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Optimizing Laboratory Pyrolysis Methods to Compliment Real World Fire Debris

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OPTIMIZING LABORATORY PYROLYSIS METHODS TO COMPLIMENT REAL WORLD FIRE DEBRIS

by

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B.S. STETSON UNIVERSITY, 2013

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ABSTRACT

Forensic analysts are tasked with determining the presence of ignitable liquid residue in fire debris. Analysis of fire debris allows the analyst to understand how the fire occurred. However, the presence of some substrates can potentially impact the identification of ignitable liquid residue and classification of a sample as positive or negative for the presence of ignitable liquid. Pyrolysis of building materials and furnishings (substrates) lead to background interference within the resulting chromatographic profile. To combat misclassification of a sample as positive for ignitable liquid residue, knowledge of the pyrolysis products from individual substrates is of utmost importance. However, unburned reference samples from a fire scene can be difficult to obtain. The use of a database in conjunction with the analysis of the samples can lead to a more complete analysis of fire debris.

Within this research, four different burn methods (modified destruction distillation method, top heat, bottom heat, and tube furnace) were utilized in burning eight different flooring substrates (polyester, nylon, and olefin carpeting, carpet padding, vinyl flooring, laminate flooring, yellow pine, and plywood) to obtain pyrolysis/combustion product profiles. Each burn method was performed at three different burn times for a total of twelve different burns of each substrate. Standard methods, ASTM E1412-12 and ASTM E1618-14, were used in the extraction and interpretation of the laboratory burn products. Principal component analysis (PCA) was used to relate the laboratory burn results to neat ignitable liquid/substrate and large scale burn data sets.

Laboratory burn data projected into the PCA space displayed that the laboratory burn data is similar to the data contained within the ILRC and Substrate databases. Differences observed within laboratory burn data projections illustrated the variability of the laboratory burn methods. The composition of the substrate dictated the pyrolysis/combustion products produced. While this

research only focuses on flooring substrates, an increase in the number of different types of materials in the Substrate Database can aid analysts in identifying common pyrolysis/combustion products observed in fire debris.

I would like to thank Dr. Sigman, Mary Williams, Dr. Bridge and the entire faculty at National Center of Forensic Science for allowing me the opportunity to pursue my dreams of obtaining knowledge in the field of forensics. My coworkers and friends alike have aided me in my pursuit of understanding. I would also like to thank my mother and father as they have impacted my life and I would love to be able to support them in the future if need be. Many trials and tribulations have come up along the way, but we have had the determination to overcome those obstacles together. I cherish their love and support as words cannot fully display my thanks for them, this is for you.

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LIST OF ABREVIATIONS (or) ACRONYMS

ACS	activated charcoal strip
AR	Aromatic
ASTM	American Society for Testing and Materials
BFFEA	Bureau of Forensic Fire and Explosive Analysis
BH	Bottom Heat
˚C	Celsius (centigrade) in degrees
cm	centimeter
C_n	Hydrocarbon range with n as a number (C_8)
CS_2	Carbon Disulfide
EIC	Extracted Ion Chromatogram
FURN	Furnace
GAS	Gasoline
GC-MS	Gas Chromatograph – Mass Spectrometer
HCl	Hydrochloric acid
IL	Ignitable Liquid
ILR	Ignitable Liquid Residue
ILRC	Ignitable Liquid Reference Collection
ILRCC	Ignitable Liquid Reference Collection Committee
Inc.	Incorporated
ISO	Isoparaffinic
LSB	large scale burn

m	meter
m/z	mass-to-charge ratio
MDDM	Modified Destructive Distillation Method
Min	minute
MISC	Miscellaneous
mL	milliliter
mm	millimeter
MPD	Medium Petroleum Distillate
MS	Mass Spectrometer
n-alkane	Normal Alkane
NA	Normal Alkane
NCFS	National Center for Forensic Science
NIST	National Institute of Standards and Technology
NP	Naphthenic-Paraffinic
OXY	Oxygenate
PC n	Principal Component n (where n refers to a number; PC1)
PCA	Principal Component Analysis
PD	Petroleum Distillate
PET	Polyethylene Terephthalate
PVC	Polyvinyl Chloride
SRN	Standard Reference Number
SUB	Substrate

TWGFEX	Technical Working Group for Fire and Explosions
T/SWGFEX	Technical and Scientific Working Group for Fire and Explosions
TCPP	Tris (1-chloro, 2-propyl) phosphate
TH	Top Heat
TIC	Total Ion Chromatogram
TIS	Total Ion Spectrum
TXIB	2,2,4-trimethyl-1,3-pentanediol diisobutyrate
UCF	University of Central Florida
µL	microliter

CHAPTER 1: INTRODUCTION

Arson has been an increasing problem in today's society for police investigators, analysts and everyone impacted by the fire. In the United States in 2013, there were 1.4 million fires across the entirety of the country.[1] It is estimated of those 1.4 million fires that occurred in the United States, that 31.7% of the fires were residential.[1] A residential fire is not only affecting the lives of individuals within the homes, but those around them as well. The fact that a combined 23% of the residential fires were committed intentionally or are under investigation displays the volume of arson attacks that are occurring within the United States.[1] Fires are a growing concern that cost the lives of individuals and damage the natural world with destructive force. To make matters worse, the destructive nature of fire is variable as no two fires are alike in intensity, size, and content of environment that is burning.[2] It is the job of the analyst to determine the presence of possible ignitable liquids at a fire scene. Investigative efforts in collection and analysis of the ignitable liquids are difficult as the destruction will not only yield possible ignitable liquid residue, but the breakdown of material within the fire causes interfering patterns adding another layer of difficulty.[3] This struggle is one of the main causes for arson scenes that were reported many years ago to still be under investigation to this date.

Arson scene investigation requires adequate search techniques of the perimeter of the fire scene searching for signs of forced entry and leads to the center of the burn area. The dynamics of fire can be affected by many factors, but three main components will always be present in some ratio of heat, fuel and oxygen.[2, 4] If any of the three components of fire are taken away, extinguishment will occur. Piecing together the arson scene and evaluating the fire's path will lead to an understanding of how the ratio of fuel to heat to oxygen could have impacted the force and movement of the fire within the fire scene. An increase in oxygen from a door opening that was not open previously or a window breaking could cause a myriad of effects on the strength of the fire.[5]

Collection of the material at the fire scene and observing the ventilation and different layers of damage at the scene is extremely important to the investigation. Materials collected at the fire scene will be analyzed at the laboratory and compared to appropriate reference samples that are unburned, if possible. Collection of known unburned reference samples allow for the comparison of materials to interpret the degradation of the material and possible presence of an ignitable liquid.[6] Even an experienced analyst may have trouble identifying the presence of an ignitable liquid residue within fire debris that is masked by pyrolysis and combustion interference products.[7,8] Simulation of "real life" fire debris by burning, analyzing and interpreting materials in the laboratory is the goal of this research. If a laboratory burn can simulate a real life fire debris scenario, then if an unburned reference sample is impossible to collect at the fire scene, there is an alternative that can be used for comparison purposes. Unfortunately, a full scale duplication of a fire scene is near impossible in the laboratory.[9] Therefore, focusing on creating testing conditions for laboratory burns of common household flooring materials was a more sound approach to this research.

A database of different laboratory burn methods including different substrates allows for further improved performance of investigative understanding of arson scenes. Evaluation of chromatographic profiles will yield dividends in identification of possible ignitable liquid and pyrolysis products.[6] Further investigation into the projection of simulated laboratory burn data utilizing chemometrics and contour plots will allow the analyst to observe the similarities and differences between burned materials that may or may not contain ignitable liquid. Analyzing the similarities and differences of laboratory burn data through chemometric methods will display if the substrate laboratory burns are similar to casework fire debris and substrate/ignitable liquid contained within the neat Ignitable Liquid Reference Collection and Substrate databases.

CHAPTER 2: BACKGROUND AND LITERATURE RESEARCH

2.1 Pyrolysis

Pyrolysis is a process where a material breaks down or degrades into smaller components by heat alone.[2, 4] It occurs without interaction of oxygen or oxidants. It is important to recognize that some of the smaller components (pyrolysis products) formed can be observed during analysis using GC-MS instrumentation. Most of the pyrolysis products released by the substrate will be fueling the flame, while part of the product will be adsorbed onto the substrate.[10] Not only will pyrolysis products be observed, but partial combustion products will be produced as well, if they are not lost during the burning process. Pyrolysis/combustion products formed during the laboratory burning process may be representative of the products obtained in real-world fire debris.[10] If ignitable liquid is present in a fire debris sample, then ignitable liquid residue (ILR) will likely be observed in the chromatogram in addition to pyrolysis/combustion products. The destructive nature of fire makes investigation difficult due to evidence being damaged and altered by the fire and firefighting efforts.[11] The different compositions of materials increase the difficulty of identifying possible ILR in the chromatographic profile.

Stauffer previously stated there are three separate mechanisms of degradation observed in pyrolysis of polymeric material.[10] Random scission, side group scission or side elimination and monomer reversion (depolymerization) are commonly observed separating mechanisms encountered in pyrolysis of a product. There are other less commonly seen mechanisms that have been discovered including rearrangement of natural, synthetic organic material and cross-linking with char formation. Cross-linking occurs within molecules like polyacrylonitriles or phenolic resins, which strengthen the polymer product creating a minimal amount of volatile products.[12] Burned material does not always undergo only one particular type of pyrolysis mechanism. Often, multiple pyrolysis mechanism routes are taken simultaneously.[13] Pyrolysis routes that are observed will be determined by the strength of the bonds of the molecules within the substrate being burned and the temperature of the flame. Variations in pyrolysis mechanisms complicate the chromatographic profile examined by the fire debris analyst.

Random scission occurs when similar strength carbon-carbon bonds are in the backbone of the molecule and the molecule breaks apart randomly. Smaller sized components in the form of alkanes, alkenes, and alkadienes will be the outcome of random scission as the hydrocarbon chain of the molecule is forced to decompose.[10] This commonly occurs within polymers as their backbones have similar strength carbon-carbon bonds.[14] In particular, polyethylene and polypropylene will typically undergo random scission. Polyethylene burns will lead to the formation of a radical, unsaturated hydrocarbon (alkene), and saturated hydrocarbon (alkane) within the chromatographic profile.[4] The full mechanism of side group scission of polyethylene is shown within **Figure 1**.

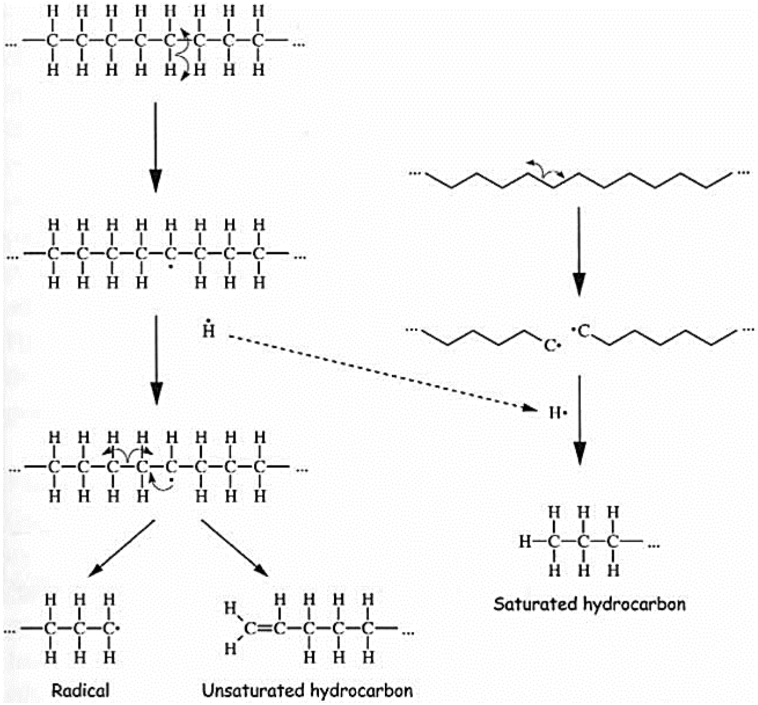


Figure 1: Random Scission of Polyethylene [10]

Polypropylene, on the other hand, contains methyl substituents along its backbone. This means that every other carbon within its chain that is attached to a methyl group is tertiary.[15] Random scission of polypropylene will result in scission of the carbon chain predominantly between the tertiary and secondary carbon.

Side group scission occurs when groups attached to the side of the carbon backbone of the polymer are lost, resulting in a polyunsaturated structure. Then, the polyunsaturated structure undergoes additional reactions of scission, aromatization and char formation.[16] Polyvinylchloride, or PVC, undergoes side group scission. Polyvinylchloride, a polymer material, experiences loss of HCl to yield a conjugated double bond backbone.[4] The conjugated double bonds in the backbone undergo further degradation forming aromatic components and smaller fragments. Side group scission of the carbon-to-carbon backbone in PVC yields aromatic components such as benzene, toluene, ethylbenzene, styrene, and naphthalene.[17, 18] The full mechanism of side group scission of polyvinylchloride is displayed within **Figure 2**.

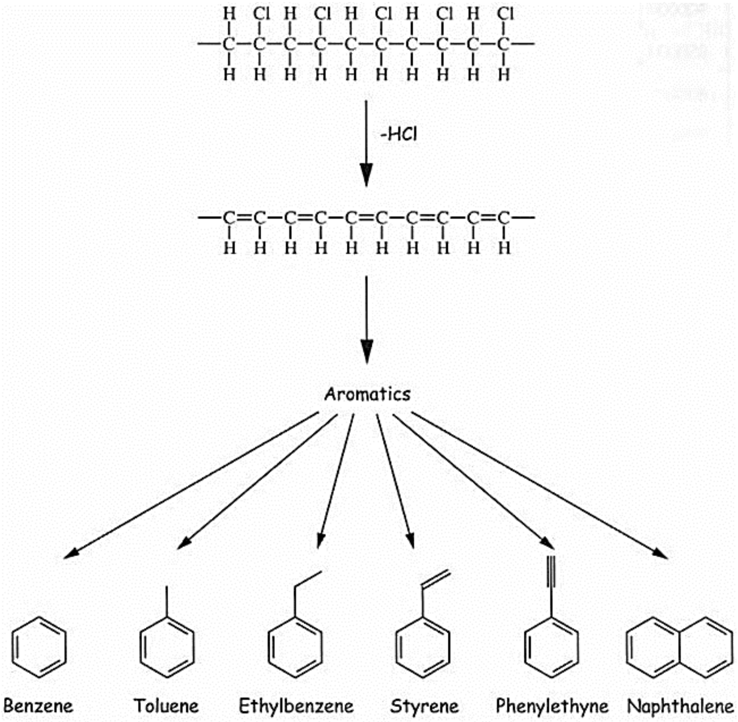


Figure 2: Side Group Scission of Polyvinyl Chloride (PVC) [10]

Similar polymers such as polyvinyl acetate, polyacrylonitriles, and polyacrylate containing side groups other than HCl will experience the side group scission mechanism.[19] For these polymers, similar aromatic derived products will be present once the side groups are eliminated.

Depolymerization occurs when a polymer undergoes a free radical mechanism that reverts the polymer back to the single monomer or group of monomers used in the synthesis of the polymer. The depolymerization mechanism will generate a simple chromatogram with large peaks corresponding to the monomers that were created from the polymer degradation. Two polymers that undergo depolymerization, often referred to as monomer reversion, are polystyrene and polymethacrylates.[18] In particular, polymethacrylates undergo scission to liberate an unsaturated smaller component (monomer) and a free radical. The free radical from the end of the polymer chain will facilitate further cleaving of the polymer and the continued breakdown of the polymer is commonly referred to as “unzipping”. The associated chromatographic profile for polymethacrylates will display the smaller unsaturated monomer as the major peak within the chromatogram.[19] If the polymer exclusively undergoes depolymerization, the chromatographic profile will be easier to analyze with one peak corresponding to the monomer. However, the depolymerization process can be subsequent to the side group scission process that was discussed previously, which will lead to additional peaks within the chromatogram.

Substrates that are burned at a fire scene will undergo one or multiple pyrolysis process(es). Estimation of the pyrolysis mechanism each material will undergo has been studied extensively. Stauffer observed polymers and their relative pyrolysis products commonly found within fire debris.[10] Commonly encountered polymers and favored degradation mechanisms are displayed in **Figure 3**.

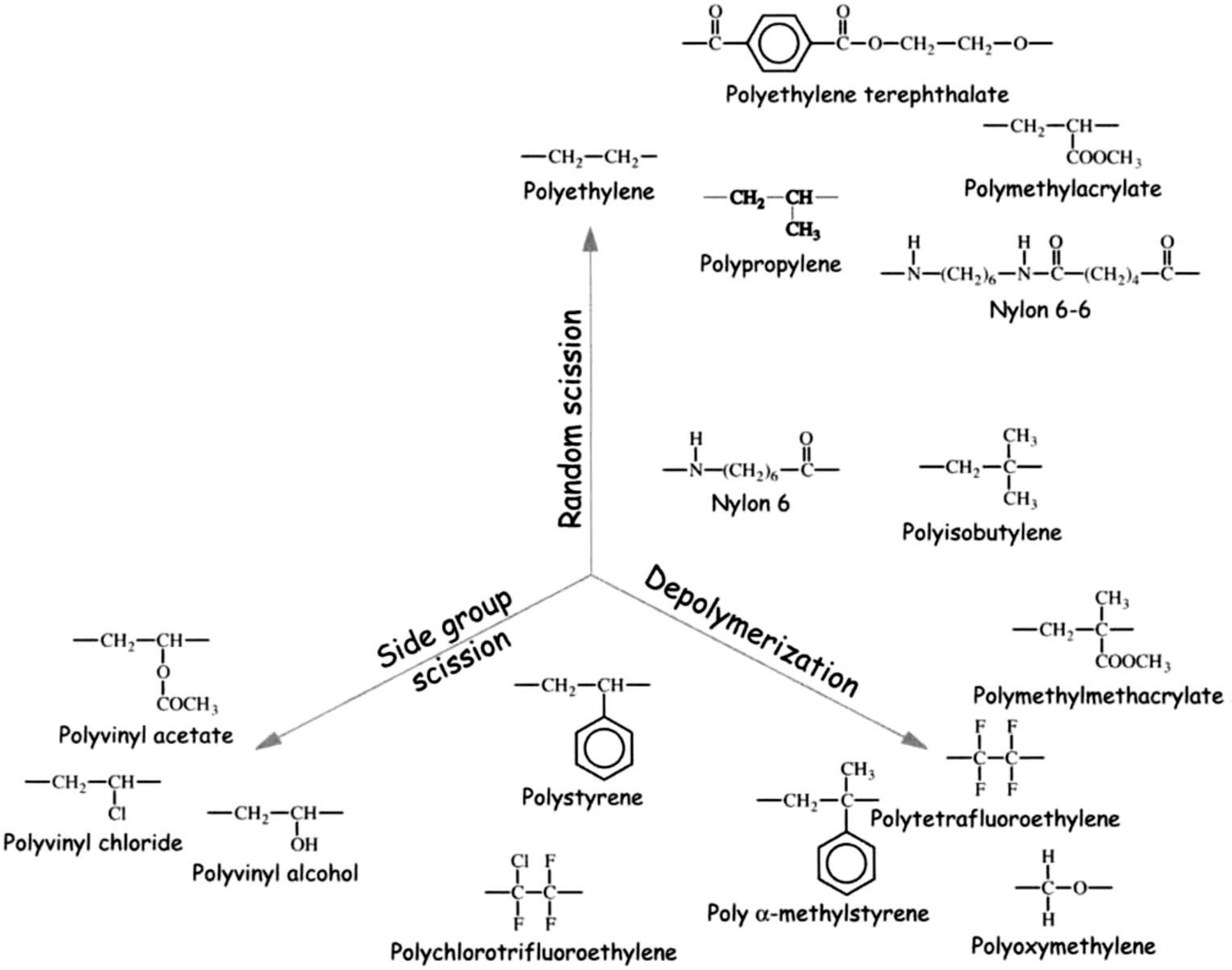


Figure 3: Common Polymers and Polymer Degradation Mechanisms [10]

For the purposes of this research, flooring material substrates and their favored degradation mechanisms were the focus. Specifically, the pyrolysis of carpeting, wood, and processed flooring will yield products that are related to the type(s) of degradation mechanisms utilized and the substrate composition.

