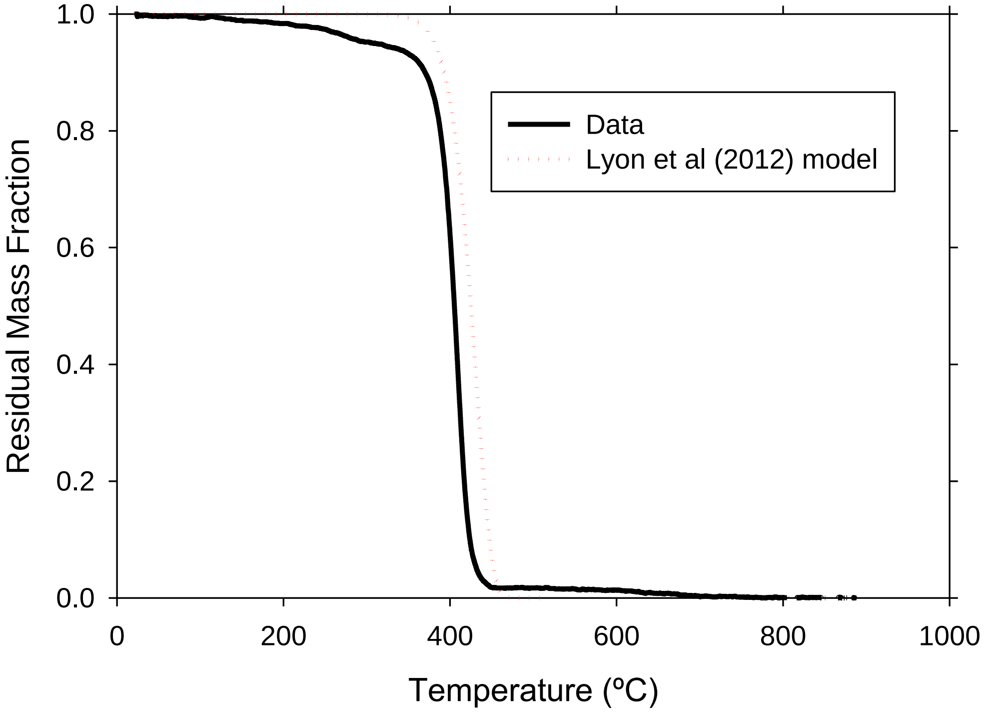

Figure 7. A comparison of polystyrene pyrolysis between data and model

Summary

Polystyrene block material provided for analysis matches well the theoretical values for pure polystyrene. The extensive existing data found in the literature on polystyrene is therefore thought to be applicable to this particular form of polystyrene material, and the existing data are probably reliable enough to predict the behavior of the material. Polystyrene is a fairly simple polymer and can be described adequately with existing data. Polystyrene is not particularly flammable but will decompose completely when engulfed in a fire. It has a heating value close to most hydrocarbon fuels, suggesting that it will readily combust if it is vaporized. Polystyrene goes through an intermediate phase change to a liquid as it is heated. In bulk configuration (with sufficient material and a large enough fire), the liquid will flow and pool below the decomposing polystyrene blocks. The liquid that spreads beneath the decomposing foam that was formed from decomposing material will then burn as a pool fire. If a dust cloud is formed, the polystyrene can detonate in a dust explosion.

4. SONEX FOAM

SONEX foam is a commercial product used to reduce sound reflections in a room. According to the Material Safety Data Sheet (MSDS) that was provided by the KUMMSC fire protection team (Pinta Acoustics, 1996), it is composed of a melamine-formaldehyde polymer. Compared to polystyrene, this material class is not nearly as common. The data on melamine-formaldehyde foams are more scarce than for polystyrene, as it presumably has fewer industrial applications. And it is not clear that the provided material is composed 100% of the fundamental melamine-formaldehyde polymer. It was therefore necessary to perform testing of the samples that were provided as part of this project to assess whether other studies of melamine-formaldehyde materials might also be applicable to this material.

Although several other papers were found that study melamine-formaldehyde polymers, the one most significant to the current effort is by Hirata et al. (1991). Based on the chemical model from Hirata et al. (1991), melamine-formaldehyde polymers have a fundamental composition of $C_{11}H_{16}O_5N_{12}$. The monomer molecule consists of two melamine rings (alternating nitrogen and carbon in a six-molecule ring structure). Compared to traditional polymers, this is very high in nitrogen content; the reader is referred to the paper for more structural information on the molecule. The characterization work by Hirata et al. (1991) will be referred to heavily throughout this section, with corroborating information from other studies as available.

The MSDS makes several statements with respect to the material. First, it lists "Flammability: None," which would seem to imply that it will not burn. What this typically means is that there is a characteristic test it was tested to, and no flaming was observed. This does not mean that it will not burn under conditions that are more extreme than were used for the test. Second, the MSDS indicates "Hazardous Combustion Product: None," but later states, "Specific Hazards: Carbon Monoxide (CO), carbon dioxide, hydrogen cyanide (HCN), fumes/smoke." The MSDS goes on to recommend that firefighters "always use self-contained breathing apparatus, as nitrogen oxide and carbon monoxides may be involved." The MSDS suggests extinguishing media for the material, once again suggestive that there is a chance for flammability. Taken as a whole, these statements appear to be contradictory. The subsequent material analysis should help give a more detailed understanding of what the expected behavior of the material might be to helpfully clarify the confusing MSDS statements.

Girods et al. (2008) study the thermal decomposition of urea-formaldehyde and melamine-formaldehyde resins in the context of wood waste containing these as binder materials. They present kinetics and focus on the fate of the nitrogen in the product gases. Hirata et al. (1991) evaluate the kinetics of decomposition and the product species from the decomposition process with a focus on the HCN. Girods et al. (2008) also look at combustion products. They find ammonia and isocyanic acid are formed in moderate amounts at lower temperatures, with no evidence of HCN or nitrous oxides (NOx).

This precipitated an examination of the toxicity of these products. Alarie (2002) describes the mechanistic understanding of the toxicity of HCN. It is a cellular disruptor (mitochondrial disruptor) and a respiratory disruptor (changes respiratory frequency). Alarie indicates lethal levels are 1-6 mg/l of blood. It has a cumulative effect with CO, so lethal levels can be lower if there is CO present. At an exposure level of 873 ppm for 30 minutes, 100% of animals are killed, and 50% of animals are dead in 29 minutes at a concentration of 177 ppm. The International Organization for Standardization publication ISO 13571 (2007) suggests it is 25 times more toxic than CO and, unlike CO, has an exponential behavior to concentration. Thus, with a large concentration, it takes only a short exposure to reach lethality. British Standards ISO 13344 (2004) lists lethal concentrations for 50% fatality (LC_{50}) for various products of fire. The 30-minute LC_{50} for rats for HCN is 165 µl/l (this is equivalent to ppm), 5,700 for CO, 170 for NO_2, and 750 for formaldehyde.

The evolution of HCN is most pronounced during the last stage of pyrolysis (as per Hirata et al., 1991). Morimoto et al. (1978) tested melamine-formaldehyde for ignition properties along with many other polymers. They found that it does indeed ignite and that it has an ignition temperature of 729 ºC, the highest of the polymers in their study. Babrauskas (2003) cites several studies that examine the ignition behavior of melamine-formaldehyde polymers. Studies uniformly suggest that melamine-formaldehyde materials do combust. However, it remains to be determined how well the formulations reported in the literature correspond to the SONEX material in question in this study.

Thermal Properties

Thermal data was not nearly as plentiful for this material as for the polystyrene. Limited data are summarized in Table 6. Density was provided in the MSDS, and it was also independently measured for the current analysis. The manufacturer suggests 10 kg/m^3, whereas our measurements suggest 9 kg/m^3 +/- 1 kg/m^3. The uncertainty factor is due to the irregular shape of the material on the side designed to diffuse sound. The uncertainty represents a dimensional measure of the valley and peak; thus, the true value is thought to reside closer to the middle of the range. Our measurements and MSDS density data are in good agreement, although our sample was slightly less dense than implied by the manufacturer.

We were unable to find data on the heat capacity and the conductivity for the material. However, the conductivity is probably very similar to that of the polystyrene foam, becasue the material is mostly air. It likely has a bulk conductivity of around 0.02 W/mK. Dielectric constants are often a good predictor for conductivity and are found in Babruskas (2003). The volume resistivity of melamine-formaldehyde is a few orders of magnitude lower than that of polystyrene, which suggests that the melamine should be more conductive. This is unlikely to change the bulk properties significantly for the foam, however, as the conductivity will mostly be a function of the air properties and porosity when expansion ratios are high (~20). The heat capacity might also be similar and usually varies by only a moderate amount for most materials. Thus, the error induced by assuming specific heat capacity similar to those for polystyrene or other similar polymers is not thought to be high. Similarly, the best estimate for the thermal diffusivity is that it is approximately the same as for the polystyrene foam.

Although no information on the heat of pyrolysis was found in the literature, heats of combustion can be evaluated from existing data. The SFPE handbook lists melamine as having a gross heat of combustion of 15.58 MJ/kg, and formaldehyde 18.76 MJ/kg. It is not clear if the polymeric melamine with formaldehyde will have a similar heat of combustion, or if the bonding process induces an unexpected variation. The material provided for this study was tested and analyzed for heating value. The data are presented in the next section and suggest that the SONEX material has a heat of combustion in the range of the two primary constituencies, melamine and formaldehyde.

Measurements for the thermal radiation absorptivity were found in Babrauskas (2003). The range was narrow, and these data are probably good through the decomposition process of the material. This is inferred because char typically has an absorptivity of around 0.9, which is in the proximity of that of the SONEX material.

Table 6. Thermal properties for the SONEX melamine-formaldehyde material

Property	**Units**	**Value**	**Source**
Density	kg/m^3	10.0	MFGR Product Sheet
	kg/m^3	9 +/- 1	This work
Thermal Absorptivity		0.8-0.9	Babrauskas (2003)
Heat of Combustion	MJ/kg	17.25	This work

Chemical Analysis

Proximate analysis was performed on a sample sent to ALS Environmental laboratories. Table 7 shows the results of the analysis. The material was surprisingly high in moisture at nearly 6%. Fixed carbon and ash were both below 1% but were not negligibly low, which was the case for the polystyrene. The remainder of the material was volatile matter.

Table 7. Proximate analysis results for the SONEX melamine-formaldehyde material

Sample	**Moisture** *wt%*	**Volatile Matter** *wt%*	**Fixed Carbon** *wt%*	**Ash** *wt%*
Sonex	5.81	92.73	0.69	0.77

The ultimate analysis is shown in Table 8. The theoretical SONEX weight fractions of the various elements are based on the basic monomer that was taken from the Hirata et al. (1991) paper.

Table 8. Ultimate analysis results for the SONEX melamine-formaldehyde material

Sample	**Carbon** *wt%*	**Hydrogen** *wt%*	**Nitrogen** *wt%*	**Oxygen** *wt%*	**Sulfur** *wt%*
Sonex	39.45	4.75	47.19	14.65	0.856
Theoretical MF	33.33	4.04	42.42	20.2	0.0

Analysis suggests that the materials are similar; however, it is noted that the SONEX material was measured with higher carbon and lower oxygen than the theoretical values. The presence of a minor amount of sulfur is surprising. Sulfur is often an impurity in organic substances and is less likely to be a design element. Not knowing the design process of the material, the presence of this element is difficult to explain in more detail.

Halogen species are often used to reduce flammability. This material was tested for bromine, chlorine, and fluorine, none of which was detectable at the minimum detection level of 0.02 wt%.

The heating value of the material was tested and found to be 17.25 MJ/kg on an as-received basis (including moisture). Dry SONEX material might have a slightly higher heating value. This lies between the heating values noted earlier for melamine and for formaldehyde.

Because this material produced significant ash, the ash was analyzed for metal content. The ash analysis yielded the results in Table 9, which is limited to the top four constituencies found in the ash.