2.2 Flooring Material Substrate Information

Flooring materials that are collected at the crime scene can have a large impact on the spread of the fire due to their composition. This can cause product background interference in the chromatographic profile of fire debris that can be misinterpreted if the analyst is not careful. With an increase in selectivity of instrumentation and analytical techniques, forensic scientists have become more aware of the contributions decomposition of different materials can have on the impact of fire debris and the fire itself.[9] Building materials, for example, are amongst the most submitted samples for analysis of fire debris.[20] They are used in the construction and furnishings of homes that are commonly affected in arson cases. The focus is not only on the composition of material that is used in the construction of homes, but the finishings, additives and adhesives that have been added to those materials, which will also impact the analysis process. Through the analytical process, analysts can overcome these distinctive difficulties in analysis of debris by collecting unburned reference samples away from the fire, if possible. Knowledge of burning characteristics of materials utilized in building and outfitting households is crucial in fire testing and analysis.[2] A deeper understanding of different building materials will also give insight into the effect these different potential fuel contributors are relaying to the fire path, intensity, and speed at which the fire spreads.

2.2.1 Carpeting

In an upholstered structure that contains carpeting, there will be multiple layers to the flooring consisting of the carpeting face, carpet padding acting as an underlayer and then subflooring as the bottom-most layer. The composition of a commonly found synthetic carpet and padding underlayer is presented within **Figure 4.**

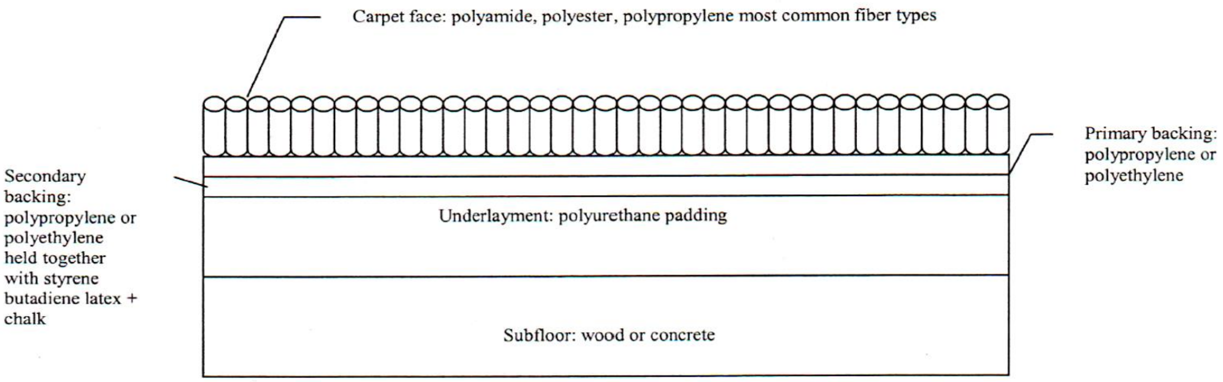


Figure 4: Structure of Synthetic Carpeting

While the carpet face may be initially burned in a fire scenario, the lower and backing layers found between the carpet face and padding need to be recognized as well. A combination is created with the carpet seated on the carpet padding and the carpet fiber is essentially woven or glued to a backing.[4] Common microfiber, or one main fiber, carpeting types include nylon, polyester, and olefin. The carpet backing is usually composed of a polymer, commonly propylene or polybutadiene.[4] Propylene is commonly identified as the ribbon-like appearance that is found on the back of most carpets. Carpets may have a rubber or urethane-foam backing that is installed over a separate foam pad.[2] The most common underlayer of the carpet is carpet padding; it is created using polyurethane polymer. The synthetically created monofiber carpets, that have been mentioned, will burn easier than carpets that are handmade with cotton due to the inclusion of synthetic material. Synthetic carpets are known to melt and reduce the specific materials' burning rate while simultaneously increasing the heat release rate of the fire.[5] Their flammable nature tends to support open-room combustion and propagate a flashover effect where the carpet ignites and directly adds to the heat rate of the fire.[4] The synthetic carpeting creates a phenomenon of conflicting natures with an insulating fiber on the face in combination with padding that acts as additional fuel for the fire to persist. Previously, the burning of the synthetic carpet material and padding have been mistaken for circular halo patterns that were thought to be formed by burning ignitable liquid, so caution in interpretation is necessary.[21, 22] If the propylene backing is exposed to a room fire, it tends to melt causing the entire carpeting to shrink. This exposes the carpet padding to the fire, thus allowing it to add additional fuel to the flame.[2]

Product formation is not only established from the decomposition of carpet fibers seated above the carpet padding, but from the polymer adhesive that strengthens the hold of multiple components as well. Assumedly, solvents that are utilized in the process of creating the adhesive would evaporate overtime. However, solvents tend to remain trapped in the polymer creation and will be detectable through the analysis process.[20] Some pyrolysis products, such as those from burned carpet face, may appear similar to an ignitable liquid like gasoline. With the addition of the breakdown of the polymer adhesive that is used in the mixture of carpet and padding, it can further increase the difficulty in understanding what allowed the fire to occur and/or persist. In fact, it is not unusual to find C_3-and C_4-alkylbenzenes, indanes and naphthalenes in samples of burned carpets.[8, 9, 23]

Specifically, the fiber content for the carpeting will further lead to different chromatographic profiles being observed. The most common synthetic carpet fibers (polyester, nylon, and olefin) will require unburned reference samples for comparison purposes to allow the analyst to observe chromatographic differences between burned and unburned flooring materials.

Polyester synthetic carpeting is manufactured using terephthalic acid and ethylene glycol which act as a precursor to the creation of the polymer, polyethylene terephthalate, also known as PET. PET will likely undergo random scission yielding small amounts of oxygenated aromatics.[10] Nylon synthetic carpeting, similarly, is a polyamide polymer that is frequently used in commercial carpeting. In fact, nylon comes in two polymeric forms that are used for carpeting in Nylon 6 and Nylon 6-6.[24] Both Nylon 6 and Nylon 6-6 undergo random scission, but Nylon 6 will further degrade by depolymerization yielding caprolactam.[10] Nylon 6-6 will yield a characteristic cyclopentanone peak.[25] Olefin synthetic carpeting is a polypropylene polymer that is relatively cheaper than both nylon and polyester carpeting and will also undergo random scission.[26]

The breakdown of these individual polymers will be facilitated by the pyrolysis mechanisms that have been discussed previously. The additional decomposition of the carpet backing composed of polypropylene will melt and mix with the detection of the adhesive still affixed in the creation of the combination of carpeting.[20] The breakdown of the fibers in the carpeting will not produce significant pyrolysis/combustion products that could interfere with observation of possible ignitable liquid residue patterns. However, the carpet backing will be a source for alkylbenzenes and aromatic compounds that may complicate the identification process of ILR.[8, 27] All of these factors interwoven into carpeting that could be found at a fire scene could potentially be observed in the analyzed chromatographic profile of an unknown carpet sample.

2.2.2 Wood

Wood is commonly utilized as a household building material. Older buildings in particular will still have interiors constructed with some form of wood compared to businesses or offices in today's world.[2] Additionally, furnishings around the household have been outfitted using different types of wood. Fire impacts wood through the thermal degradation process, which will produce changes in the structure that can be accelerated by an increase in heat. Volatile components expelled from the decomposition of flames interacting with the wood allow for the analysis of characterizing different types of wood.[28]

Wood is composed of three main components: cellulose, hemicellulose and lignin that are polymeric materials making up a wood cell.[29] Approximately 50% wood composition is cellulose, while hemicellulose and lignin are both 25% of the remaining composition.[25] Cellulose is a sugar molecule that is a polymer composed of repeating units. Cellulose composes the cell walls and sturdiness of the wood. Hemicellulose is found in the cell walls as a polymeric carbohydrate with a random structure that is less strong than cellulose. Lignin is a polymer that adds to the strength of the wood molecule while acting as an adhesive keeping cells closely bound and aiding in keeping trees upright.[29]

Although the pyrolysis of wood will be significant in the breakdown of these cellulosic components, the molecular composition of the wood is not the only concern. Solvents and finishes that are applied to wood flooring, commonly found in commercial homes, will impact the chromatographic profile of a burned wood material.[30] Analysts cannot dismiss the possibility of additives being applied to the wood, as the chosen material can seep within the wood and persist. It has been reported in previous studies that through thermal degradation, wood has produced toluene, styrene and limonene readily observed in the chromatographic profile.[20, 23, 28]

From finishing to fire retardant treatment, the composition of commercial flooring should be analyzed diligently to observe if there was an impact from the additives on the pyrolysis/combustion products within the chromatographic profile. Fire retardant is used to delay ignition, reduce heat release and attempt to reduce the spread of the flame.[31] In fact, the wood structure will absorb the additive, where the cell walls will act as pores and take in fire retardant in an attempt to protect the structure from fires. Fire retardants aim at delaying the ignition time and the rate of heat release during combustion and reduce the spreading of flames throughout the structure.[31] Char formation also plays a large role in slowing decomposition by increasing thermal resistance between wood and pyrolysis.[29] The two types of wood that were analyzed in this research include yellow pine and plywood.

Plywood is a combination of pine wood that has been manmade with an adhesive to allow for pieces to be stuck together on the bottom surface.[2, 60] However, the top surface is composed of plywood material. Pyrolysis of the material should yield contribution from both surfaces plus the addition of any additives that may been used in the manufacturing process. Other woods are used without being affixed through an adhesive, like yellow pine, but may have finishes or fire retardants that can alter the chromatographic profile. Addition of ignitable liquid only increases the difficulty of attempting to identify the components that are found in fire debris with potential interferences from multiple sources in the wood. Background interference is dependent on all possible contributions on the origin of the substrate.[23] Realizing the impact coatings and finishes can have on wood materials will allow the analyst to consider the path of the fire. Additionally, where certain burned and unburned samples need to be collected to better accurately observe and identify potential pyrolysis/combustion products during the analysis process is important as well.

2.2.3 Processed Flooring

In addition to carpets and woods, other flooring materials are common both in residential and business structures. Processed flooring is synthetically created using additives and raw materials, combining them and recreating a final product with some sort of finishing. The amalgamation of multiple layers or materials to create a synthetic product is the cornerstone of these products. Adhesives will most likely be representative in the chromatographic profile that will result from pyrolysis of a sample of this flooring type.[20] Ultimately, the background interferences observed will depend on the origin of the substrates being analyzed.[23] No matter the material used in the creation of flooring, the material and synthetic combination will have a strong influence on the spread of fire and alter the fuel load and ease of ignition. Thus, this will affect the overall contribution on the fuel content that is reflected in the pyrolysis product profile.[2] Two common examples of these processed floors are vinyl and laminate flooring.

Vinyl flooring is a product that is made in combination with vinyl resin and different plasticizers, stabilizers, pigments and fillers to create a finished amalgamation of adhesive and building material.[32] Vinyl flooring is currently one of the most popular types of flooring chosen by consumers.[33] In recent studies, an analysis of vinyl flooring revealed a number of volatile components like toluene, C_2 and C_3 alkylbenzenes detected in pyrolyzed vinyl flooring.[23] Several layers compose the vinyl flooring material that include a wear layer, print layer, foam layer, and felt backing layer.[33] Similar to carpeting, vinyl flooring contains multiple layers that are held together with an adhesive that is applied between the layers to ensure the material will not deteriorate or peel easily. In addition to adhesive, plasticizers are utilized in the mixture of vinyl flooring specifically 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) and normal alkanes, which have recognizable ignitable liquid residue patterns when analyzed.[33] Polyvinyl chloride (PVC), a synthetic plastic, is utilized in the manufacturing of vinyl flooring and treated with plasticizers to improve rigidity.[34] Possible interference results from the plasticizers mixed with the volatile components have been observed from analyzing vinyl flooring fire debris exhibiting the difficulty in understanding the chromatographic profile.

Laminate flooring is a synthetic product that is composed of multiple layers sealed together through a manufacturing process. Similar to vinyl flooring, there are four distinct layers to laminate flooring that include: wear resistant layer, decorative print layer, core layer made of fiberboard and a backing layer for support.[35, 36] The wear resistant layer is composed of melamine which acts as a fire retardant material and is the topmost clear covering.[36] The decomposition of the polymer utilized in laminate flooring production, poly(melamine-co-formaldehyde), yields products such as methanol and formaldehyde.[34] Wood based-products may contain important variations in their pyrolysis processes that are difficult to predict.

The pyrolysis of cellulosic products, which includes wood-based products like laminate, will decompose to commonly yield 2-furaldehyde, 2-furanmethanol (also known as furfuryl alcohol), and 5-methyl-2-furancarboxaldehyde (also known as 5-methylfurfural).[10] The definition of laminate, in fact, is the bonding together of two or more layers of material.[37] There are no adhesives that are used to combine the different layers together for this type of flooring, so there will be no potential interference in the chromatographic profile from adhesives. However, there is potential for there to be fire retardant material on the outer layer of the laminate flooring and the flooring to burn from the inside out. A space is created between the laminate flooring and the sub-flooring material where it “floats freely” above the sub-flooring.[38] Laminate flooring is likely to be burned from beneath as it allows the fire to spread upwards and limits any chance at isolating the flame to one specific area.[2]

2.3 Extraction and Analysis of Interference Points

Along with possible pyrolysis/combustion products that can be observed chromatographically, it is important to realize that additional interference patterns from ignitable liquid residue may also be observed within fire debris evidence. Decomposition products formed during the pyrolysis processes will be released into the gas phase, where they could react with other pyrolysis products or undergo partial or complete combustion reactions. Some pyrolysis products remain in the fire debris and are released during the analytical process. The amount of pyrolysis/combustion product that is consumed or released depends on the material analyzed and the burn method utilized. Ignitable liquid residue may add additional contributions to the chromatographic profile of a sample, increasing the complexity of the chromatographic profile. Depending on the type of substrate that is being burned, and if an ignitable liquid was administered on or near the material, both ignitable liquid residue and pyrolysis/combustion products can cause background interference in the analysis of the produced chromatogram.

The possible detection of ignitable liquid residue in fire debris will be displayed through the combination of extraction method ASTM E1412-12 and analysis and interpretation method

ASTM E1618-14. ASTM E1412-12 is the passive headspace sampling method and it is the most commonly used extraction method because it is extremely sensitive and essentially nondestructive.[39, 40] The method is ideally completed by suspending a 100 mm^2 activated charcoal strip (ACS) in the sample container and placing it into an oven for 16 to 24 hours.[39, 41] The ACS is utilized for adsorption of the residue from the sample, but if the correct parameters are not observed, product may be lost. The analyst must ensure the sample is heated at an appropriate temperature as too little or too much heat may be insufficient to volatize components or displace more volatile pyrolysis product respectively.[39] Under ideal conditions, the analyst can observe the full range of hydrocarbons from C_6-C_{20} on the activated charcoal strip with the correct analytical technique ASTM E1618-14.[42] ASTM E1618-14 is the standard test method for analyzing samples from fire debris using GC-MS instrumentation.[6]

GC-MS, or gas chromatograph-mass spectrometer is the “gold standard” for analysis of possible ignitable liquid and pyrolysis/combustion product in fire debris samples. The E1618-14 method utilizes CS_2 as a solvent to displace the residue adsorbed onto the charcoal strip. A syringe is used to inject the extract into the instrument. The gas chromatograph is where the mixture will be separated in a column before it is sent to the mass spectrometer for detection. It takes time for the molecules to traverse the column and reach the mass spectrometer for detection. The time it takes for the molecules to travel through the column is referred to as the retention time, which is utilized to identify the presence of different components in the sample. There is a specific breakdown of molecules into smaller fragments within the MS source. The peak pattern and target compounds are identified by the analysts and cross referenced against a database.[43] A qualitative search of an ignitable liquid database for comparable components and similar product pattern to those found within the sample aids in the identification of ignitable liquid residues. A similar search of a substrate pyrolysis database can help to explain components arising from pyrolysis. Ultimately, the analyst must have the experience, knowledge, and understanding to interpret results based on the match quality. The classification of ignitable liquids and the subsequent sub-classification is done by following the ASTM E1618-14 classification guide.[6] The penultimate question is whether an analyst can identify the chromatographic patterns of fire debris as substrate pyrolysis/combustion products and possible addition of ignitable liquid residue when it is present within the mixture. An ignitable liquid is not always discovered, but looking at the total ion chromatogram (TIC) and extracted ion chromatograms (EIC) yields valuable information about the pyrolysis/combustion products present in the substrate from the fire debris.

2.4 Automated Fire Debris Classification

Attempting to classify ignitable liquids into the ASTM E1618-14 classes and subsequent sub-classifications by hydrocarbon range is important when analyzing samples that are collected from a fire scene. Classifications can be automated and fire debris better understood by compiling and analyzing existing data. Principal component analysis, or PCA, offers several advantages and insights into fire debris classification and analysis. Principal component analysis allows for the reduction of dimensionality by combining factors that are being interpreted for a given set of data.[44] PCA is ideal when working with multivariate data because it allows the analyst to reduce the number of variables that will be utilized in interpretation of data.[45] Chromatographic profiles will be clustered to be in arrangement with the previously mentioned

ASTM E1618-14 classification system for ignitable liquid classes.[6] Total ion spectra (TIS) for ignitable liquids, pyrolysis samples and fire debris will be simplified with the aid of PCA. Scores from the first three principal components will provide enhanced understanding of fire debris. The TIS corresponds to the average mass spectrum across the chromatographic profile for a given sample.[43] The TIS of the fire debris will be analyzed by PCA and the scores from the first three principal components (PCs) will be plotted and labeled by their ASTM E1618-14 classifications. These plots will be useful in displaying the similarity between the fire debris data and compared database data sets. Two particularly interesting ignitable liquid classes are gasoline and distillate. Distinct patterns of specific major ions appear in gasolines regularly and a dominant Gaussian-like shape of the spectra in pure distillates.[6] Because of the defining pattern seen within the composition of non-weathered gasoline and distillates in the chromatographic profile, an analyst is more likely to recognize the source of the pattern and identify the classification of ignitable liquid based on the ASTM E1618-14 classification system.

TIS is one of several data representations that have been studied as alternatives to the TIC. Sigman et al. extensively studied the use of covariance mapping of different groups of ignitable liquids from the ASTM classification guide to allow for groupings of chromatographic ion data to physically plot on or toward a region of ignitable liquid.[46,47] The covariance map of a sample could be searched against a library of standards for ignitable liquids and substrates to identify those most similar to the sample. This will allow similar grouped burn data points to be observed graphically. To overcome the complexity and data storage challenges, Sigman et al. simplified the data representation by summing the intensities of each ion over the chromatographic profile to output the TIS.[43] The TIS has been used as the data representation for automated chemometric-based classification of fire debris as positive or negative for ignitable liquid residue and for classification of residue into the ASTM E1618-14 classes.[48, 49] TIS allows for inter laboratory comparisons, as the retention time no longer complicates the data representation.[11] This facilitates quicker interpretations of ignitable liquids against a database.

CHAPTER 3: METHODS/EXPERIEMNTATION

3.1 Materials

Eight different flooring substrates (polyester, nylon, and olefin carpeting, laminate flooring, vinyl flooring, yellow pine, plywood, and carpet padding) were utilized in the burning process for this experimentation. Three different mixtures using polyester carpeting and carpet padding (polyester and padding, polyester and padding with distillate, and polyester and padding with gasoline) were created to simulate what would likely be observed in an actual fire with carpet padding residing under the top carpet layer. The ignitable liquid addition in two mixtures will be used to display the impact of different ignitable liquids to substrate material. The flooring material was purchased from Home Depot® near Orlando, Florida. The ignitable liquids that were collected for use in the mixtures were from the Ignitable Liquid Reference Collection (ILRC) maintained by National Center for Forensic Science (NFCS). The ignitable liquids utilized exclusively for the mixtures were SRN 30 (Klean-Strip® Odorless Mineral Spirits) for distillate and SRN 105 (Phillips 66® Unleaded Regular Gasoline; neat liquid) for gasoline. Paint cans were of 1 quart size and purchased online from bestcontainers.com retailer. Activated charcoal strips were purchased from Albrayco Technologies Inc. and crimp top vials used for analysis were purchased from Thermo Scientific. A Carbolite brand tube furnace was utilized for the tube furnace burn method. GC-MS instrumentation, 5977E MS/7890B GC, was purchased from Agilent Technologies and used for the analysis portion of this experimentation with the Chemstation software. A purchased library from the National Institute of Standards and Technology (NIST) and the compiled ILRC database were employed for comparison of spectra with fragmentation identification. PCA calculations and projections onto contour mapping plotted regions were performed using the freeware software, R.