Table 9. Ash analysis for the SONEX material

Element	**Abundance in Ash** *wt%*
Sodium	47.64
Carbon	34.56
Copper	8.24
Silicon	6.76

Curiously, there was no sulfur found in the ash even though it was found in the volatiles (see Table 8). It is also curious that carbon was found to be one of the major constituencies of the ash. This suggests that some of the carbon is fixed carbon and will not emerge under pyrolysis condition. The propensity for fixed carbon is not unusual, and is often seen in coal pyrolysis.

TG Analysis

TGA analyses were performed on samples of melamine foams. The melamine foam is a Sonex acoustic foam that is supplied by Pinta Acoustics. The polystyrene foam is a Styrofoam Highload foam produced by Dow. An image of the foam before TGA analyses is shown in Figure 8.

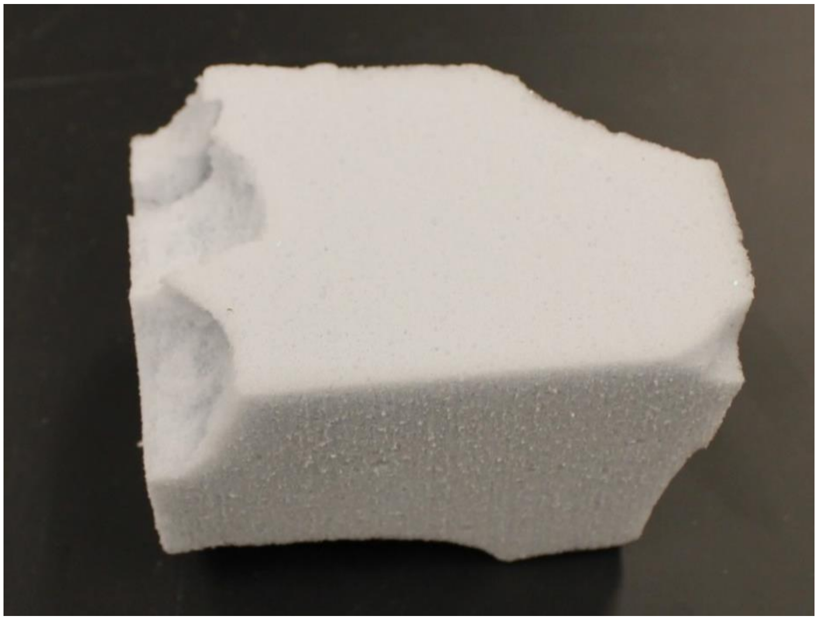

Figure 8. Picture of the Sonex melamine foam before TGA analysis.

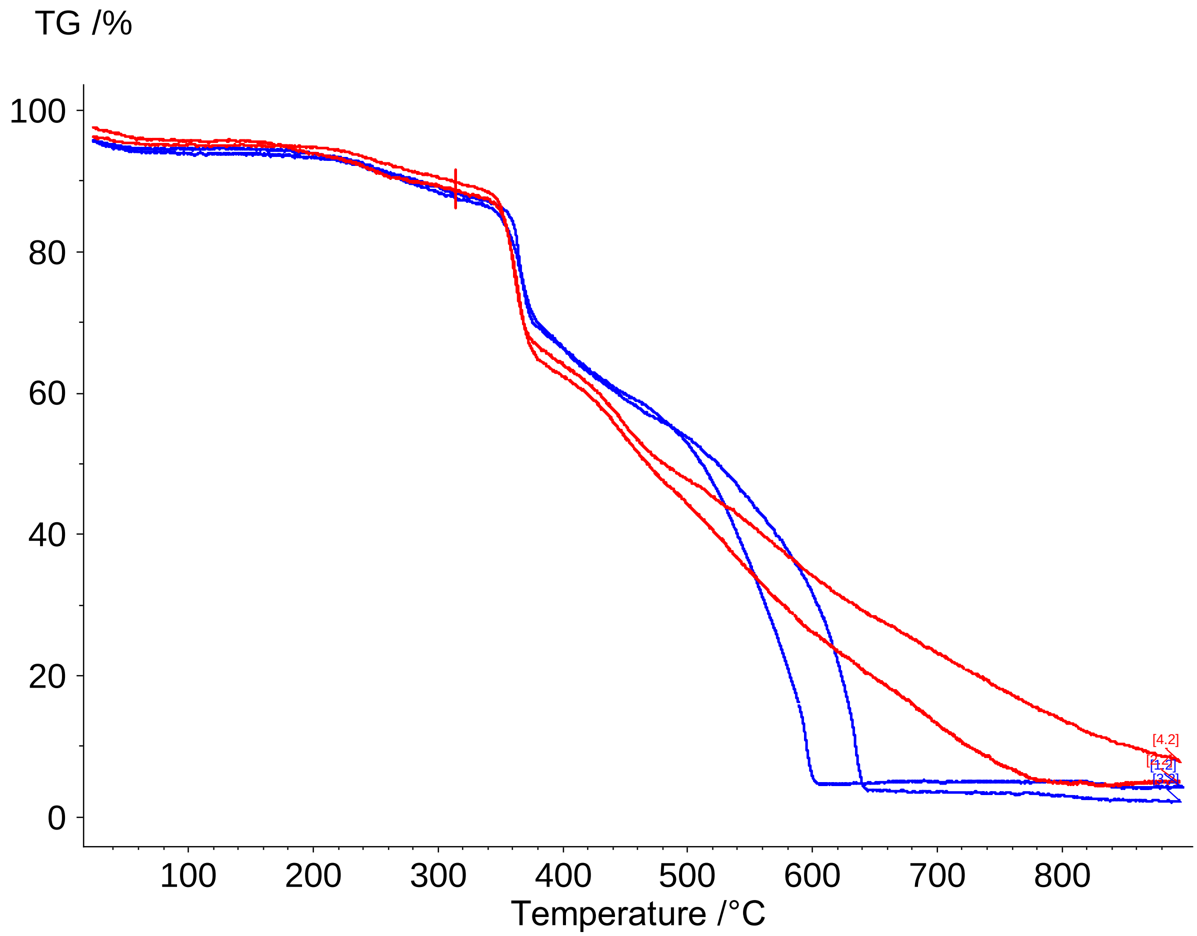

Figure 9. TGA results for melamine foam heated at 1°C/min in air (blue) and nitrogen (red). Differences between the nitrogen and air kinetics do not appear until after 400°C. The small spike in the nitrogen run at ~ 325°C should be ignored. There is some uncertainty in the kinetics at T > 500°C.