3.1.1 Large Scale Burn Data Set

The large scale burns (LSB) were completed at the Florida Fire College using four 2.4 x 2.4 x 6.1 m^3 Konex shipping containers that were constructed to simulate a two room structure that would be found in a real world scenario.[51] Containers were constructed with sheetrock walls and ceilings. Each shipping container housed similar items that would be found within common homes. A window opening was at the rear of the containers that would allow for minimal control of the air that could potentially support the strength of the fire. Additionally, building and flooring materials in chairs, carpet, carpet padding, sofas, tables, beds, and dressers were all found within the shipping containers. The backroom housed the bed and dresser to simulate a bedroom. The front room housed the sofa, table and chair to resemble a living room. Floors were made of plywood and were covered with carpeting and carpet padding and there was a small space covered in vinyl or wood laminate in each shipping container. Building and flooring material was purchased from Home Depot while the furnishing was purchased from either IKEA or Wal-Mart. Clothing, plastic and paper items were added within some of the shipping containers to add “fuel” to the fire and present additional material that could be found within the analysis of the burns that would be completed. 500 mL of different ignitable liquid classes were used in separate containers, where one specific ignitable liquid was used for each different shipping container. The ignitable liquid was poured from the front of the container near the couch and lead back towards the bed. The fire was started when a fire fighter used a torch near the couch. The fires lasted for 5 to 15 minutes in duration and usually “flashover” occurred. Flashover ensues when all fuels within a room burst into flaming combustion simultaneously and could occur if the window opens and ventilation changes allow a fresh source of air to enter the system.[5] After the fire persisted for the allotted time duration, fire fighters would extinguish the fire using water. An initial cool down period would take place, then material was collected near the ignitable liquid pour trail and material was collected away from the pour path for comparison purposes. The material samples were analyzed using the GC-MS instrumentation and the ASTM E1618-14 method. Classification of the experimental fire debris was performed by an “informed analyst” who had knowledge of the ignitable liquid that was used to initiate the fires and examined the outputted chromatographic profiles in an attempt to determine if any patterns from the liquid could be observed.[50] If any trace ignitable liquid pattern was observed, then the analyst classified the sample as IL otherwise the analyst classified the sample as SUB. If the analyst observed a pattern that was similar to pyrolysis product formation, then the analyst would recognize that and label the sample as SUB. The data set is composed of 159 different IL and SUB samples that were collected and analyzed by NCFS. Ideally, these fire scenarios will be representative of casework fire debris that would be collected from arson scenes.

3.1.2 Neat IL/SUB Data Set

The neat ignitable liquid (IL) and substrate (SUB) data set is a collection of pure ignitable liquids and substrates that have been analyzed using GC-MS instrumentation. The pure ignitable liquid portion of the data set was gathered by NCFS and maintained as the Ignitable Liquid Database and Reference Collection (ILRC), which was developed by the Technical and

Scientific Working Group for Fire and Explosives (T/SWGFEX) Ignitable Liquids Reference Collection Committee (ILRCC) in conjunction with NCFS and UCF.[52] The NCFS-UCF group updates and administers the collection as well as performing analyses on additional ignitable liquids that will be added to the database. The ignitable liquid is classified according to the ASTM E1618-14 test method.[6] Only pure ignitable liquid samples were chosen for the neat IL/SUB data set. The substrate portion of the data set was maintained and administered by the same ILRCC that allowed the NCFS-UCF group to perform the burns and analysis of the substrates within their laboratory.[53] All of the current substrates that are found within the Substrate Database were burned and analyzed using the Modified Destructive Distillation Method (MDDM) burning method. The ASTM E1412 standard method was used to passively collect the headspace adsorption onto the suspended activated charcoal strip. These substrate and ignitable liquid data sets were collected into a data set in 2014 with 567 representative samples composed of 445 pure ignitable liquid and 122 substrate samples.[50] A comparison of the neat IL and SUB data to casework fire debris and laboratory burn data will be explored further within the *Results and Discussion* section of this research.

3.2 Laboratory Burning Methods

Controlled heating of flooring materials was completed in an attempt to replicate fire debris samples that would be observed in real world situations. The controlled heating was completed using four separate burn methods to compensate for the variances that are seen from one fire to another. The first burn method is a modified version of normal destructive distillation method, which was produced by the Florida Bureau of Forensic Fire and Explosive Analysis

(BFFEA).[54] It is important to note that the "top" surface of the material is a reference to the side of the material that would normally be initially exposed to the flame during a fire. The "top" will be used to indicate side of the material that will be exposed to the heat source for the application of these different methods. Each burn method is performed within a fume hood for safety purposes. An attempt to be consistent in each burn method for each substrate is important to increase reproducibility among experiments.

3.2.1 Modified Destruction Distillation Method (MDDM)

Modified destructive distillation method (MDDM) requires placing a substrate that is 5 x 5 cm into a paint can taking note of the "top" side of the material that will be placed facing the bottom of the can. The lid of the paint can will be punctured with nine holes about 1 mm in diameter and placed onto the labeled paint can with information as to the composition of the material being burned, method being used and the laboratory burn time. The paint can is placed onto the ring apparatus that will allow for the paint can to sit directly above the flame, which is placed about 4 cm away from the bottom of the paint can, as displayed in **Figure 5**. Three different burn time intervals of 30 seconds, 1 minute, and 2 minutes were used for each substrate. Timing is started when smoke first appears. The flame is continuously applied to the bottom of the can for the allotted time. After heating has persisted for the designated time period, the heat is removed and the hole-punched lid is immediately replaced with a new lid containing no holes, to contain the substrate product within the can. The can is allowed to cool to room temperature before being placed into an oven for the extraction process. An activated charcoal strip is suspended by un-waxed dental floss in the headspace of the paint can and placed into the oven to allow the extraction process to occur that is described in depth in the *Passive Headspace Adsorption Technique for Extraction* method section that is discussed later in this research.

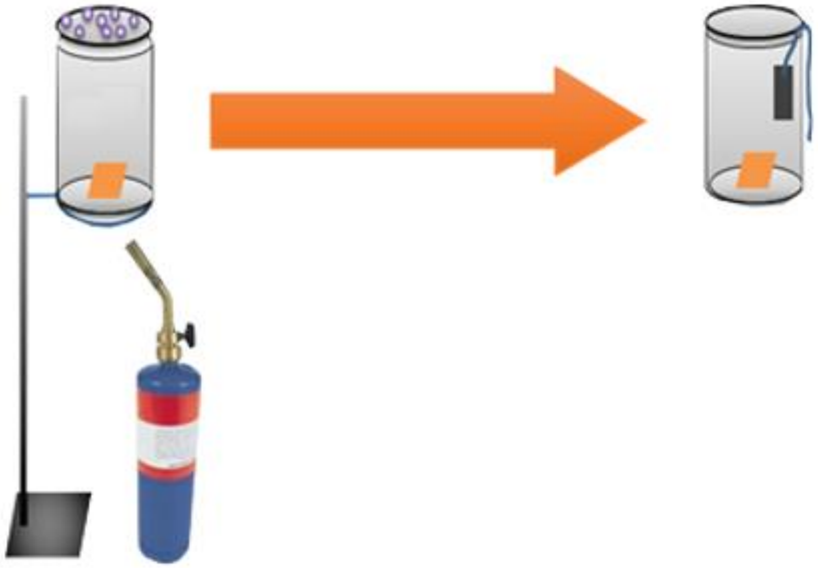


Figure 5: MDDM Burning Method and Passive Headspace Extraction Method

3.2.2 Top Heat Burn Method (TH)

The top heat (TH) method requires placing a substrate that is 5 x 5 cm into a tin boat that is constructed in a way similar to the one in **Figure 6**. The substrate should be able to sit completely in the tin boat so that the substrate will stay contained within the boat during the entire burn process. Burning of the substrate in this method will allow the flame to directly impact the material instead of being burned through a material. The flame from the torch is positioned 4 cm away from the “top” of the substrate, ensuring it is not directly touching the material. Timing of the burn is started as soon as the flame hits the material. Once again three separate burn times were used: 30 seconds, 1 minute and 2 minutes. After the burn time has passed, the flame is removed and the substrate is transferred in the tin boat to an unused paint can that is labeled with the burn time and substrate information. The sample is allowed to cool to room temperature before being placed into an oven for the extraction process. An activated charcoal strip is suspended by un-waxed dental floss in the headspace of the paint can and placed into the oven to allow the extraction process to occur that is described in depth in the *Passive Headspace Adsorption Technique for Extraction* method section that is discussed later in this research.

Figure 6: Top Heat Burning Method

3.2.3 Bottom Heat Burn Method (BH)

The bottom heat (BH) method requires placing a substrate that is 5 x 5 cm into a tin boat constructed in a way similar to the previously described top heat method. The substrate should be able to sit completely in the tin boat so that the substrate will stay contained within the boat during the entire burn process. The bottom heat method has the flame situated 4 cm from the bottom of a stainless steel pan holding the tin boat that contains the substrate, which is illustrated in **Figure 7**. Note that the “top” of the sample is facing down. Heat is applied to the substrate until smoke is seen. Once smoke is seen, the timing of the burn begins. Three separate burn time intervals were used: 30 seconds, 1 minute and 2 minutes. After the time has passed, the flame is removed from the substrate and the substrate in the tin boat is transferred to a correctly marked unused paint can that is labeled with the correct time and substrate information. The can is allowed to cool to room temperature before being placed into an oven for the extraction process.

Figure 7: Bottom Heat Burning Method

3.2.4 Tube Furnace Burn Method (FURN)

The tube furnace (FURN) method was designed to mimic similar tube methods that have been explored for imitating pyrolysis.[55] The substrate that is 1 x 1 cm is placed into the vial and inserted into the tube furnace, as shown in **Figure 8**. The sample situated within a tube furnace near to the center, where the desired temperature was noted. A temperature of 400˚C was the target temperature that was chosen to allow for the pyrolysis of substrates within the vial. Before situating the vial within the tube furnace, a “faux lid” is created using aluminum foil with punctured holes in an attempt to replicate the punctured lid that was utilized in the modified destructive distillation method and placed over the vial ensuring it is secure. Once smoke is seen, the burn timing is started. Three separate burn time intervals were used: 2 minutes, 5 minutes and 10 minutes. After the burn time, the vial is slowly removed from the tube furnace following shut off of the power as a safety precaution. The vial and the faux lid are punctured with a glass stopper and allowed to cool to room temperature. Once it has reached room temperature, the activated charcoal strip is suspended into the vial using a paperclip and a cap is tightened to seal the opening of the vial. The vial is then placed into the oven to allow the extraction process to occur that is described in the *Passive Headspace Adsorption Technique for Extraction* method section.

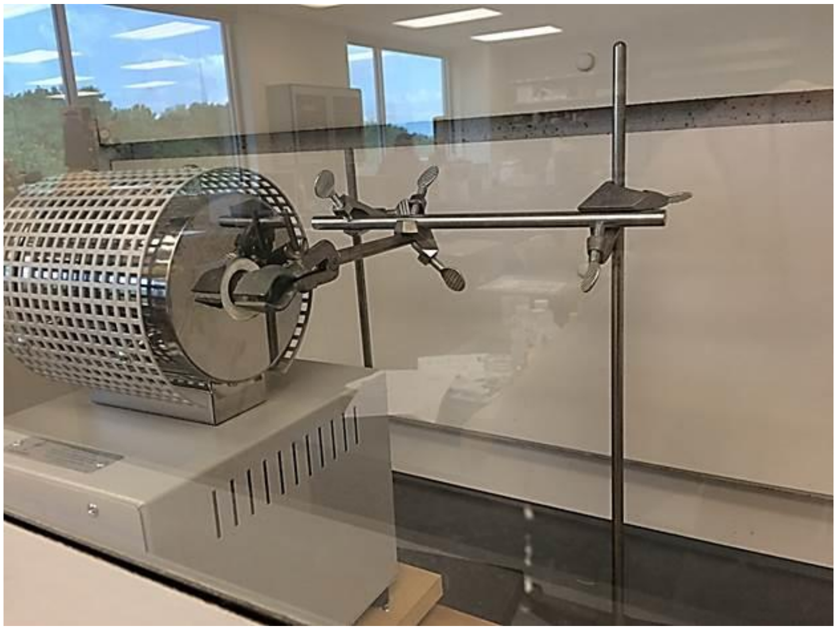


Figure 8: Apparatus used in Tube Furnace Method

3.2.5 Ignitable Liquid Addition

The ignitable liquid addition burn procedure was performed on two substrate “mixtures” that were done to simulate actual flooring that would commonly be found in homes. Carpet and carpet padding was selected as the mixture that would be analyzed using one of the previously described methods. The method that was chosen (MDDM) was performed on the mixture without ignitable liquid addition and with two different ignitable liquids. The chosen ignitable liquids were petroleum distillate and gasoline due to their recognition in a spectrum based on pattern recognition and major ion fragmentations formed and displayed to the analyst. In preparation for the procedure, the chosen ignitable liquids were slowly added dropwise onto the carpet and padding mixture that was layered like that of actual carpeting in a home. 500 µL of ignitable liquid was added to the mixture using a micropipette distributing across the entirety of the top surface of the carpeting. Because this was done using the MDDM method, all MDDM methodology was followed past the point where ignitable liquid was slowly added to the substrate mixture. Sterile tongs were used to place the material within the can before the method was applied.

3.3 Passive Headspace Adsorption Technique for Extraction

The laboratory oven is set to 66˚C and the pyrolyzed substrate sample in the quart paint cans is heated for 16 to 18 hours. The activated charcoal strip is suspended into the headspace of the can and the lid is resealed prior to heating. This allows enough time for the transfer of material from the side walls of the paint can or the pyrolyzed sample and adsorption onto the activated charcoal strip. The passive headspace adsorption technique is perfect for extracting ignitable liquid residues over the entire range of concentration due to its high level of sensitivity and non-destructive nature.[39] When the paint can is placed into the oven with the activated charcoal strip, the pyrolysis product will vaporize and adsorb preferentially onto the carbon strip, which results in extraction of the components that derive from heating of the substrate. A 100 mm^2 area carbon strip is utilized for extraction of the products at temperatures below $80\,^0C$ because a higher temperature can cause the increase of concentration of headspace. An increase in the concentration of headspace will increase the likelihood of displacement of lighter volatiles by heavier, less volatile residue.[41] After the substrate is heated, the paint can is removed from the oven and allowed to cool to room temperature.

3.4 GC-MS Instrumental Parameters

All samples were analyzed on an Agilent 7890B gas chromatograph with a G4567A series autosampler and interfaced to a 5977E mass spectrometer. The samples are introduced through a split injector and 1 µL of sample was split 50:1 and is injected at a temperature of 250°C. The initial oven temperature was held at 50°C for three minutes and then ramped up at a rate of 10°C per minute until it reaches 280°C and held for four minutes for the total run time of thirty minutes. The chromatographic column is a HP-1 methyl siloxane column of 0.2 µm diameter, 24.36 meter length, 0.50 µm thickness and 38 cm per second linear velocity. Helium gas was maintained throughout the system at a constant flow of 34 cm per minute on the column. The mass analyzer scanned from 30 to 350 m/z where the detector is turned off between 1.54 to 2.00 minutes that was programmed as a timed event to account for solvent delay. An additional timed event turns off the detector from 1.08 to 1.13 minutes to avoid air peak elution. The mass spectrometer quad temperature was set to 150°C and the source temperature at 230°C and both are monitored and maintained.

3.5 GC-MS Analysis Process

The paint can from the extraction process is unsealed after cooling to room temperature and the carbon strip is removed. The carbon strip is placed into a vial with 500 µL of CS_2 that will act as a solvent extract material off of the activated charcoal strip. The extraction of material from the adsorbed carbon strip into carbon disulfide, CS_2, provides a sample for subsequent GC-MS analyzes. CS_2 is used as a solvent because it is a better absorber and will displace the hydrocarbon residue that has been adsorbed by the activated charcoal strip. When the carbon strip is submerged in the CS_2 in the vial during this analysis process, the GC-MS will be able to identify the pyrolysis/combustion products that were formed during the burning process and extracted from the headspace of the can. It is important for the CS_2 solvent to have greater affinity to activated charcoal than the adsorbed components from the substrate material and for the adsorbed molecules to be readily soluble in the solvent.[4] The vial is labeled appropriately with the method used, sample composition and the laboratory burn time used for that particular run. The chromatographic profile is analyzed to detect and identify the major components and the information is recorded for comparison purposes that will later be discussed in the *Results and Discussion* section.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Fire Debris Samples

In order to recreate fire debris samples for the purpose of interpreting fire debris results, nine different flooring substrates were burned within a laboratory using four different burn methods. Different laboratory burns were completed with three different burn times to simulate real world fire debris with differing levels of pyrolysis/combustion products. Each substrate (or substrate mixture) has a total of 12 different burns that were compared to reflect the variability in the laboratory burn methods and the resulting chromatographic profile of each burned substrate. The materials used include: polyester carpeting, nylon carpeting, olefin carpeting, carpet padding, vinyl flooring, laminate flooring, yellow pine, plywood, and polyester/padding mixture. These materials were discussed extensively in the *Materials* section of this research, but were revisited for the observation of the pyrolysis/combustion products found within each chromatographic profile of each substrate. In all, 108 laboratory burns were analyzed, interpreted, and projected against both “real world” fire debris and neat ignitable liquid and substrate data sets. All substrate laboratory burn data projected neatly into both LSB and neat IL/SUB PC spaces. Therefore, similarity between the laboratory burns and the different data sets could be observed. Analysis of projected laboratory burn data into the LSB and neat IL/SUB PC spaces and TICs of the laboratory burns yielded information regarding the similarities and differences between the laboratory burn methods.

4.2 Projection of In Silico Data into Fire Debris Data Sets

Sigman et al. prepared a data set by mixing the total ion spectrum from ignitable liquid with the total ion spectrum from randomly selected substrate data that served as a training set for fire debris model development.[50] If any ignitable liquid contribution was present in a sample, it was labeled as ignitable liquid and samples that contained no presence of ignitable liquid contribution were labeled as substrate. Therefore, a sample that was labeled as ignitable liquid had at least 1% of ignitable liquid contribution. The ignitable liquid database that was utilized in creating fire debris models was the ignitable liquid reference collection (ILRC) database administered by the National Center for Forensic Science (NCFS). The Substrate Database is currently administered by NCFS and ILRC Committee of the Technical Working Group for Fire and Explosives (TWGFEX). The Substrate Database currently contains 212 common household building materials and furnishings at the time of this project.[53] Only one controlled laboratory burn method, MDDM, was utilized in the preparation of burned substrate material for the Substrate Database.

Principal component analysis was completed on large scale burn (LSB) and neat IL/SUB data sets to produce scores and eigen vectors. Scores are compiled and plotted onto a principal component space that displays the relative variance covered for a chosen number of principal components. For purposes of this research, the first three principal components (PCs) were utilized. The first three PCs covered 74% of the variance in LSB data. The first three PCs covered 61% of the variance in neat IL/SUB data. Contour maps of substrate and IL scores are plotted for the LSB and neat IL/SUB PC spaces.

LSB PC space contained the map of the contour region of the mixture of ignitable liquid and substrate from the analysis of burned material that was collected within the large scale burn data set. Projection of pure ignitable liquid and substrate data into the LSB PC spaces displayed the potential difference between the substrate and ignitable regions within the LSB contour. The pure ignitable liquid and substrate data was not mixed compared to the burn data contained within the LSB data set. Therefore, if there was a distinction between the SUB/IL regions within the LSB contour, it would be observed within this projection of pure IL and SUB data points. The projection onto the three principal component spaces is displayed in **Figure 9**.

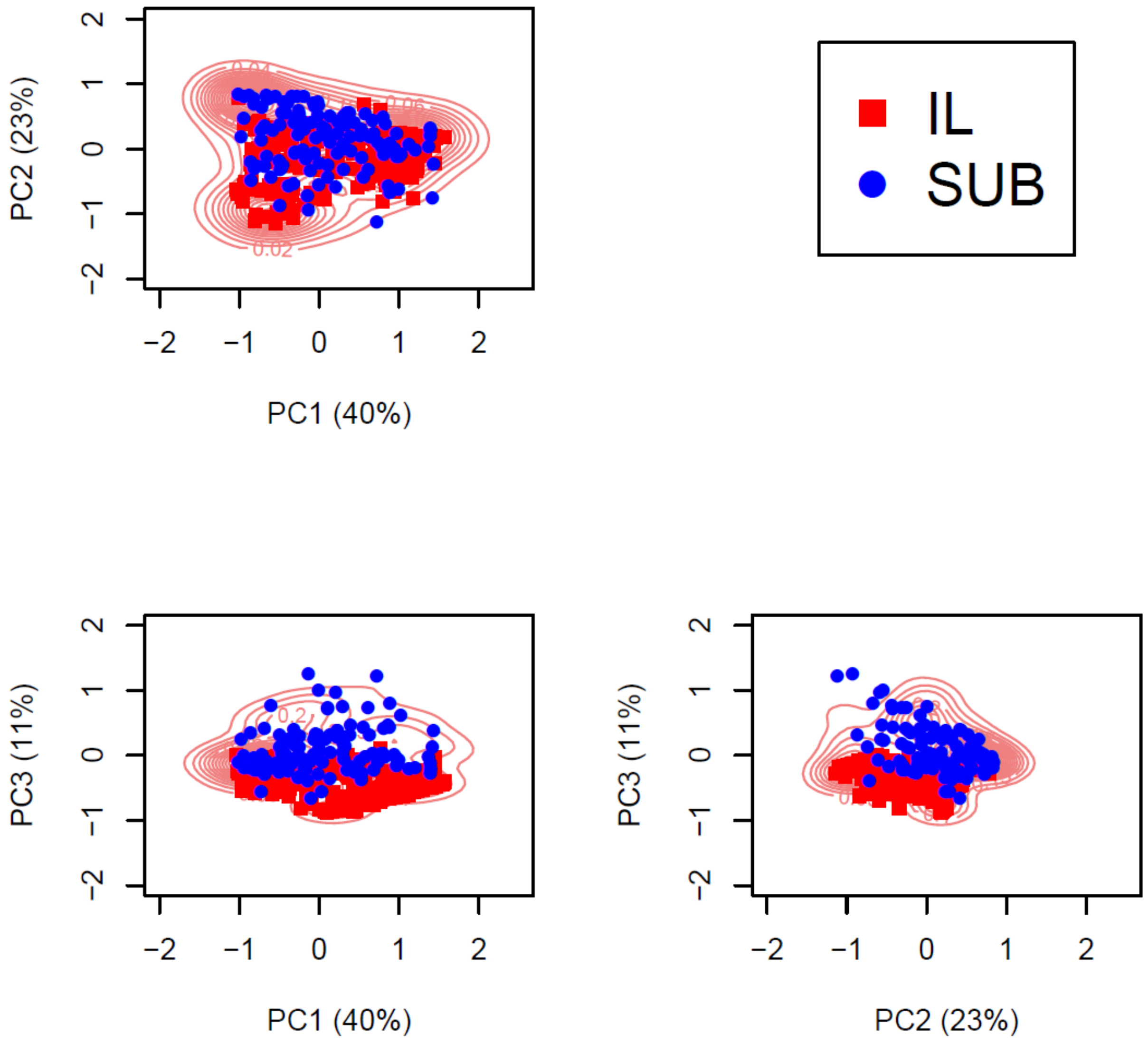


Figure 9: Projection of pure IL and SUB into LSB PCA space

There was overlap of both substrate and pure ignitable liquid data points with no clear distinction between ignitable liquid and substrate within the first two principal components space. A highly populated area only containing pure ignitable liquid points displayed near the bottom right of the PC1 and PC3 space and bottom left of the PC2 and PC3 space. The pure IL and SUB data points projected mostly within the contour region, which means that the IL and

SUB data was similar to the LSB data set. The projection of the in silico data set into the LSB contour region further revealed the similarity of the data to the LSB burn data set, but classification of data points as either substrate or ignitable liquid cannot be completed.

For the *in silico* data set, *only* the first two principal components were utilized. The *in silico* data set acted as a test set against the model LSB contour region. Projection of *in silico* data into the LSB space displayed the similarities between IL and SUB data and the LSB data set. **Figure 10** below displays the projection of *in silico* data points into the LSB PC space.

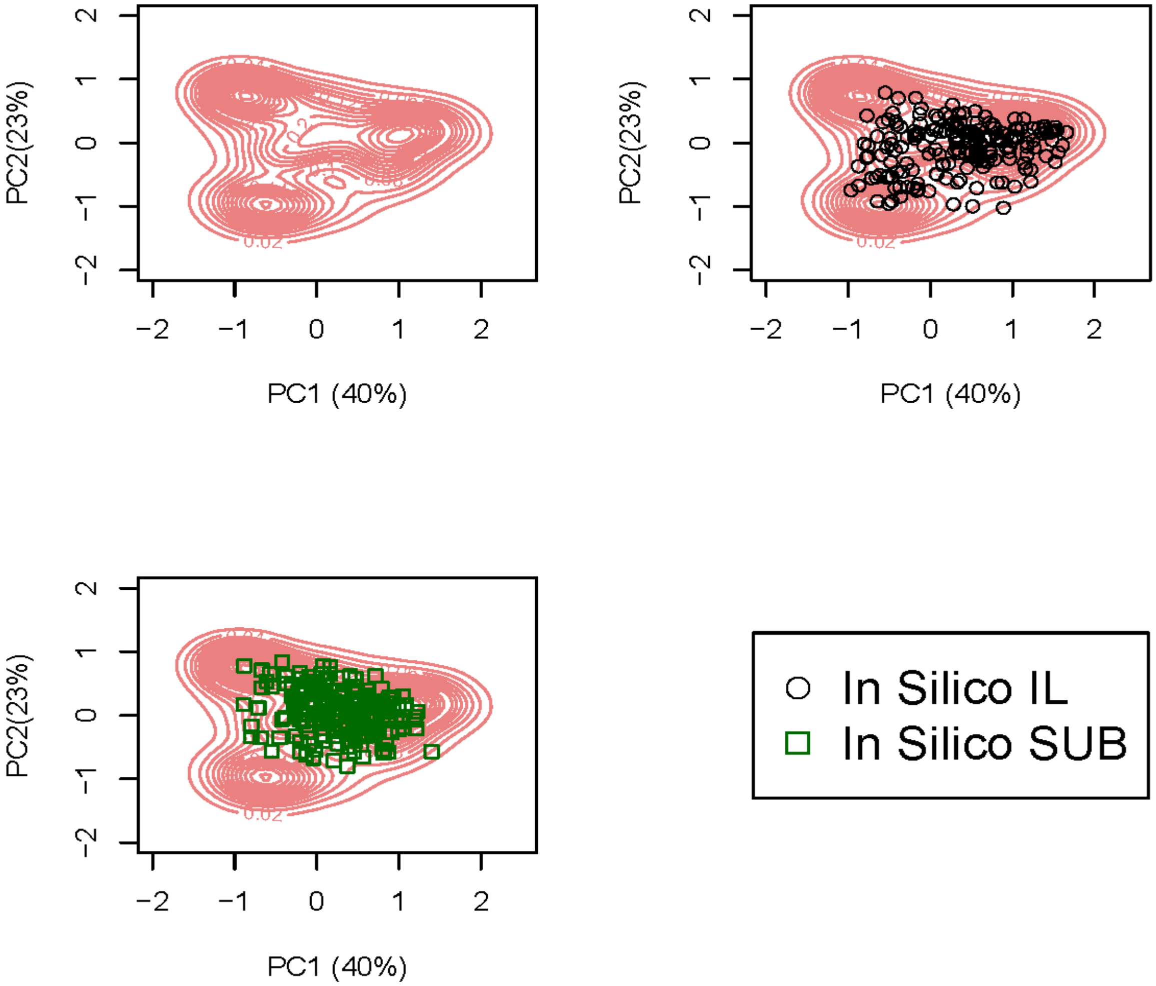


Figure 10: Projection of in silico data into large scale burn PCA space

Projection of *in silico* data into the large scale burn principal component space revealed the similarity between *in silico* data and LSB fire debris. No clear distinction between ignitable liquid and substrate regions could be made as **Figure 9** displayed previously. The points labeled as ignitable liquid that were projected likely included a percentage of substrate as the data set was a mixture of both substrate and ignitable liquid data. As expected, the *in silico* data projected into the large scale burn PC space neatly as both data sets contained ignitable liquid and substrate data. The computational *in silico* data set was similar to the large scale burn data.

Two distinct classifications, designated SUB and IL, corresponded to samples containing only pyrolysis and samples containing pyrolysis and ignitable liquid residue (ILR), respectively. The IL designation could be further sub-divided into ignitable liquid classes defined by ASTM E1618-14. The substrate sample region was identified with the “SUB” marker and the “IL” region included the ASTM classes with various class-clustering regions being marked on the contour. The different ignitable liquid classes included in the data set were: aromatic (AR), oxygenate (OXY), normal alkane (NA), petroleum distillate (PD), gasoline (GAS), isoparaffinic (ISO), naphthenic paraffinic (NP) and miscellaneous (MISC). Projection of the *in silico* data into the neat IL/SUB PC spaces displayed the similarity between the *in silico* data and the neat IL/SUB data sets. The projection exhibited the challenge in attempting to discriminate *in silico* points as either ignitable liquid or substrate as the *in silico* data points projected into both substrate and IL regions. Projection of *in silico* data into IL/SUB PCA space was performed and displayed in **Figure 11** with ignitable liquid regions (in red) and substrate regions (in blue) labeled.

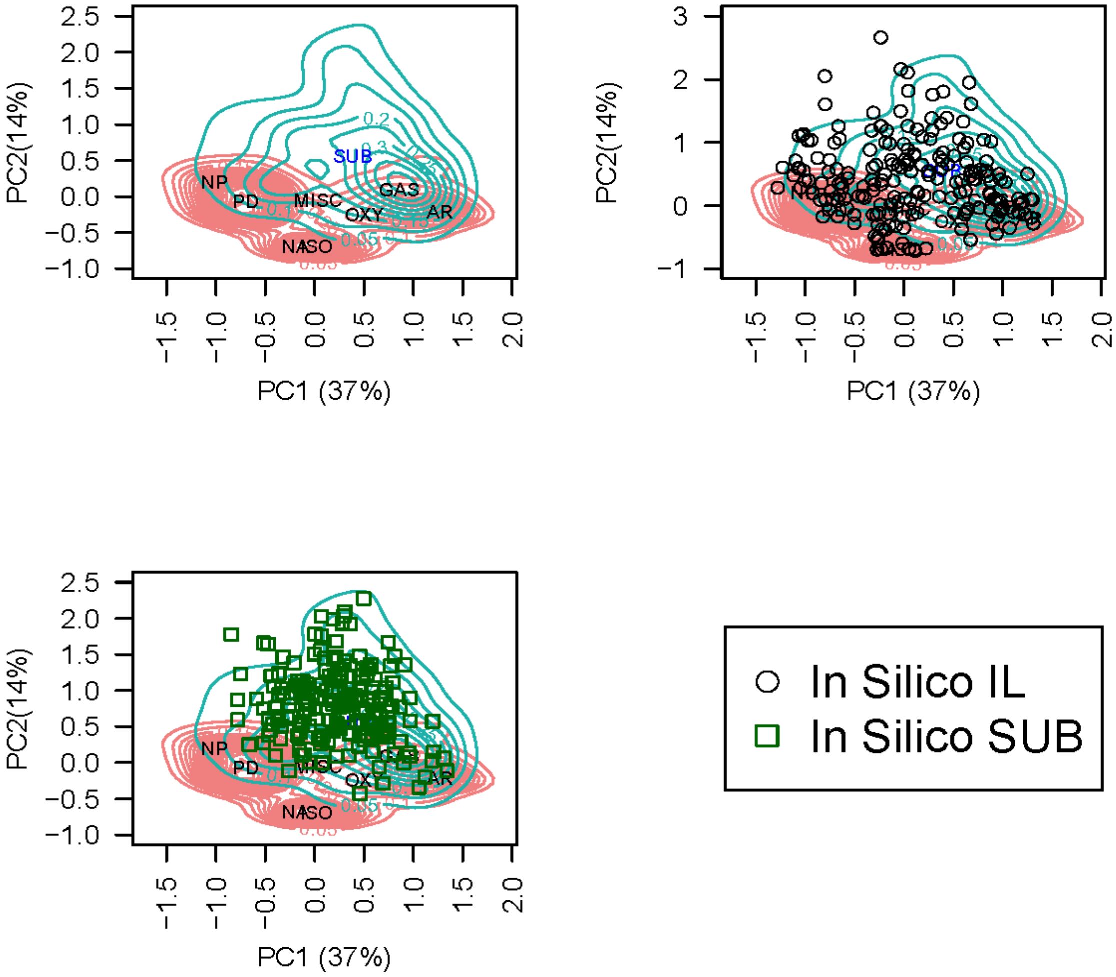


Figure 11: Projection of in silico data into neat IL/SUB PCA space

In silico data projected into the contour mapping region of IL and SUB presented in the neat IL/SUB PC plot due to *in silico* data being a mixture from the neat IL/SUB data set. It closely resembled the neat IL/SUB data set within the projection as most points tended to correspond to either the substrate or ignitable liquid regions. However, few points projected outside of the contour mapping region of neat IL/SUB. Some projected *in silico* points that were labeled as IL contained contribution from substrate leading to projection of points toward the SUB contour region. Projected data points outside of the contour region in the principal component space could be viewed as substrate and ignitable liquid mixtures that were not represented in the database or occur infrequently. Expansion of the database with additional substrates using other laboratory burn methods increased the coverage of the database.

Flooring substrates were the focus of this research. The Substrate database currently contains laboratory data for burns that were performed by the MDDM burn method only burned for 2 minutes. Analysis and interpretation of additional pyrolysis products within chromatographic burn profiles allowed for the further expansion of the database. The TIS from laboratory burns completed for this research were projected into both the previously shown LSB and neat IL/SUB PCA spaces. The results facilitated an increased understanding of how additional substrate pyrolysis methods and products can enhance the Substrate database.

4.3 Polyester Carpeting

4.3.1 Projection of Laboratory Burns into Fire Debris Data Sets

Polyester carpeting burns were completed using four different laboratory burn methods (MDDM, BH, TH, and FURN) with three different burn times and projected into the same principal component space and map of the contour regions that were used for projection of the *in silico* data. Laboratory burn data was projected into LSB and neat IL/SUB principal component spaces. The first three principal components were utilized for projection of polyester laboratory burn data. Projection of the polyester laboratory burn data into the LSB PCA space is provided in **Figure 12**.

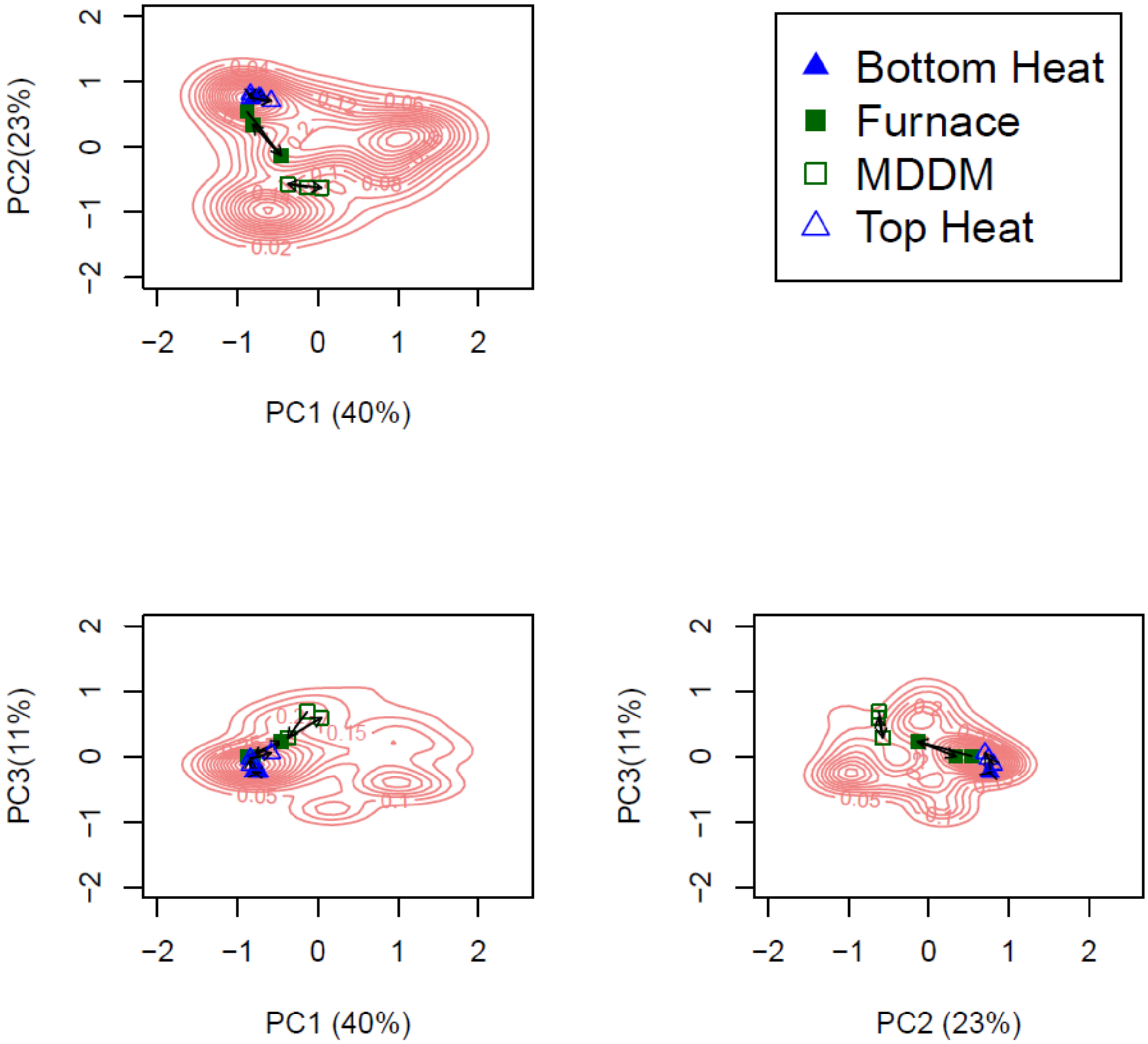


Figure 12: Polyester laboratory burns projection into LSB PCA space

Due to similarities in the properties of BH and TH methods, they were grouped together into similar shapes and color for easier interpretation. FURN and MDDM were also grouped together with similar shapes and color.

In the three different orthogonal views covering 74% variance in the data, all polyester carpeting burn data projected into the LSB map of the contour region. Clustering was observed between TH and BH laboratory burn projections. Shifts in projection of the FURN laboratory burn data occurred with increase in burn time. MDDM laboratory burn data shifted slightly in projection with increase in burn time, but clustered together. Projection of the polyester laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 13**.