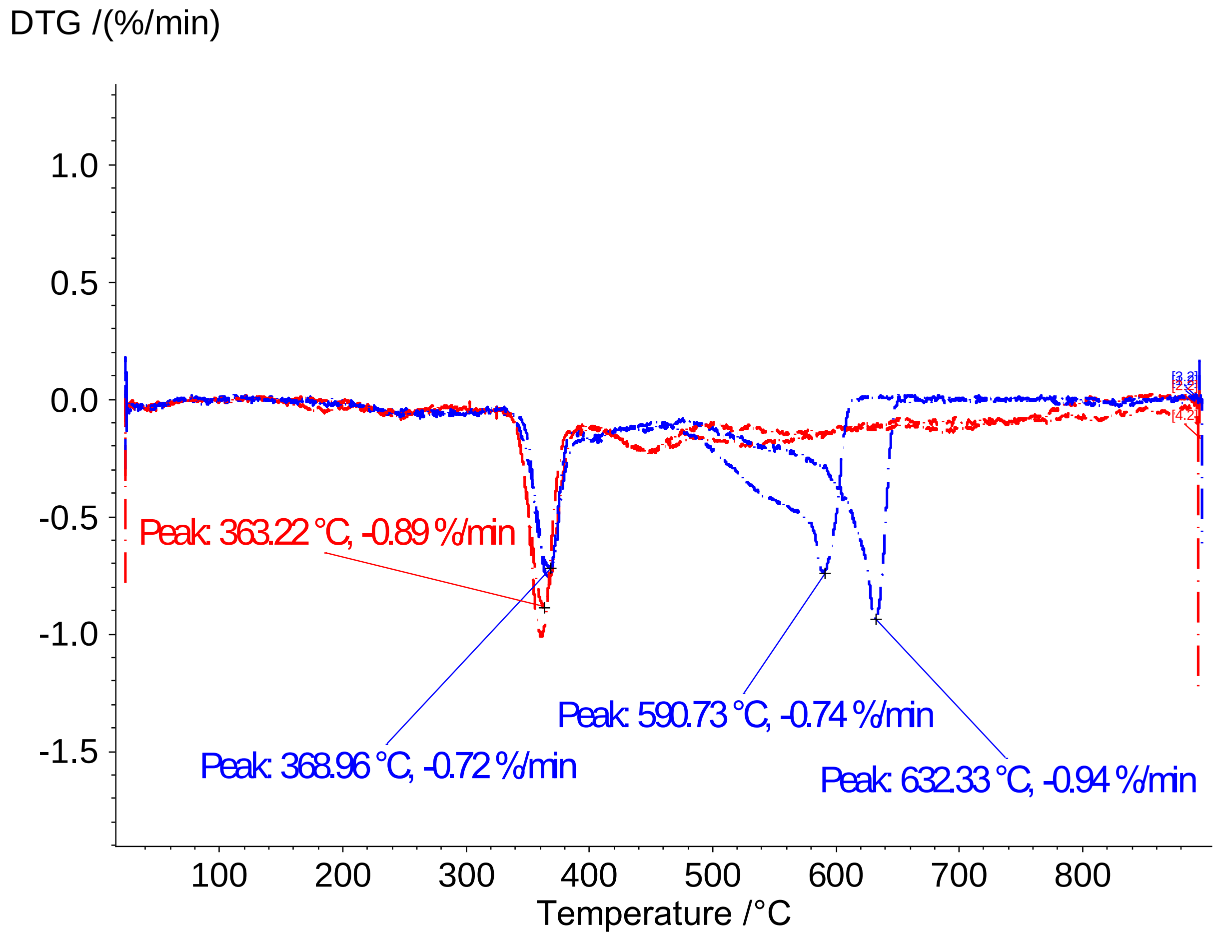

Figure 10. DTG curve for melamine foam heated at 1°C/min in air (blue) and nitrogen (red).

Figure 9 shows the TGA results for the melamine foam heated at 1°C/min. The first derivative in temperature is shown in Figure 10. Noticeable oxidation does not occur until around 400°C. The mass-loss profile shown in Figure 9 and Figure 10 is consistent with the results of Hirata et al. (1991) in the location of peaks, although the mass-loss rates for the material tested tend to be less than those shown in Hirata et al. (1991).

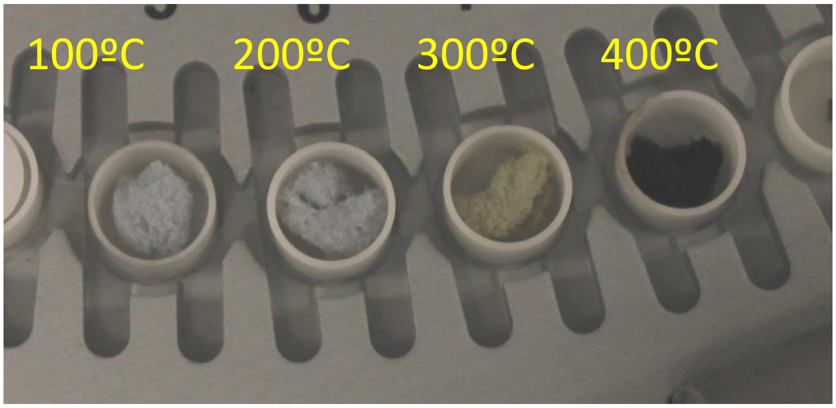

Figure 11. Image of Sonex foam heated at 100°C, 200°C, 300°C, and 400°C from left to right.

Figure 11 shows an image of ~3-mg samples of SONEX foam that were heated in nitrogen (150 ml/min) in a Netzsch TGA at 20°C/min, to 100°C, 200°C, 300°C, and 400°C (from left to right), and then held at that temperature (100°C, 200°C, 300°C, and 400°C) for 30 minutes. The crucibles were then cooled to room temperature and photographed to look for evidence of liquefaction. No evidence of liquefaction can be seen, which would be expected to appear as a morphological change in the form of the material.