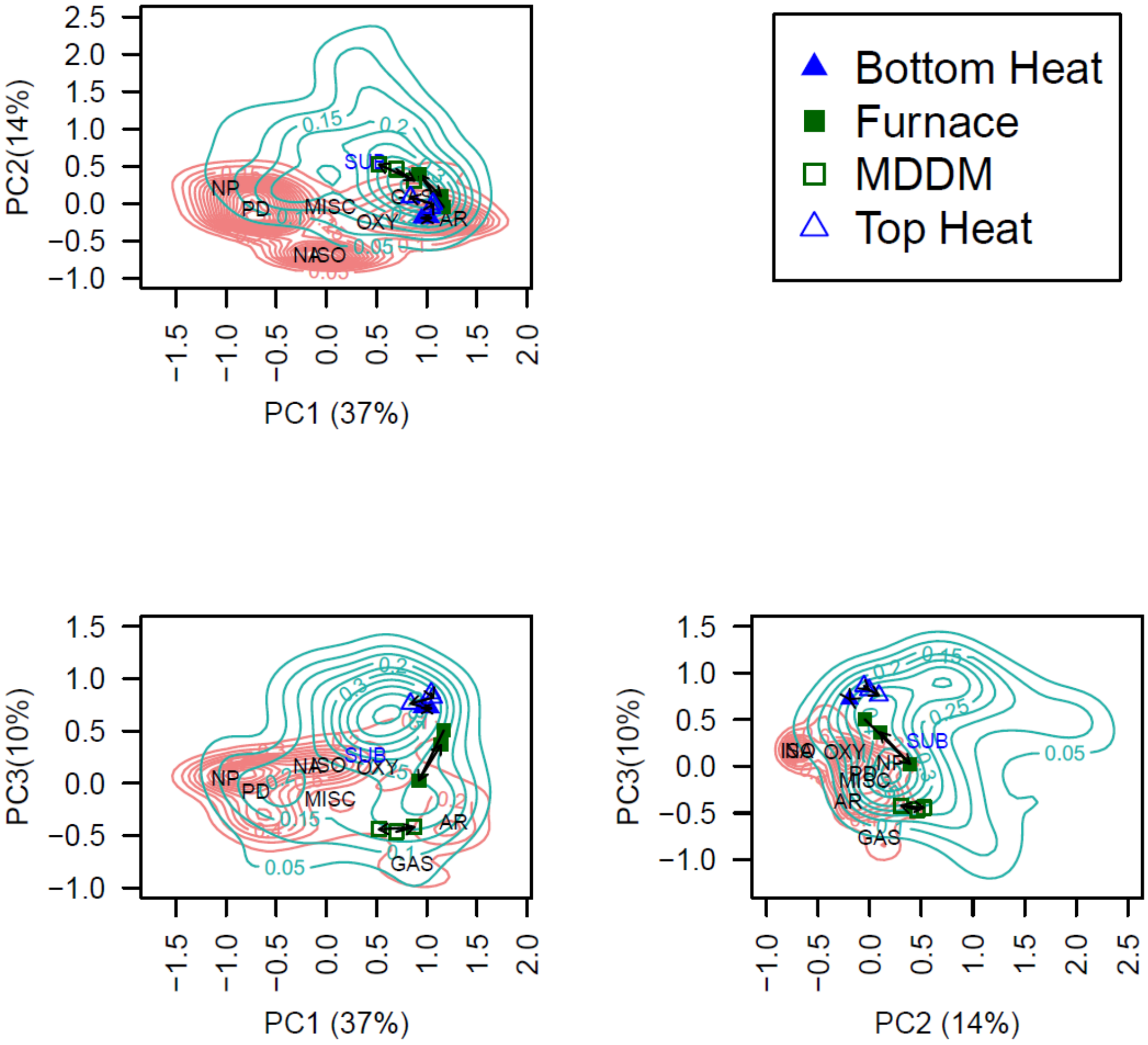


Figure 13: Polyester laboratory burns projection into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn of polyester carpeting projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burns project within the mapping space, all laboratory burn data for all PCs shown in **Figure 13** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all polyester laboratory burns projected within the neat IL and SUB PC map of the contour region. Clustering occurred between TH and BH laboratory burn data. Shifts in projection of the FURN laboratory burn data occurred with increase in burn time. MDDM laboratory burn data shifted slightly, but were clustering together.

4.3.2 TICs from Laboratory Burns

Polyester carpeting was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared between the burns. Major pyrolysis products expected for polyester carpeting were produced from the random scission of PET and polypropylene or polybutadiene backing of the carpeting, which yields small amounts of aromatics like toluene, benzene and styrene. Polyester carpeting laboratory burns were performed without any carpet padding. Pyrolysis products were confirmed through mass spectra comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and TH laboratory methods are displayed in **Figure 14**. The TICs from the BH and FURN laboratory burn methods are displayed in **Figure 15**.

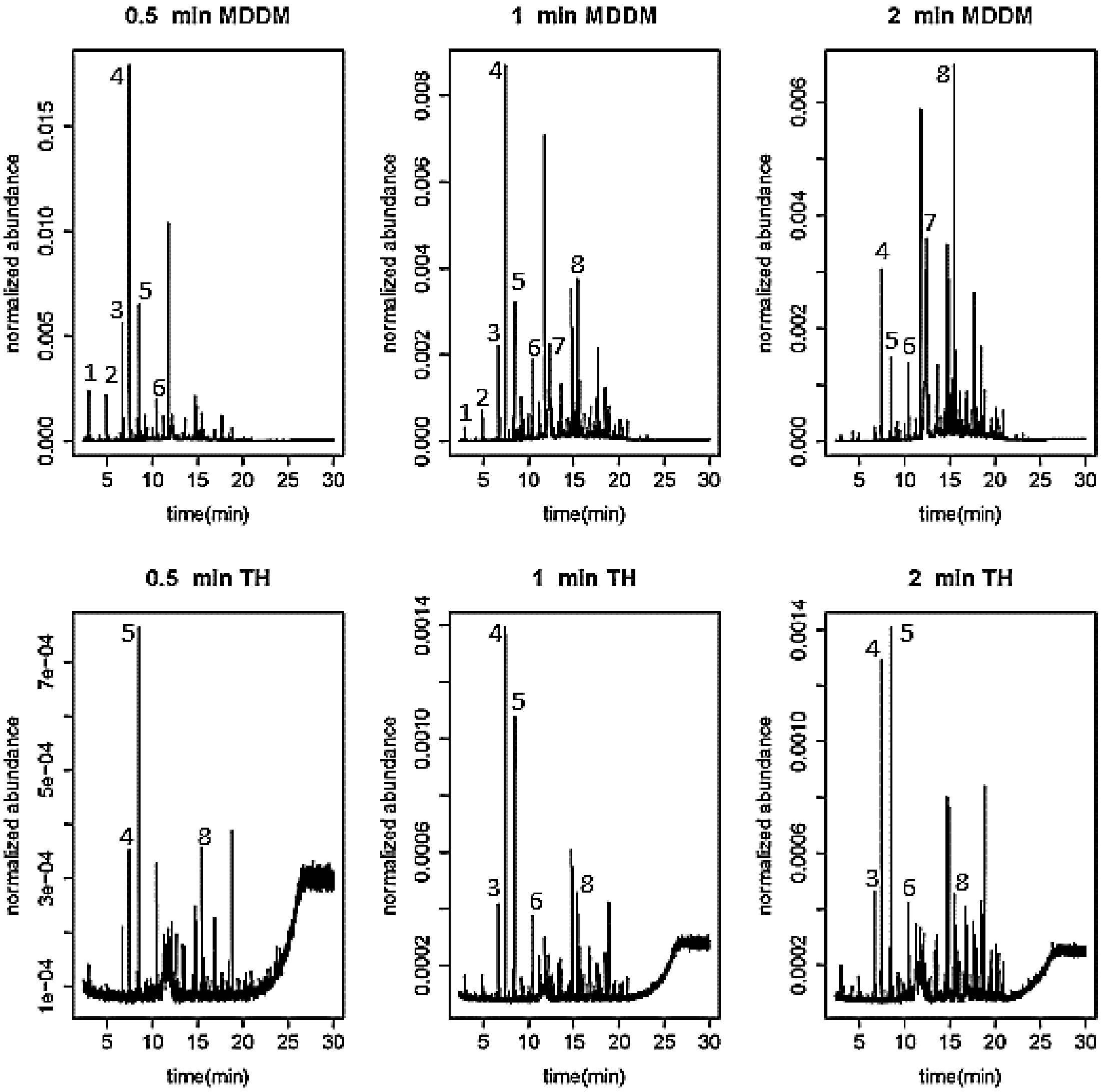


Figure 14: Compounds (1) benzene, (2) toluene, (3) 2,4-dimethyl-1-heptene, (4) styrene, (5) benzaldehyde, (6) acetophenone, (7) benzoic acid, (8) biphenyl

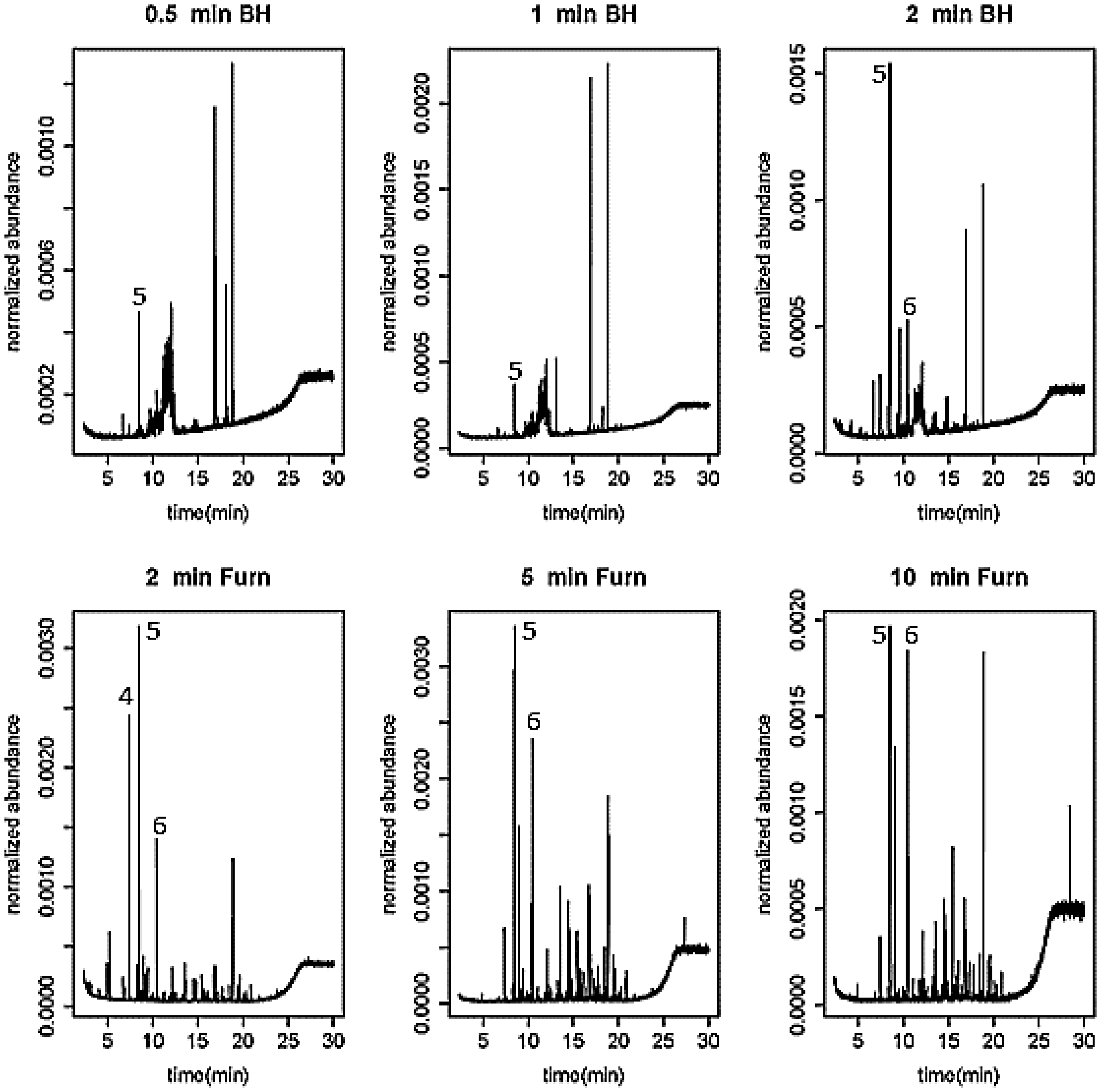


Figure 15: Compounds (4) styrene, (5) benzaldehyde, (6) acetophenone

From the above figures, multiple conclusions about the substrate and laboratory burning methods could be reached. The MDDM burning method produced the largest number of identified products. With increase in burn time, MDDM laboratory burn TIC peak intensities decreased in the front portion of the chromatographic profiles, which contained volatile pyrolysis/combustion products. Additionally, an increase in peak abundance of less volatile components was observed at the tail end of the chromatogram. Thus, 2 min MDDM laboratory burn revealed a difference in chromatographic profile relative to shorter burn times, with fewer identified pyrolysis/combustion products in the front of the TIC. TH laboratory burns displayed an increase of pyrolysis/combustion products throughout the chromatographic profiles. The 0.5 min TH laboratory burn showed fewer identified compounds in the TIC, compared to increasing burn times. The 1 and 2 min TH laboratory burns displayed an increase in abundance of volatile components in the front of the product profile. BH laboratory burns produced the least amount of identified pyrolysis/combustion products in the front portion of the chromatographic profiles at all burn times. Only benzaldehyde was identified in 0.5 and 1 min BH burns and benzaldehyde and acetophenone in the 2 min BH burn. Similarities between TH and BH laboratory burns were observed in the clustering of projections in the previous plots of LSB and neat IL/SUB PC spaces. Similar burn product patterns were observed within the TH and BH TICs. All MDDM laboratory burns of polyester carpet yielded similar chromatographic profiles. FURN laboratory burns yielded few observed pyrolysis/combustion products in the front of the TIC with only styrene, benzaldehyde and acetophenone identified.

Across all polyester laboratory burns, benzaldehyde was present in all chromatographic profiles. Intense benzaldehyde product was observed in the front portion of the chromatogram, possibly due to oxidation of toluene. Toluene, a major component commonly found within gasoline, was a product that was observed in the 0.5 min and 1 min MDDM laboratory burns. Polyester in combination with carpet padding will be discussed later within this research. Different burn method parameters and the laboratory burn time affected the chromatographic profile of polyester pyrolysis/combustion products that were produced.

4.4 Nylon Carpeting

4.4.1 Projection of Laboratory Burns into Fire Debris Data Sets

Nylon burns were completed using four different laboratory burn methods (MDDM, BH, TH, and FURN) with three different burn times and projected into the same principal component space and map of the contour regions that were used for projection of the *in silico* data. Laboratory burn data was compared graphically to LSB and neat IL/SUB principal component spaces. The first three principal components were utilized for projection of nylon laboratory burn data. Projection of the nylon laboratory burn data into the LSB PCA space is provided in **Figure 16**.

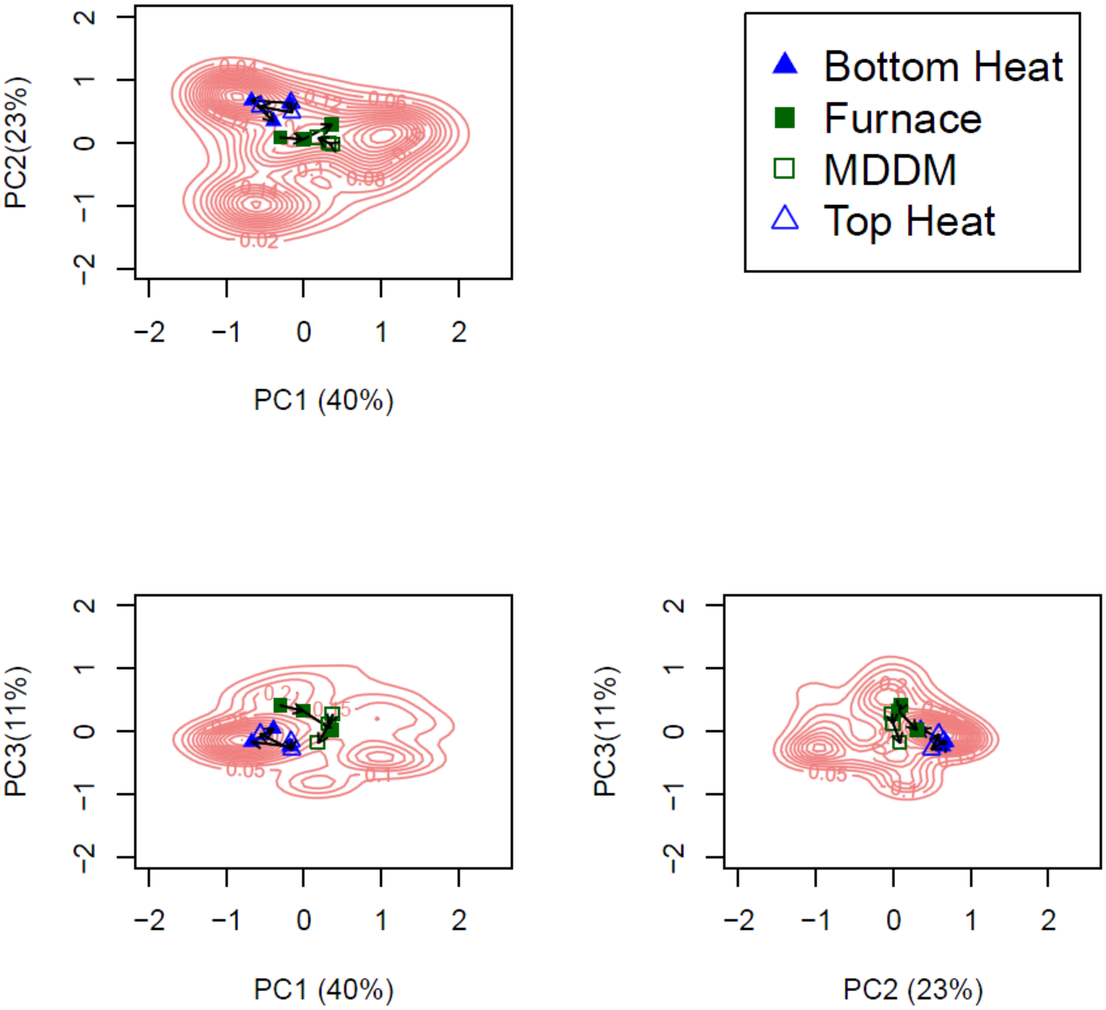


Figure 16: Nylon laboratory burns projection into LSB PCA space

As stated for the previously discussed substrates, BH/TH and MDDM/FURN were grouped together due to their similarities in properties. In the three different orthogonal views covering 74% variance in the data, all laboratory burn data projected into the LSB map of the contour region. Clustering was observed between TH and BH laboratory burn projections. Additional clustering was observed between MDDM and FURN laboratory burn projections.

Projection of the nylon laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 17**.

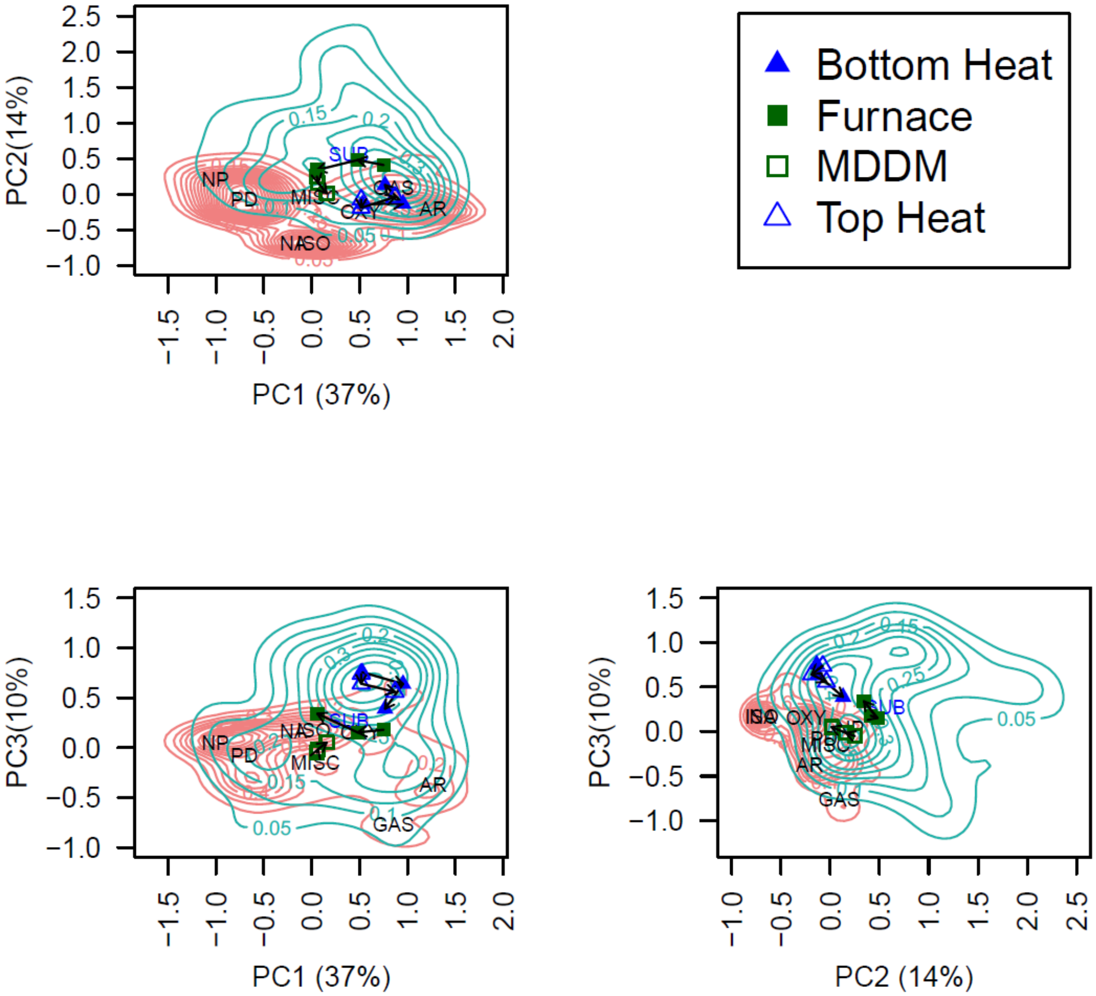


Figure 17: Nylon laboratory burns projected into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn of nylon carpeting projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burn data project within the contour space, all laboratory burn projections shown in **Figure 17** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all nylon laboratory burns projected within the neat IL and SUB PC map of the contour region. Clustering occurred between the TH and BH laboratory burn projections. The 2 minute FURN and MDDM laboratory burn data clustered as well. BH and FURN laboratory burn data did not cluster and were noticeably different in all three orthogonal views. Shifting in projection of the FURN laboratory burn data occurred with increase in burn time.

4.4.2 TICs from Laboratory Burns

Nylon carpeting was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared between the burns. Major pyrolysis products expected for nylon carpeting were produced from the random scission of either Nylon 6 or Nylon 6-6 polymers and propylene or polybutadiene backing of the carpet. Pyrolysis of propylene or polybutadiene backing of carpet yielded small amounts of aromatics like toluene and styrene. Nylon 6 underwent random scission and additional depolymerization that yielded caprolactam.[25, 56] Nylon carpeting laboratory burns were performed without any carpet padding. Pyrolysis products were confirmed through mass spectral comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and TH laboratory methods are displayed in **Figure 18**. The TICs from the BH and FURN laboratory burn methods are displayed in **Figure 19**.

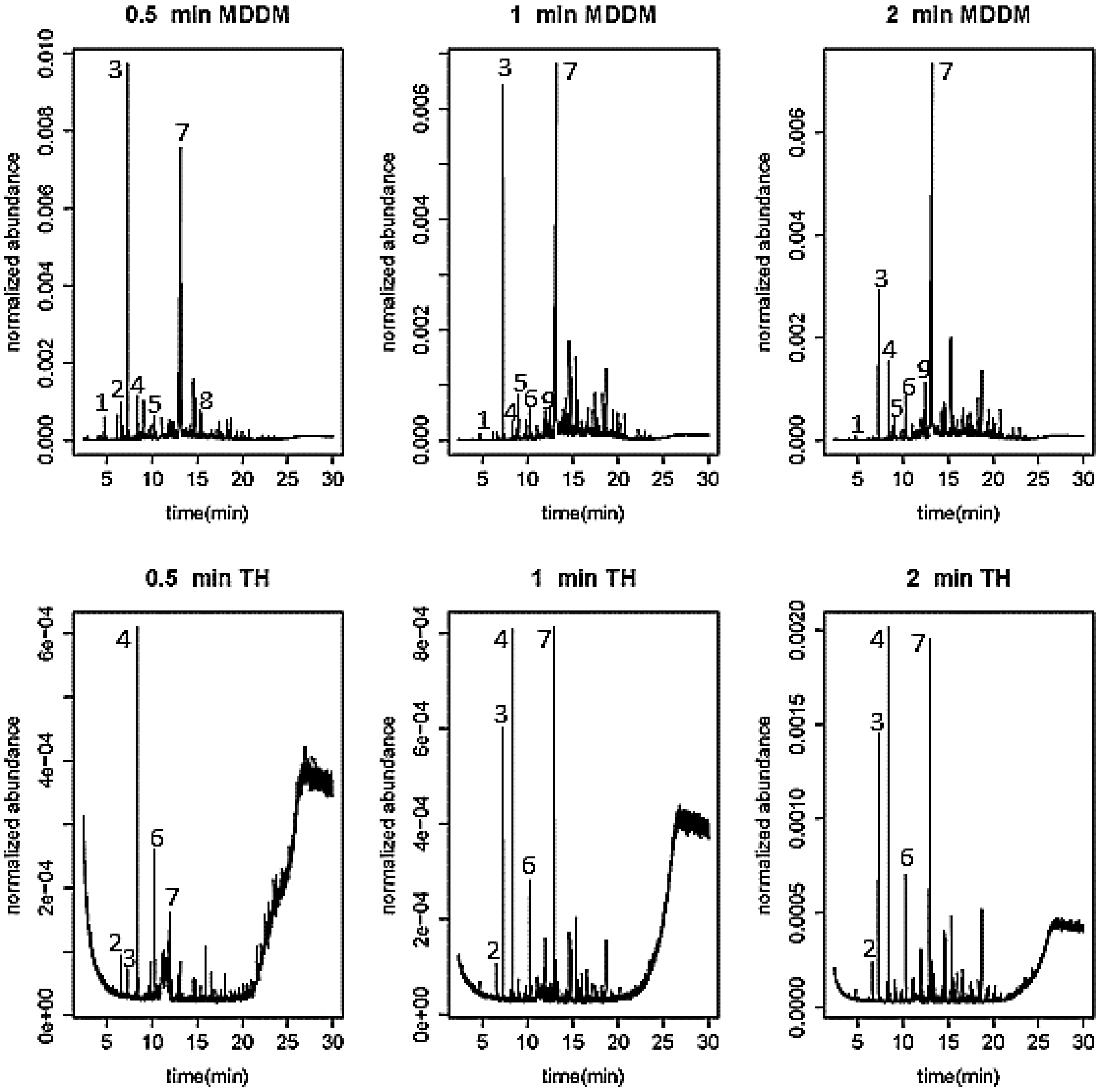


Figure 18: Compounds (1) toluene, (2) 2,4-dimethyl-1-heptene, (3) styrene, (4) benzaldehyde, (5) alpha methylstyrene, (6) acetophenone, (7) caprolactam, (8) biphenyl, (9) naphthalene

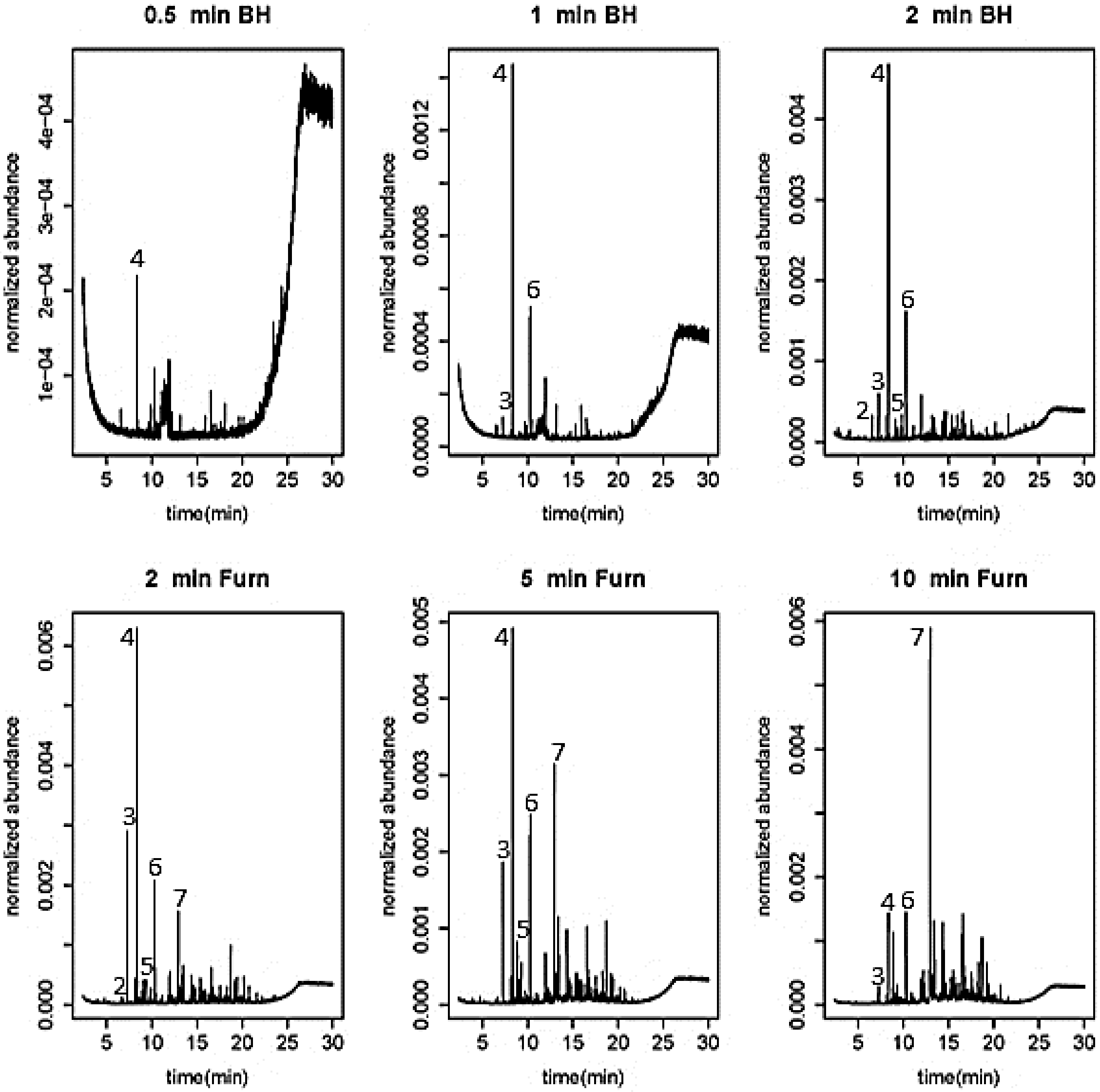


Figure 19: Compounds (2) 2,4-dimethyl-1-heptene, (3) styrene, (4) benzaldehyde, (5) alpha methylstyrene, (6) acetophenone, (7) caprolactam

From the above figures, multiple conclusions about the substrate and laboratory burning methods could be reached. As observed for polyester carpeting, the MDDM burning method produced the largest number of identified products. The 0.5 and 1 min MDDM laboratory burns observed an increase of less volatile components in the front portion of the chromatographic profiles. The 2 min MDDM laboratory burn displayed intense peaks of less volatile components at the tail end of the chromatogram. TH laboratory burns of nylon carpeting exhibited an increase of volatile components in the front portion of the chromatograms with increasing burn time. BH laboratory burns exhibited an increase in the number of identified pyrolysis/combustion products in the front of the TIC with increasing burn time. The 2 min BH laboratory burn TIC observed additional volatile components in the front portion of the chromatogram. With increasing burn time, FURN laboratory burns displayed a decrease in volatile components in the front of the TICs. The 10 min FURN burn displayed increased peak abundance of caprolactam compared to the other FURN laboratory burn times. Similarities between TH and BH laboratory burns were observed in the clustering of projections in the previous plots of LSB and neat IL/SUB PC spaces. All MDDM laboratory burns of nylon carpet yielded similar chromatographic profiles and clustered together in previous plots of LSB and neat IL/SUB PC spaces.

Caprolactam was identified in all chromatographic profiles of nylon carpet laboratory burns except in the BH laboratory burns. Identification of caprolactam was important within synthetic nylon carpeting; it could be indicative of the Nylon 6 polymer being utilized in the manufacturing process. There was an increase of caprolactam peak abundance with increasing burn time within MDDM, TH and FURN laboratory burn TICs. Across all nylon laboratory burn profiles, benzaldehyde was present in all chromatographic profiles in the front portion of the chromatograms. Different burn method parameters and laboratory burn time affected the chromatographic profile of nylon pyrolysis/combustion products that were produced.

4.5 Olefin Carpeting

4.5.1 Projection of Laboratory Burns into Fire Debris Data Sets

Olefin burns were completed using four different laboratory burn methods (MDDM, BH, TH, and FURN) with three different burn times and projected into the same principal component space and map of the contour regions that were used for projection of *in silico* data. Laboratory burn data was compared graphically to LSB and neat IL/SUB principal component spaces. The first three principal components were utilized for projection of olefin laboratory burns. Projection of the olefin laboratory burn data into the LSB PCA space is provided in **Figure 20**.

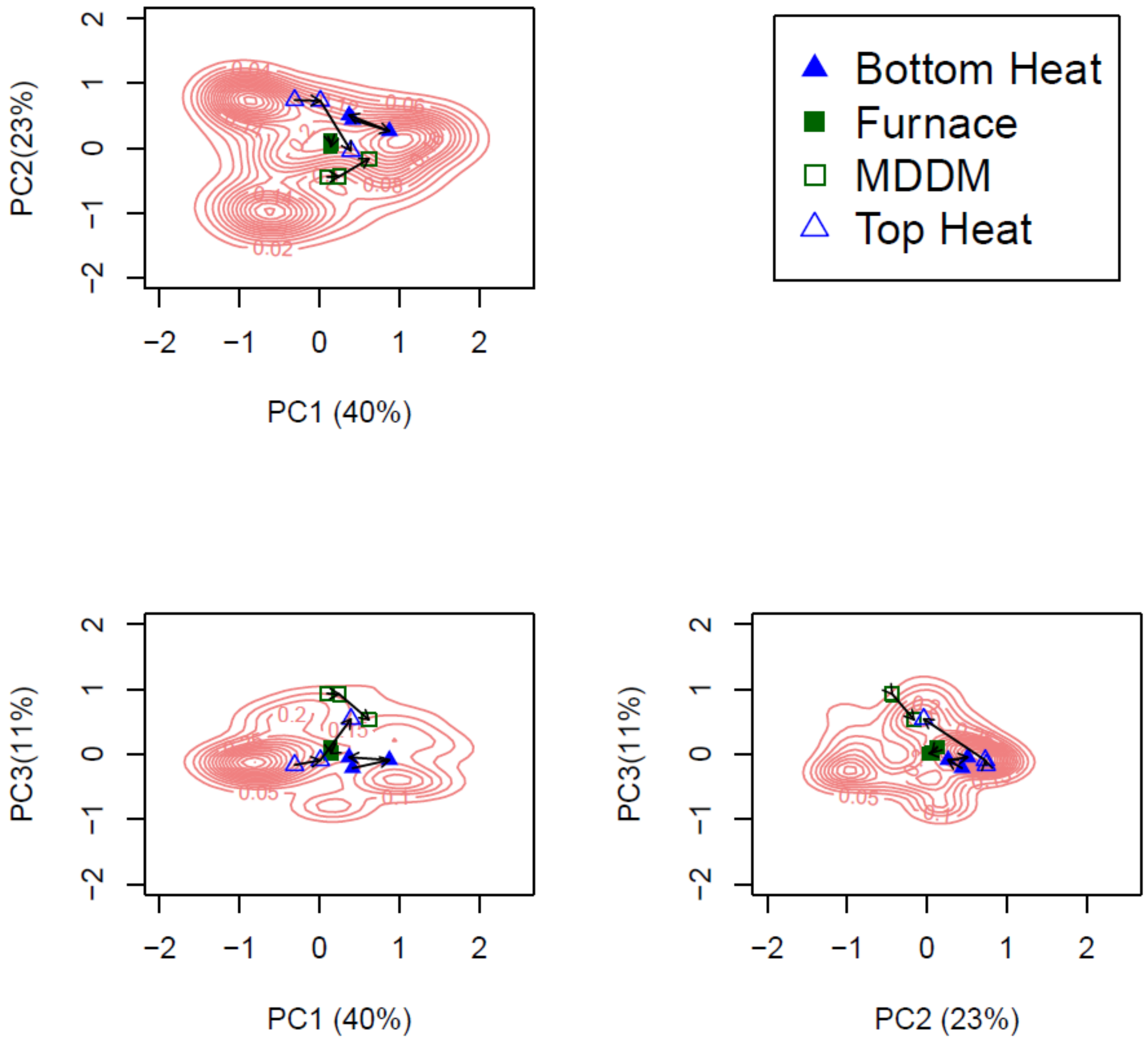


Figure 20: Olefin laboratory burns projection into LSB PCA space

As for the analogous graphs for polyester and nylon pyrolysis, similarities in the properties of BH/TH and MDDM/FURN allowed for grouping together into similar shapes and color for easier interpretation. In the three different orthogonal views covering 74% variance in the data, all laboratory burn data projected into the LSB map of the contour region. Clustering of FURN laboratory burn data with increase in burn time was observed. Shifts in projection of TH and BH laboratory burn data occurred with increasing burn times without any clear clustering. MDDM laboratory burn projections shifted slightly with increase in burn time. The 2 minute MDDM laboratory burn data shifted away from the 0.5 and 1 minute MDDM laboratory burn cluster. Projection of the olefin laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 21**.

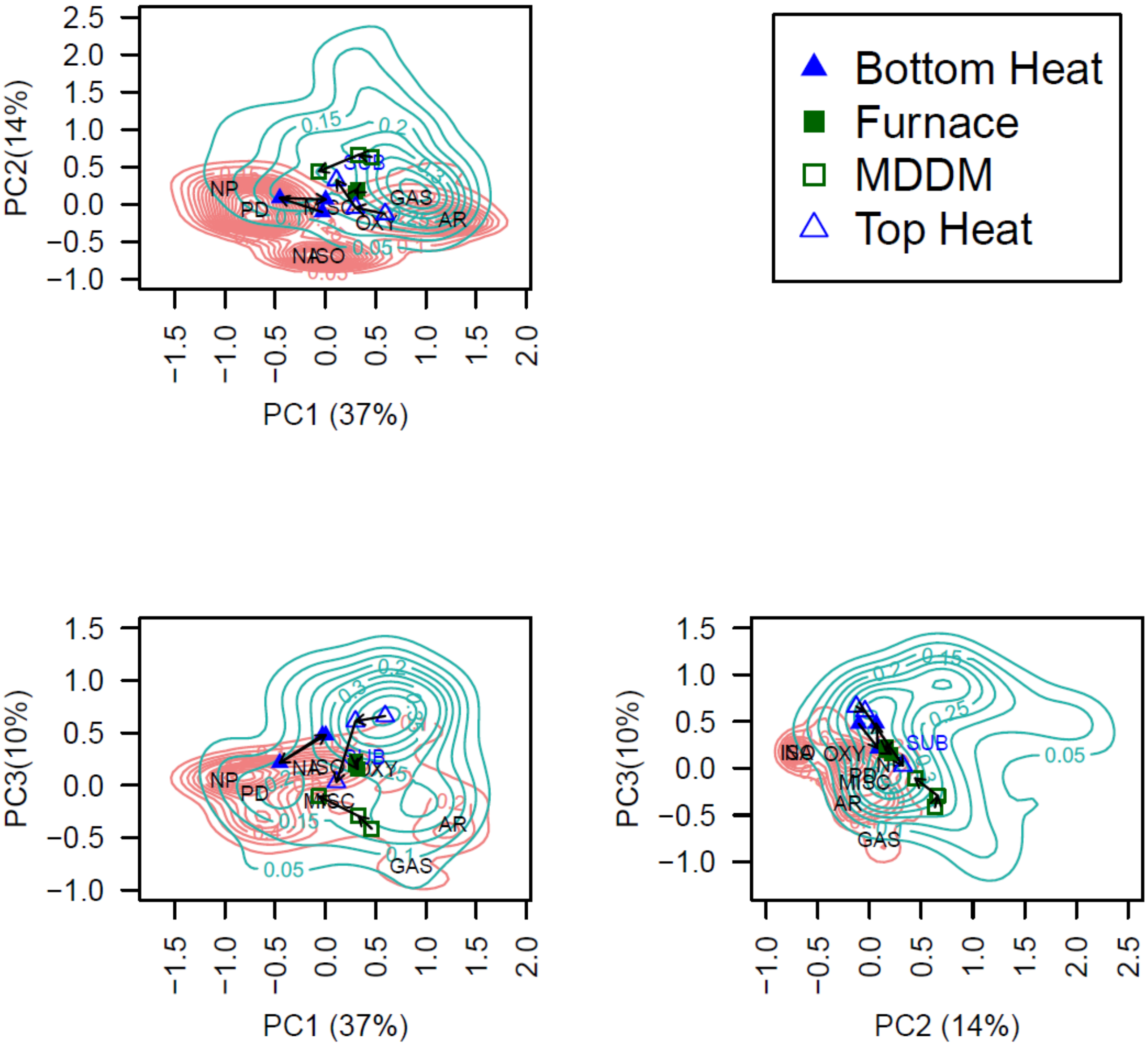


Figure 21: Olefin laboratory burn projection into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn of olefin carpeting projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burn data project within the mapping space, all laboratory burn data for all PCs shown in **Figure 21** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all olefin laboratory burns projected within the neat IL and SUB PC map of the contour region. Clustering occurred between the FURN laboratory burn data as the points were shifting slightly with increase in burn time. Shifting in projection occurred for the TH and BH laboratory burn data with increasing burn time. Shifting in projection occurred for the MDDM laboratory burn data as well with increase in burn time. MDDM and BH laboratory burn data appeared to be different with no clustering in all three orthogonal views.