Rheological Results

Figure 12 shows the rheological response of a slice of melamine foam that was obtained in a TA Instruments ARES rheometer at temperatures up to 200°C in nitrogen. A strain sweep and frequency sweep were performed at 30°C to determine the linear viscoelastic region for the melamine foam. The melamine foam was analyzed using the torsion bar fixtures with a 5.0 g of tension. Oscillatory data were collected every 2°C over the temperature range of 30 – 200°C with a strain of 2% and a frequency of 1 Hz. The foam was allowed to thermally equilibrate for 300 seconds at each temperature prior to data collection. In addition, the sample was oscillated for 5 cycles prior to data collection. The graph shows the storage and loss modulii of the material during oscillatory stress-strain measurements under a fixed imposed oscillatory strain. The storage modulus is the response of the material that is in phase with the applied stress and represents the solid-like behavior of the material. The loss modulus is the response of the material that is out of phase with the applied stress and represents the viscous or liquid-like response of the material. The results show that the storage modulus is always much greater than the loss modulus, indicating that the material is solid-like over the temperature range investigated.

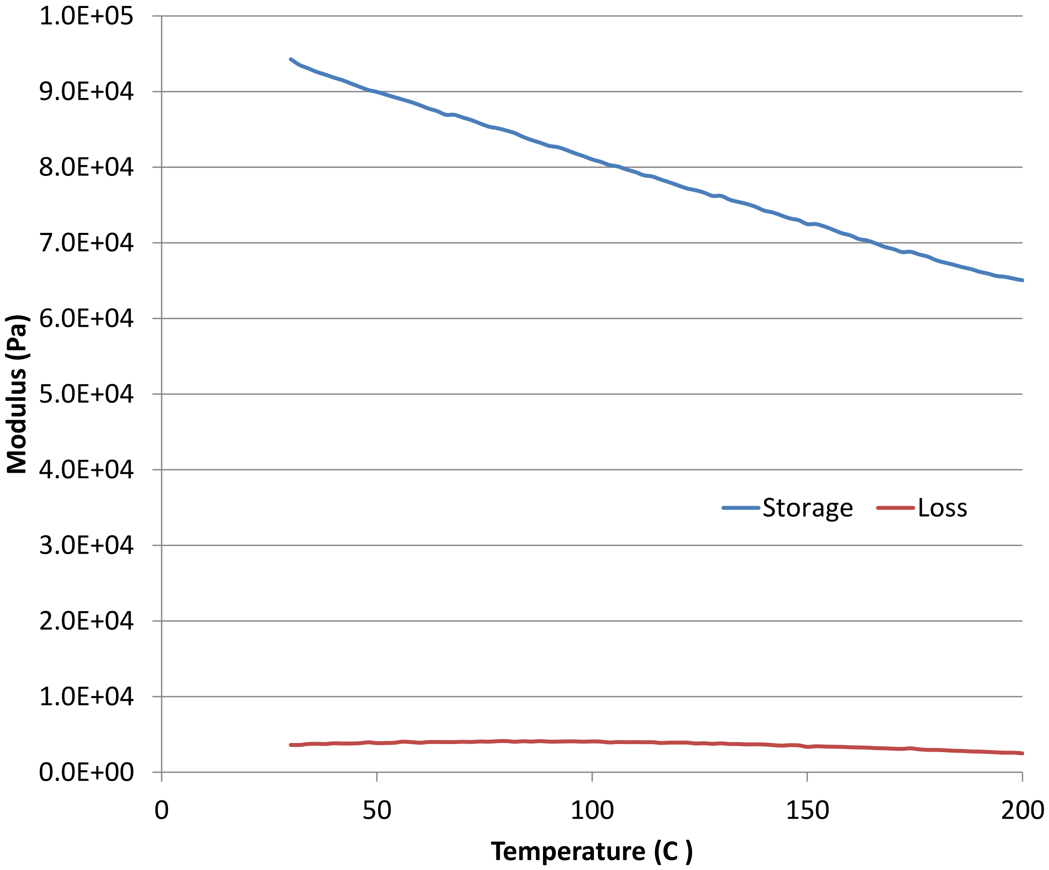

Figure 12. Rheological results of melamine foam up to 200°C.

Kinetics

Besides the TGA kinetic analysis performed in the previous section, there are two sources in the literature for melamine-formaldehyde material reactions. The first is Hirata et al. (1991). They noted three primary reaction rates during air and inert (He) pyrolysis. Rate constants listed in Table 10 are for melamine-formaldehyde mass loss in air. The study does not state the fraction of material that decomposes under each rate, so there is insufficient information presented to reconstruct a detailed model from the rates without inferring mass fractions that react through each pathway. In this respect, the kinetics model is incomplete and is only partially able to reproduce the measured decomposition curves.

Table 10. Kinetic parameters for melamine-formaldehyde polymers

Source	Stage	Activation Energy *kJ/mol*	Pre-exponential Factor s^{-1}
Hirata et al. (1991)	First	136	4.0e10
	Second	291	2.3e21
	Third	68	10.9
Girods et al. (2008)	First	56.1	1.37e3
	Second	130.7	2.18e9

Assuming that a third of the source material reacts to gas in each reaction stage, a simulated TGA curve can be constructed from the rate constants of Hirata et al. (1991). The schematic for the assumed model is illustrated in Figure 13. Based on this assumption, the rate data can be compared to the TGA curves presented earlier. This comparison is found in Figure 14. Note that the TGA data decrease shortly after the heating begins, which suggests loss of water. This is consistent with the findings from the proximate and ultimate analysis. The data suggest limited reactions occur before the model predicts inception. The first two steps occur somewhat later than the model suggests, but then the final step is much faster than the Hirata et al. (1991) model suggests. Using these kinetics will result in reactions that are initially a little faster than the data but at later times much slower. The fact that the model and data curves decline at similar temperatures (roughly 400ºC) suggests that the kinetic rates, although not perfect, are an adequate representation of the present material.

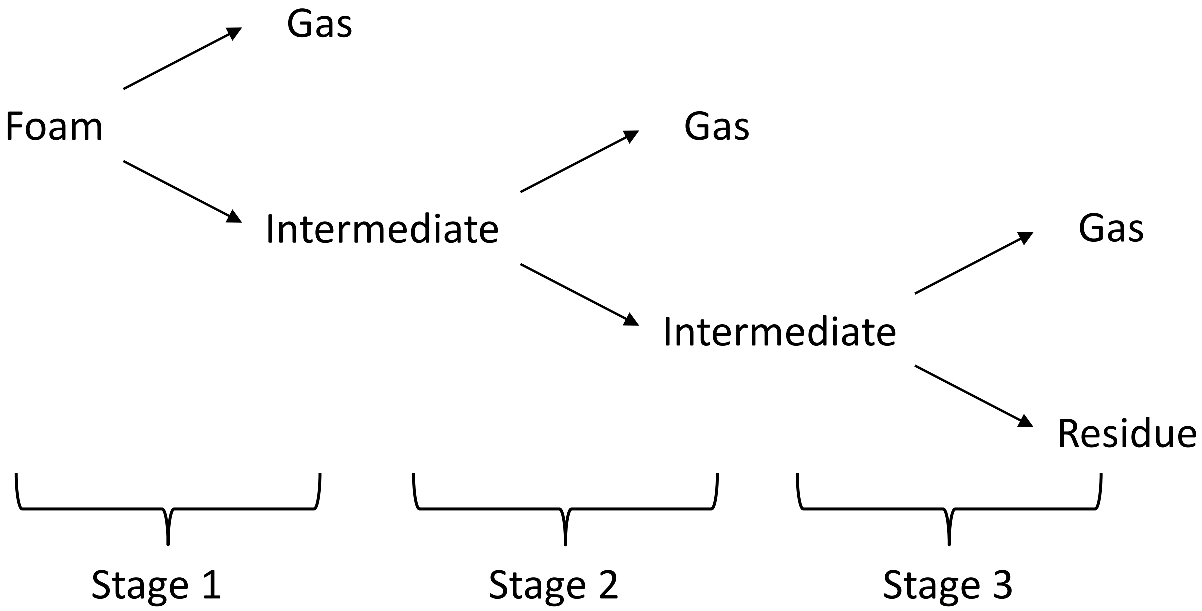

Figure 13. A schematic of the assumed Hirata et al (1991) model for melamine-formaldehyde decomposition.

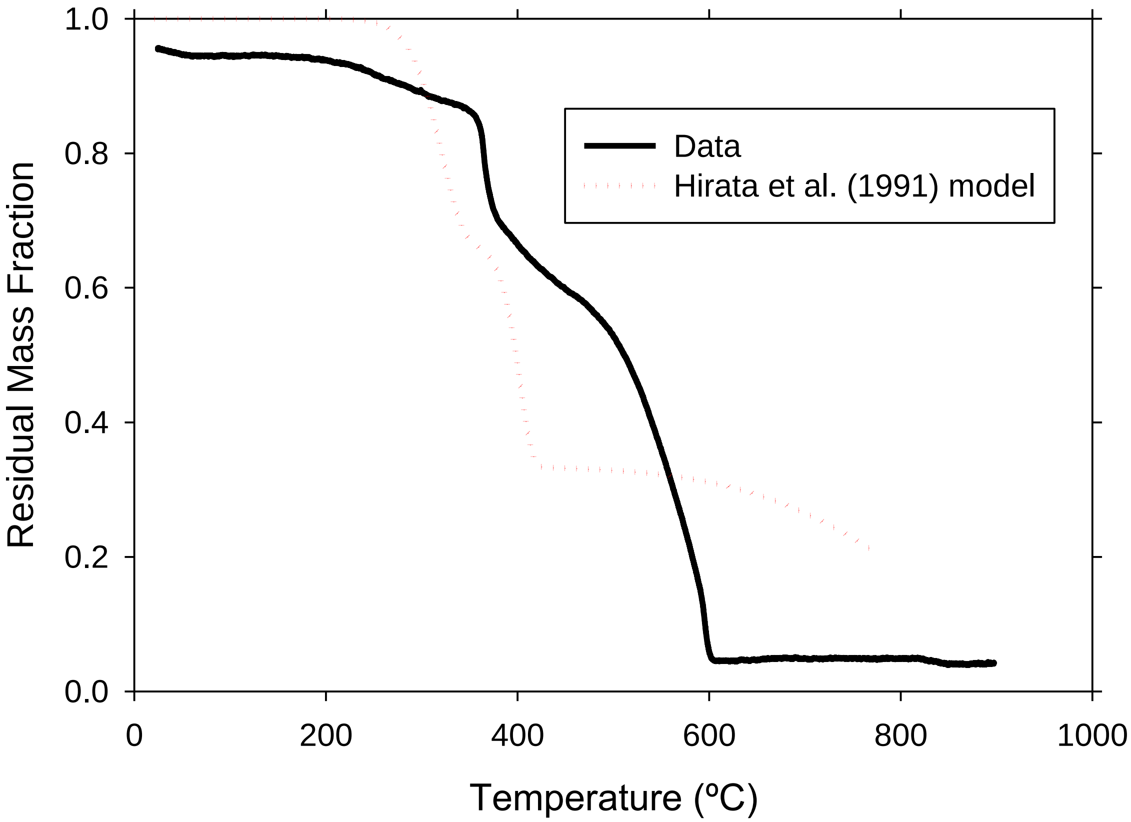

Figure 14. A comparison between the SONEX data and the model of Hirata et al. (1991)

For simplicity's sake, the Girods et al. (2008) model might make more sense to employ; however, the Hirata et al. (1991) model correlates the formation of HCN with the various stages of decomposition in their model. This correlation might be more useful because the reaction rate can be linked to the emission of toxic HCN products.

Summary

The SONEX soundproofing material is primarily a melamine-formaldehyde polymer-based foam with a very low density (10 kg/m^3). It is not a pure polymer, because there are significant quantities of inorganic and perhaps impurities in the matrix as tested. Where data exist in the scientific literature on the material properties for melamine-formaldehyde polymers, the comparison with data from the analysis of a SONEX material sample are in respectable agreement. This suggests that there is good reason to expect that literature data can be applied to estimate the behavior of the SONEX foam in a fire.