4.5.2 TICs from Laboratory Burns

Olefin carpeting was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared between the burns. Major pyrolysis products expected for olefin carpeting were produced from random scission of polypropylene polymer and propylene or polybutadiene backing of the carpet. Olefin carpet laboratory burns were performed without any carpet padding. Pyrolysis products were confirmed through mass spectra comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and TH laboratory methods are displayed in

Figure 22. The TICs from the BH and FURN laboratory burn methods are displayed in **Figure 23**.

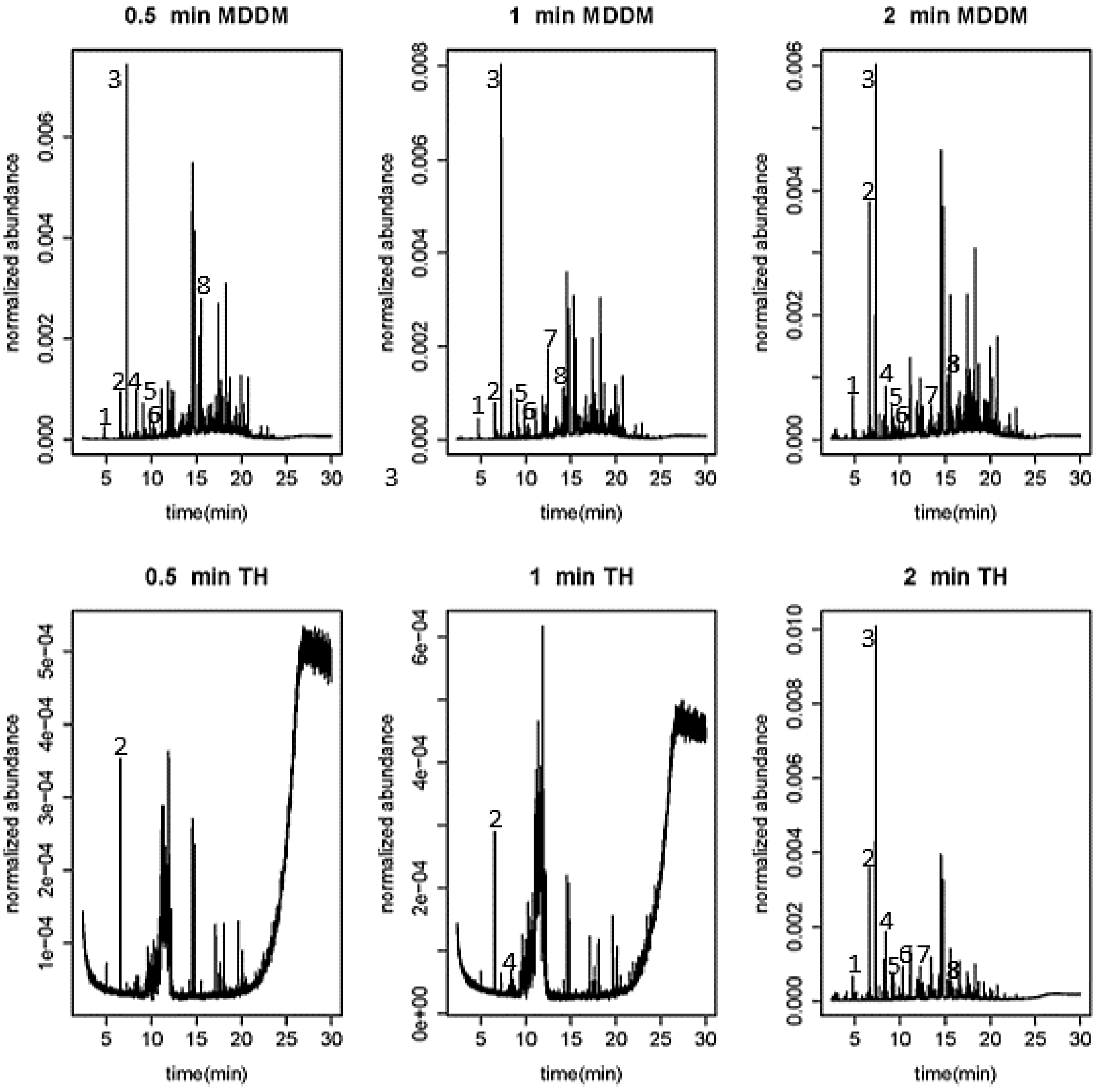


Figure 22: Compounds (1) toluene, (2) 2,4-dimethyl-1-heptene, (3) styrene, (4) benzaldehyde, (5) alpha methylstyrene, (6) acetophenone, (7) naphthalene, (8) biphenyl

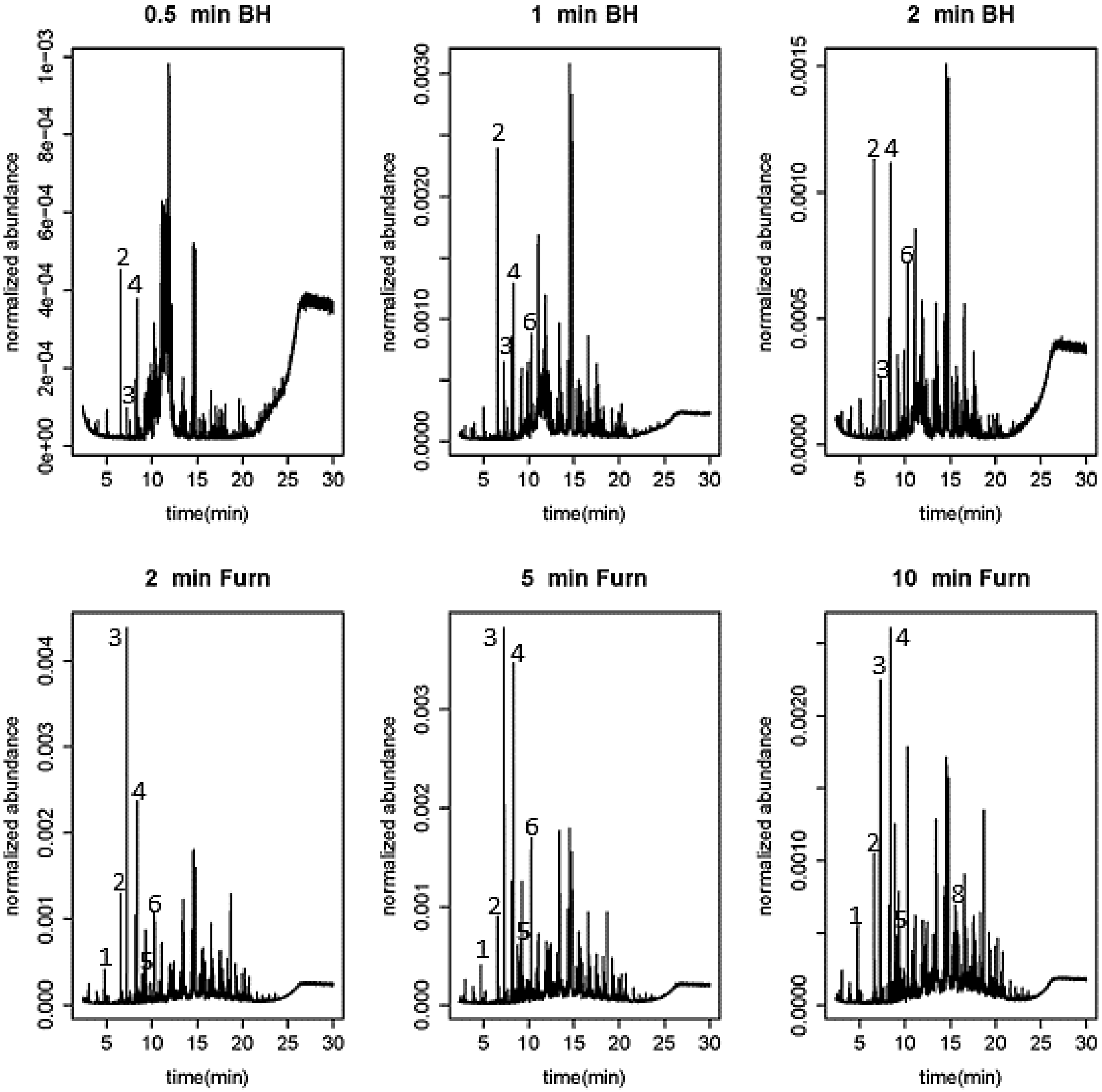


Figure 23: Compounds (1) toluene, (2) 2,4-dimethyl-1-heptene, (3) styrene, (4) benzaldehyde, (5) alpha methylstyrene, (6) acetophenone, (8) biphenyl

From the above figures, multiple conclusions about the substrate and laboratory burning methods could be reached. As observed for polyester and nylon carpeting, the MDDM burning method produced the largest number of identified products. For olefin carpeting, an increase of volatile components in the 2 min MDDM burn was observed with increase in burn time. TH laboratory burns yielded 2,4-dimethyl-1-heptene in all TH burns. With increase in burn time, additional pyrolysis/combustion products were identified in the 2 min TH chromatographic profile that were not observed in the 0.5 and 1 min TH burn TICs. BH laboratory burns yielded similar pyrolysis/combustion products in the front portion of the chromatogram with increase in burn time. All FURN laboratory burns of olefin carpet yielded similar pyrolysis/combustion products in the front portion of the TICs with increasing burn time.

Across all olefin carpeting laboratory burns, 2,4-dimethyl-1-heptene was present in all chromatographic profiles. 2,4-dimethyl-1-heptene was an aliphatic compound identified within the TICs of the other discussed carpeting burns. Within the BH and 0.5 and 1 min TH laboratory burns, 2,4-dimethyl-1-heptene was one of the few identified pyrolysis/combustion products in the TICs. Random scission occurred within all three different carpets burned for this research. Styrene, another commonly identified carpet pyrolysis/combustion product, was observed in almost all laboratory burn chromatographic profiles of olefin carpeting. Different burn method parameters and the laboratory burn time affected the chromatographic profile of olefin pyrolysis/combustion products that were produced.

4.6 Carpet Padding

4.6.1 Projection of Laboratory Burns into Fire Debris Data Sets

Carpet padding burns were completed using four different laboratory burn methods (MDDM, BH, TH and FURN) with three different burn times and projected into the same principal component space and map of the contour regions that were used for projection of the *in silico* data. Laboratory burn data was compared to LSB and neat IL/SUB principal component spaces. The first three principal components were utilized for projection of carpet padding laboratory burn data. Projection of the carpet padding laboratory burn data into the LSB PCA space is provided in **Figure 24**.

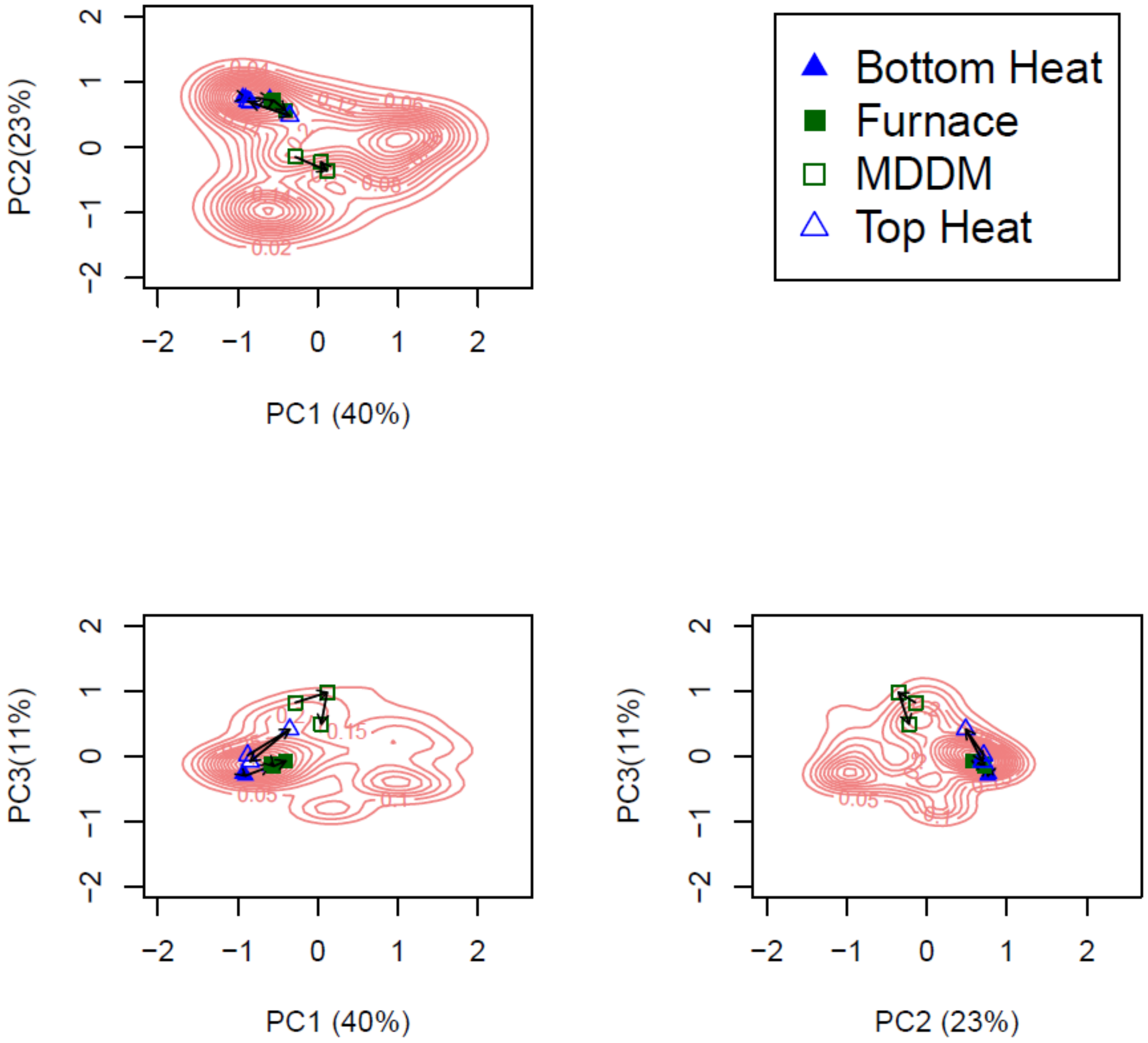


Figure 24: Padding laboratory burns projection into LSB PCA space

As stated for the previously discussed substrates, BH/TH and MDDM/FURN were grouped together due to their similarities in properties. In the three different orthogonal views covering 74% variance in the data, all laboratory burn data projected into the LSB map of the contour region. Clustering was observed between BH and FURN laboratory burn data. TH laboratory burn data projected near the cluster of BH and FURN laboratory burns, but with increasing burn time shifted from the cluster. The MDDM laboratory burn projections separated from the cluster of other laboratory burn data and shifted with increase in burn time. Projection of the carpet padding laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 25**.