Contrary to what might be inferred from conflicting statements in the MSDS, the SONEX foam material will burn. It has a heat release rate of a little less than half that of typical hydrocarbon fuels and about that of low-grade woods. While it will burn, this does not mean that it is highly susceptible to fire behavior or is easily ignited. It will probably resist active burning and may require a significant external source and large quantities of material present to sustain active burning. Unlike the polystyrene foam, it will not go through a liquid transition. It forms a char and yields a moderate amount of ash. As is suggested by the MSDS, the material can emit toxic fumes when exposed to a fire. HCN can be a major product under certain conditions, which has a fatal exposure limit much lower than many other typical combustion product gases. It also might form soot, soot precursors, CO, formaldehyde, NO_2, and ammonia.

5. HYDRAULIC OIL

Hydraulic oils are historically linked to fires under storage conditions, and also related to pressurized failure of hydraulic lines. The resulting sprays from pressurized lines can easily be ignited by a spark, and can burn intensely. Hydraulic oil is a class of material and is not necessarily a uniform or homogeneous liquid. The oils are not particularly prone to combustion and are difficult to ignite in a container or as a liquid pool. However, if these oils are part of a spray, they can ignite much easier because of the high surface-area-to-volume ratio, and this is typically where hydraulic oil fires are considered high risk. Thus, one must be cautions when using hydraulics with an active ignition heat source. Hydraulic oils are most commonly a mineral oil, although there are grades of hydraulic oil that are less susceptible to combustion that contain other constituencies. Silicon substitutions for carbons in mineral oil blends have this effect, as do other liquid compounds. Because they are naturally produced, mineral oils are likely the most inexpensive hydraulic fluids. It is therefore believed that the inexpensive mineral oils are also the most commonly used. Babrauskas (2003) provides some information on hydraulic oils, with a focus on aviation hydraulics. Other data on hydraulic oils are found in the SFPE Handbook and in a general heat transfer reference book (Holman, 1991).

Hydraulic oils are similar to many of the heavy hydrocarbons in terms of fire behavior. It takes a moderate amount of energy to vaporize oils, so oils tend to be stable and not vaporize and burn at room temperature. However, once oils begin to burn, they can be difficult to extinguish. A pool of liquid oils that is actively burning will normally have flames spread completely across the exposed surface, this (the exposed area) being the most significant component to the burn rate. The properties for hydraulic oils will vary by type. Some data have been found and summarized in Table 11 for hydraulic oils and hydraulic oil surrogates.

Table 11. Some physical properties of mineral oil hydraulic oil

Property	**Units**	**Value**	**Source**
Density	*kg/m*^{3}	800-1000	SFPE (2002), Holman (1991)
Heat Capacity	*J/kgK*	~2000	Holman (1991) (engine oil)
Conductivity	*W/mK*	1.5	Holman (1991) (engine oil)
Flash point	*ºC*	102->500	Babrauskas (2003)
Auto Ignition Temperature	*ºC*	232->500	Babrauskas (2003)
Heat of Combustion	*MJ/kg*	4.1-42.3	Babrauskas (2003)

Mineral oils are composed mostly of carbon (~90%) and hydrogen (~10%). Organic oils will burn much like organic fuels in terms of gas products. One can expect soot and carbon monoxide to be two of the more hazardous products of combustion produced in significant quantities. Other oils will not burn at all, with a range of oils between those two cases. Based on very similar properties, the mineral-oil-based hydraulic oils should burn to a first order in a way that is similar to diesel fuels or kerosene-based aviation fuels.

6. WOOD

Focusing on commercial sources of wood, the literature contains a great quantity of information on the behavior and reactions of wood to fire. Wood is most generally either hard or soft wood and can be processed many different ways. Processing commonly includes a pressurization treatment that infuses trace metals or other minerals to help improve longevity. Examples of such treatments may include chromium, copper, borates, chlorine, and potassium. Other treatments include painting, staining and varnishing. Thus, the exterior of the wood may have a finish that changes the bulk combustibility in a fire. Composite woods may not be composed of all wood. Binders such as glues and epoxies can be used to adhere composite panels. Thus, a glue or binder can make up a component of the matrix for commercial fiberboards.

Woods vary significantly in their properties. A range of properties for structural woods are found in Table 12. Wood is heterogeneous, composed of various constituencies at the molecular level. It is also isotropic, having different properties depending on the direction of measurement. Detailed studies of wood pyrolysis have shown the importance of these parameters to the behavior of wood in fire-like conditions.

Table 12. Some physical properties of wood

Property	Units	Value	Source
Density	*kg/m^3*	300-800	SFPE (2002), Holman (1991); Babrauskas (2003)
Heat Capacity	*J/kgK*	1000-2000	SFPE (2002)
		1800	Babrauskas (2003) (spruce)
Conductivity	*W/mK*	0.125-0.185	Babrauskas (2003)
Auto Ignition Temperature	*ºC*	287-355	Babrauskas (2003)
Heat of Combustion	*MJ/kg*	16-20	SFPE Handbook (2002)

Bulk wood is not normally considered a fire hazard for the inception of fires. Wood fires often go out without external stoking or other such agitation. Structural wood is not a major fire-ignition hazard but will participate in a fire if it is subjected to conditions that have prolonged thermal exposures.

There are numerous models for the pyrolysis of wood in the literature. Superposition is a common assumption, which is that the wood will degrade according to the rates of the primary constituencies, namely cellulose (~40%), hemicellulose (~20%), and lignin (~35%). Constituency values also vary depending on the origin of the wood but are approximate for most woods. The value of these types of models is that they portend to be able to model a wide range of materials without having to know more than an estimate of the major constituencies. This is a nice conceptual theory; however, practical application of such models suggests they are only approximate in their ability to predict material variations and constituency product evolution. Examples of such superposition models in the literature include Kofopanos et al. (1989) and Miller and Bellan (1997). Many other models exist that are more narrowly aimed at specific materials (i.e. subspecies of wood) and are more complex derivations designed to model only one specific kind of wood. These models require knowledge of the wood source and risk error due to tree-to-tree variations that occur due to the differences in the growth environment. The superposition models will probably suffice for a first-order approximation to the behavior of woods in fires. These models were reviewed in a dissertation by Brown (2001), which contains a large number of other relevant references on wood pyrolysis.

Decomposing wood forms a char, which is a carbon residue. It also contains a moderate amount of mineral ash. The char formation is rate relevant because the rate reaction of wood can proceed in a kinetic-limited regime (temperature control) and a diffusion-control regime (species transport control). This second regime depends heavily on the details of the char layer. Char formation is not predicted well, although factors influencing the formation of char are moderately well understood.

The toxicity of wood burning is not particularly high. Common inhalation, such as campfire smoke, is tolerable at low levels. Carbon monoxide, soot, wood acids, formaldehyde, volatile organic carbons and radical hydrocarbons are expected to be present, and represent some of the more hazardous products. Treated lumber has potentially worse emissions, which are induced by the treatment. Altarawneh et al. (2009) suggest that treated wood can yield trace amounts of dichloro-benzenes (dioxins), which are highly toxic. The magnitude of the formation of these will depend greatly on the type of wood in the fire and the type of treatment imposed on the wood.

Representative molecular structures exist for wood, as presented in Rowell, (1984). These structures are large-chain molecules without significant repetition. Thus, the characterization of wood by elemental composition is complex. Compared to the other polymers in this document, the chemical constituency of wood is not well known and can vary; there are trace minerals and low (~5%) amounts of nitrogen. Thus, the potential for forming HCN in a fire is much lower compared to materials with higher nitrogen content. Wood has a significant amount of oxygen (~40%), which is one of the reasons the heating value tends to be much lower than refined hydrocarbon fuels.

7. POLYURETHANE FOAM

Sandia National Laboratories has a long history of polyurethane foam study. Some examples of recent work include Hobbs (2005, 2006), Hobbs and Lemmon (2004), and Hobbs et al. (2000). From Hobbs et al. (2000) it is understood that polyurethane is a complex polymer with six primary structural units. From Wang et al. (2014), we find a typical mass based composition of polyurethane of 62% carbon, 20% oxygen, 6% hydrogen, and 6% nitrogen. Polyurethane foam is used in packaging and is a common polymer for shipping container packing materials. It is often used in furniture design. Polyurethane is also a very common industrial material, so data are readily accessible. Table 13 lists some thermal constants found in the literature.

Table 13. Some physical properties of polyurethane foam

Property	**Units**	**Value**	**Source**
Density	*kg/m³*	38	Babrauskas (2003)
	kg/m³	353	Hobbs et al. (2000)
	kg/m³	100	Wang et al. (2014)
Heat Capacity	*J/kgK*	1300-2200	Hobbs et al. (2000)
	J/kgK	1460	Wang et al. (2014)
Conductivity	*W/mK*	0.059-0.092	Hobbs et al. (2000)
	W/mK	0.03	Wang et al. (2014)
Thermal Diffusivity	*m²/s*	1.5e-6	Babrauskas (2003)
Auto Ignition Temperature	*ºC*	518	Babrauskas (2003)
Heat of Combustion	*MJ/kg*	10.1	Grexa et al. (1996)
	MJ/kg	18.4-45.3	Babrauskas and Grayson (1992)

The density of polyurethane is dependent on the formation process. The values given in Table 13 are suggestive of the various densities encountered. The values from Hobbs et al. (2000) are likely most applicable since they pertain to foams used in the application space of the study. For conductivity, the two sources in Table 13 show moderate variation. Compare these to the similarly derived density numbers, and it can be deduced that they are consistent. As density decreases, the conductivity correspondingly decreases. The heat of combustion is not well settled, with a wide range of values found in the various sources. The variations in the Babrauskas and Grayson (1992) data are related to the imposed heat flux. This suggests that the decomposition process plays a role in the volatile release. Conservation of energy suggests that char formation would then retain much of the energy not liberated in the reaction and flaming. This further suggests that the best assumption probably tends to the higher side of the measured values, which would also be conservative when considering risk.

According to the SFPE Handbook (2002), polyurethanes do not break down below 475 K (202ºC) and tend to decompose slowly. They produce HCN, and CO in increasing quantities with increasing temperatures, along with other minor toxic products.

Numerous reports have been published that detail mechanisms and models for predicting the rates of thermal decomposition of polyurethane materials. Notably, Pau et al. (2013) review a few past studies and present the derived kinetic expressions from each study. In addition, Pau et al. (2013) present some of their own expressions. Reactions all fit the Arrhenius model presented earlier. Wang et al. (2014) also present a kinetic study that breaks down the decomposition of the polyurethane into three stages. The first stage involves only about 7% mass loss, while the remaining mass is roughly split between the last two stages. The third stage is due to oxidative reactions. Another more complex mechanism for the decomposition of polystyrene can be found in Hobbs et al. (2000). They use percolation theory to model the bond behavior in a surrogate or representative model for the polymer. A more advanced model, this method is difficult to apply in fire modeling tools without significant accommodation; however, the model might be expected to give higher fidelity predictions because it more closely approximates that which is believed to be the physical behavior of the material.

8. SUMMARY

Data for five materials were analyzed for properties related to fire modeling. In general, adequate information was found or measured for all materials. Some materials are better characterized than others. The materials are listed in Table 14, along with a brief description of the findings from this effort.

Table 14. Summary of results

Material	**Findings**
Polystyrene	Excellent data for kinetics and for heat transport, high confidence in model properties and kinetics
SONEX	Material is mostly melamine-formaldehyde, with adequate properties available, and some appropriate surrogate properties
Hydraulic Oil	Good data exist for general properties, good surrogates exist for common types
Wood	Moderate uncertainties exist in properties, mostly due to the natural and commercial variety in woods
Polyurethane Foam	Good data exist for this material, plenty of properties are published with acceptable accuracy

All materials form toxic products in fire, with the SONEX material having the highest hazard due to the high nitrogen content in the material. Polyurethane and wood have intermediate hazard due to toxicity (more complex products, nitrogen constituencies), with the lowest hazard related to the oils and polystyrene (mostly soot and carbon monoxide).

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