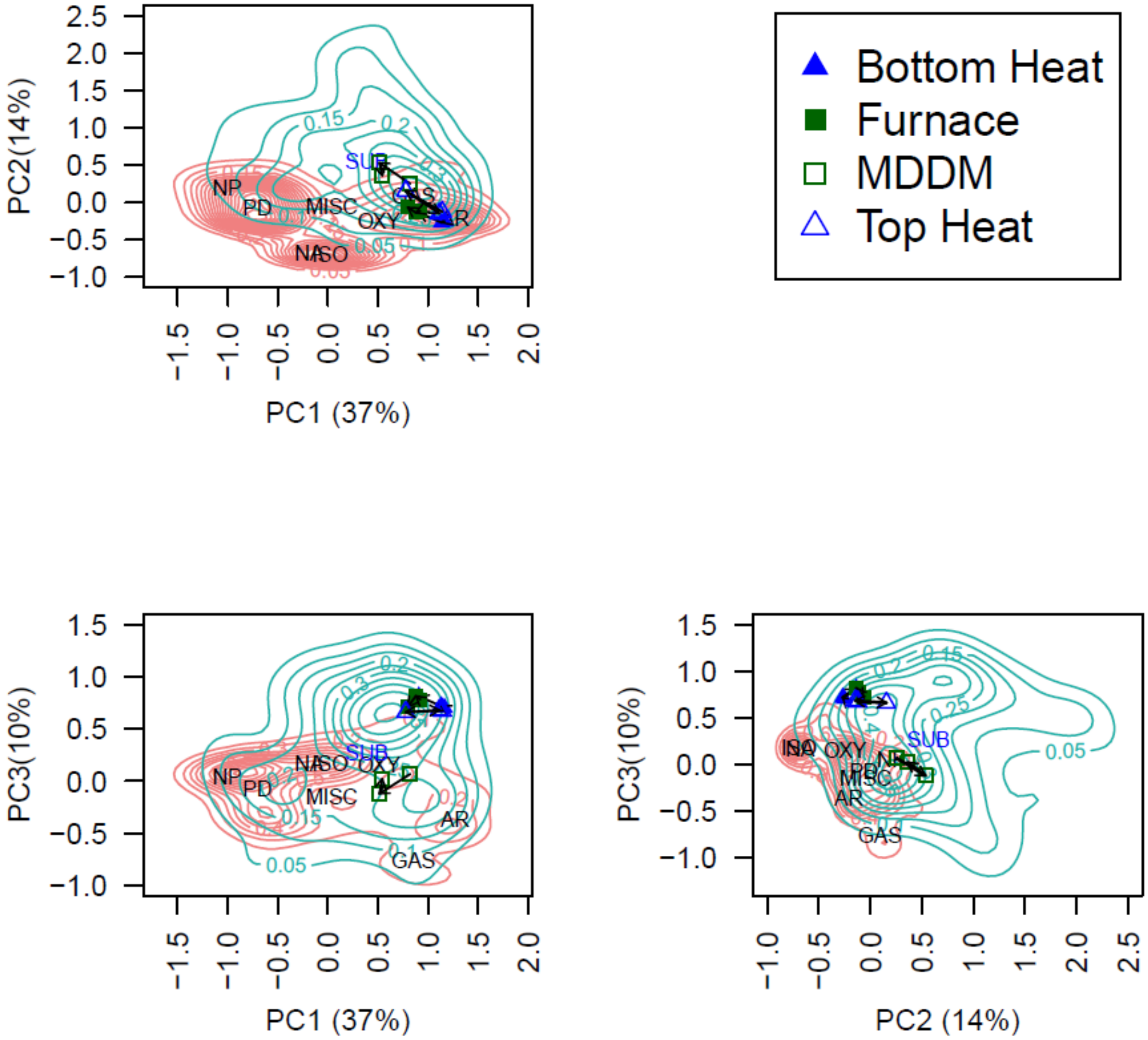


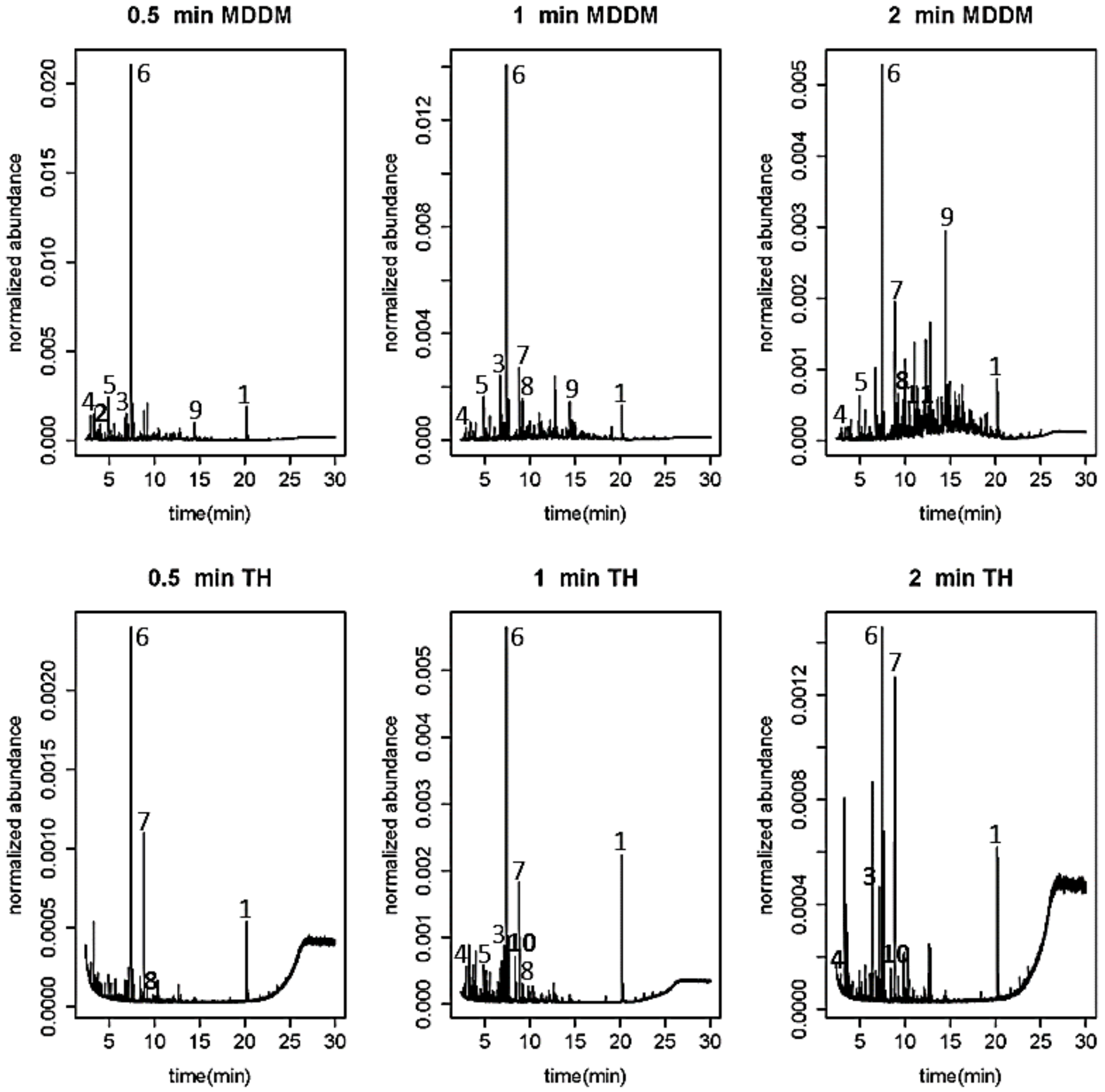
Figure 25: Projection of carpet padding into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn of carpet padding projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burn data project within the mapping space, all laboratory burn data for all PCs show in **Figure 25** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all carpet padding laboratory burns projected within the neat IL and SUB PC map of the contour region. Clustering occurred between TH, BH and FURN laboratory burn data with slight shifting with an increase in burn time. Shifts in projection occurred for MDDM laboratory burn data away from the cluster of TH, BH and FURN laboratory burn projections. The TH, BH and FURN laboratory burns appeared to project within the SUB region, which means these laboratory burns were similar to the data contained within the Substrate database.

4.6.2 TICs from Laboratory Burns

Carpet padding was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared between the burns. Major pyrolysis products expected for carpet padding were produced from decomposition of polyurethane yielding benzene, toluene, alpha methylstyrene, and styrene through random scission.[10, 25] Pyrolysis products were confirmed through mass spectra comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and TH are displayed in **Figure 26**. The TICs from the FURN and BH are displayed in **Figure 27**.



0.5 min MDDM

1 min MDDM

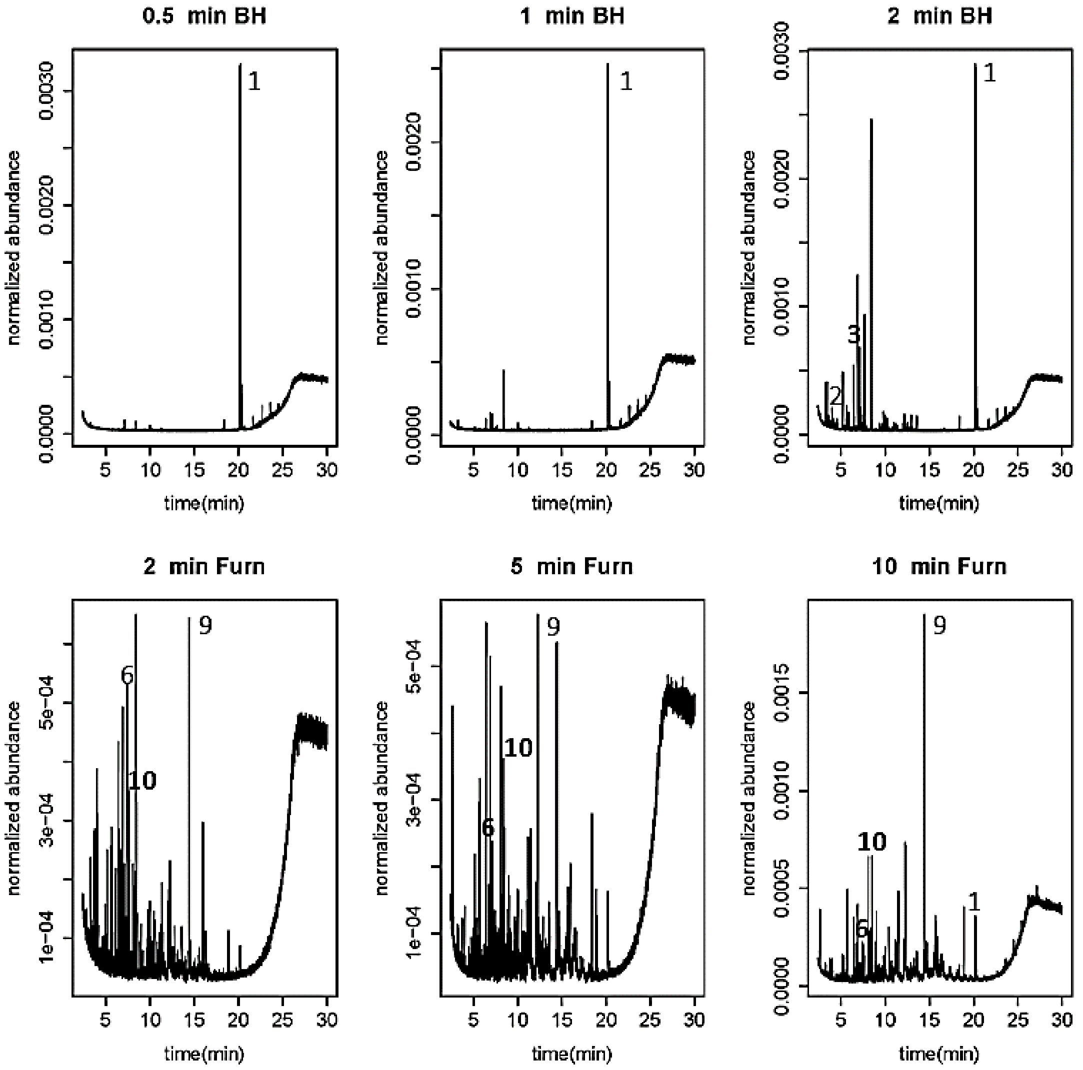
2 min MDDM

0.5 min TH

1 min TH

2 min TH

Figure 26: Components (1) 2-propanol, 1-chloro-, phosphate (3:1), (2) 1-propene, 1,3-dichloro, (3) 1,3-dichloro, 2-propanol, (4) benzene, (5) toluene, (6) styrene, (7) benzonitrile, (8) alpha methylstyrene, (9) 4-phenylbutronitrile, (10) benzaldehyde, (11) phenol


0.5 min BH

1 min BH

2 min BH

2 min Furn

5 min Furn

10 min Furn

Figure 27: Components (1) 2-propanol, 1-chloro-, phosphate (3:1), (2) 1-propene, 1,3-dichloro, (3) 1,3-dichloro, 2-propanol, (6) styrene, (9) 4-phenylbutronitrile, (10) benzaldehyde

From the above figures, multiple conclusions about the substrate and laboratory burning methods could be reached. As observed for the polyester, nylon and olefin carpetings, the MDDM burning method produced the largest number of identified products. The fire retardant, Tris (1-chloro, 2-propyl) phosphate or TCPP was identified within MDDM laboratory burns and

TH and BH burns of carpet padding. TCPP was added as a fire retardant in the manufacturing process of polyeurathane foam.[59] With increasing burn time, there was a shift in the chromatographic profile favoring less volatile components within the MDDM laboratory burns. Styrene was the most abundant peak in MDDM laboratory burns with increasing burn time. Similarly, styrene was the most abundant pyrolysis/combustion product observed in the TICs of TH laboratory burns with increasing burn time. With increase in burn time, TH laboratory burns displayed a decrease in abundance of volatile components in the front portion of the chromatogram. BH laboratory burns yielded chloro-based hydrocarbons such as TCPP, 1-propene, 1-3-dichloro and 1-3-dichloro, 2-propanol. Increase in volatile components and identified components occurred with increasing burn time for BH laboratory burns. FURN laboratory burns displayed low abundance of pyrolysis/combustion products within the TICs. TCPP was identified in the 10 min FURN laboratory burn TIC. The mixture of carpeting and carpet padding was discussed later within this research. Different burn method parameters and laboratory burn time affected the chromatographic profiles of pyrolysis/combustion products that were produced.

4.7 Vinyl Flooring

4.7.1 Projection of Laboratory Burns into Fire Debris Data Sets

Vinyl burns were completed using four different laboratory burn methods (MDDM, TH, BH and FURN) with three different burn times and projected into the same principal component space and map of the contour regions used for projection of the *in silico* data. Laboratory burns data was compared to LSB and neat IL/SUB principal component spaces. The first three principal components were utilized for projection of vinyl laboratory burn data. Projection of the vinyl laboratory burn data into the LSB PCA space is provided in **Figure 28**.

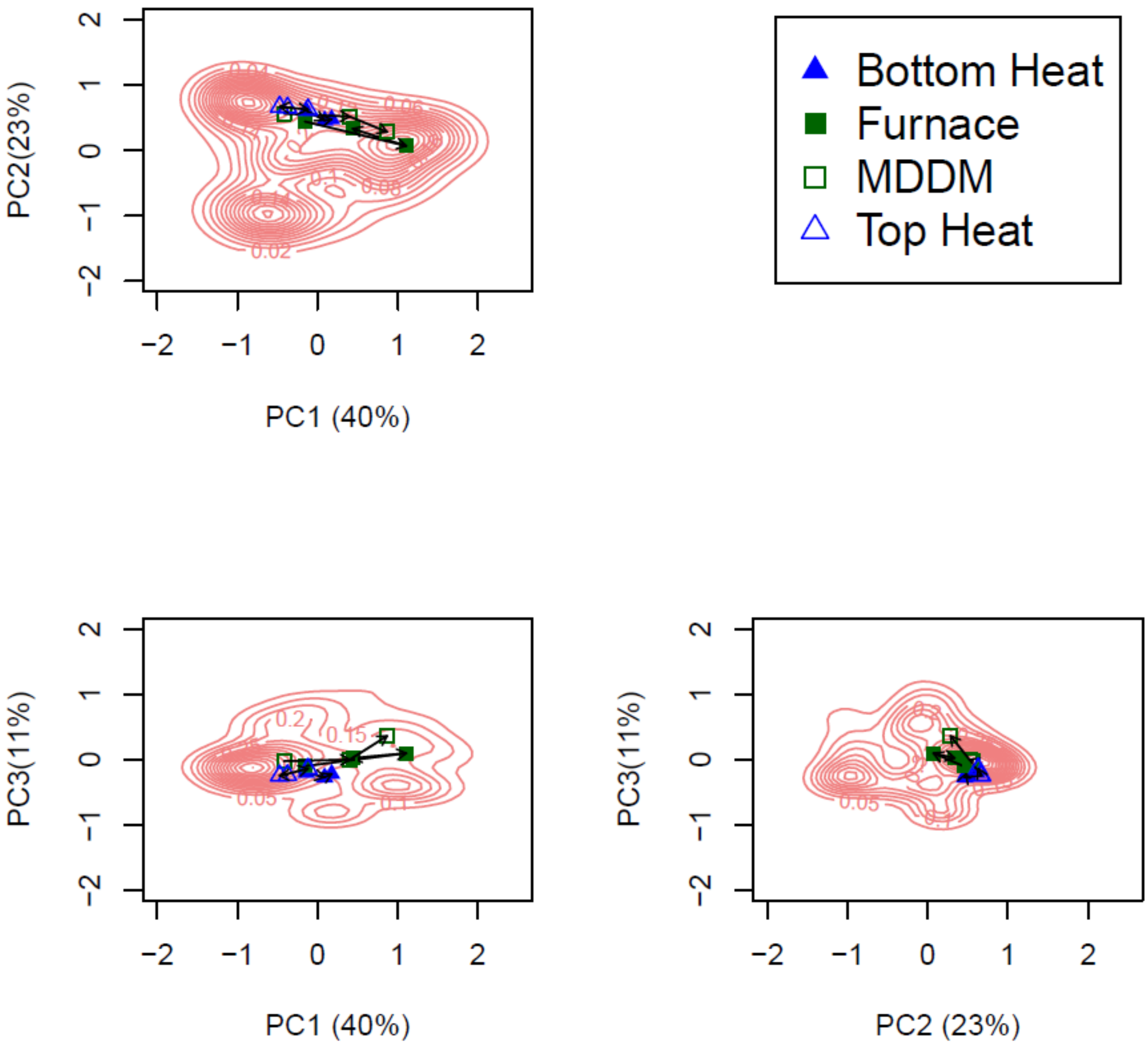


Figure 28: Vinyl laboratory burns projection into LSB PCA space

As stated for the previously discussed substrates, BH/TH and MDDM/FURN were grouped together due to their similarities in properties. For the first two principal components covering 74% of the variance in the data, all laboratory burn data projected into the LSB map of the contour region. Clustering was observed between the TH and BH laboratory burn projections. Shifts in projection of the FURN laboratory burn data was occurring with increase in burn time. MDDM laboratory burn data shifted as well with increase in burn time. Projection of the vinyl laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 29**.

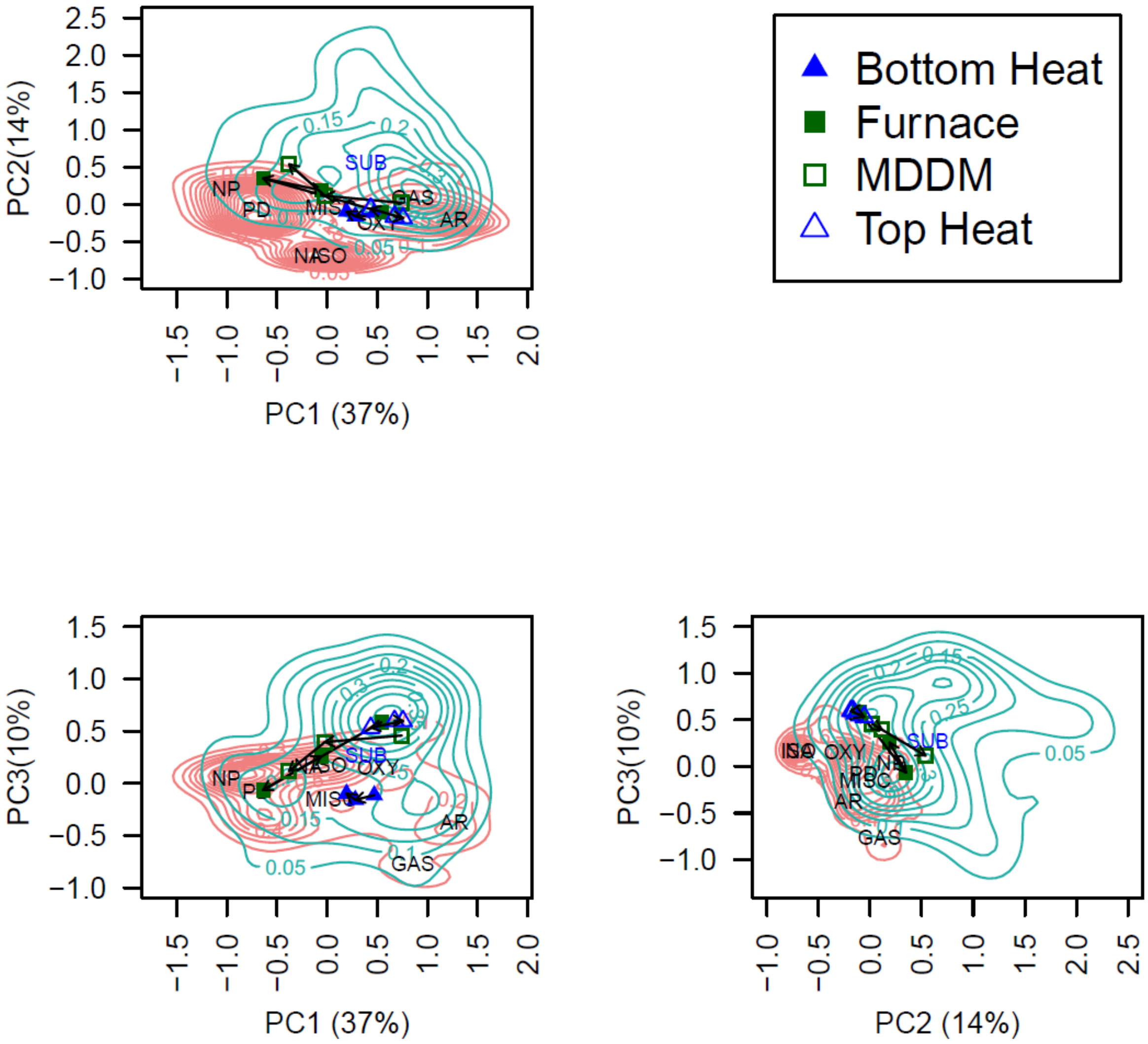


Figure 29: Vinyl laboratory burns projected into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn of vinyl flooring projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burn data project within the mapping space, all laboratory burn data for all PCs shown in **Figure 29** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all vinyl laboratory burns projected within the neat IL and SUB PC map of the contour region. Shifts in projection of the TH and BH laboratory burn data occurred with increase in burn time. FURN laboratory burn projections shifted as well with increase in burn time. MDDM laboratory burn data clustered near the FURN laboratory burn data and shifted with increase in burn time.

4.7.2 TICs from Laboratory Burns

Vinyl flooring was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared between the burns. Major pyrolysis products expected for vinyl flooring were produced from side group scission of polyvinyl chloride (PVC) polymer and vinyl resin with different plasticizers, stabilizers, pigments and fillers. The conjugated chain within PVC broke randomly at a C-C bond, yielding aromatic compounds such as benzene, toluene, and naphthalene.[10, 16, 17] Comparisons between different burning methods was provided using PCA projections into the LSB and neat IL/SUB data sets. Pyrolysis products were confirmed through mass spectral comparisons from NIST and NCFS ILRC libraries and retention time comparisons. The TICs from the MDDM and TH laboratory methods are displayed in **Figure 30**. The TICs from the BH and FURN laboratory burn methods are displayed in **Figure 31**.

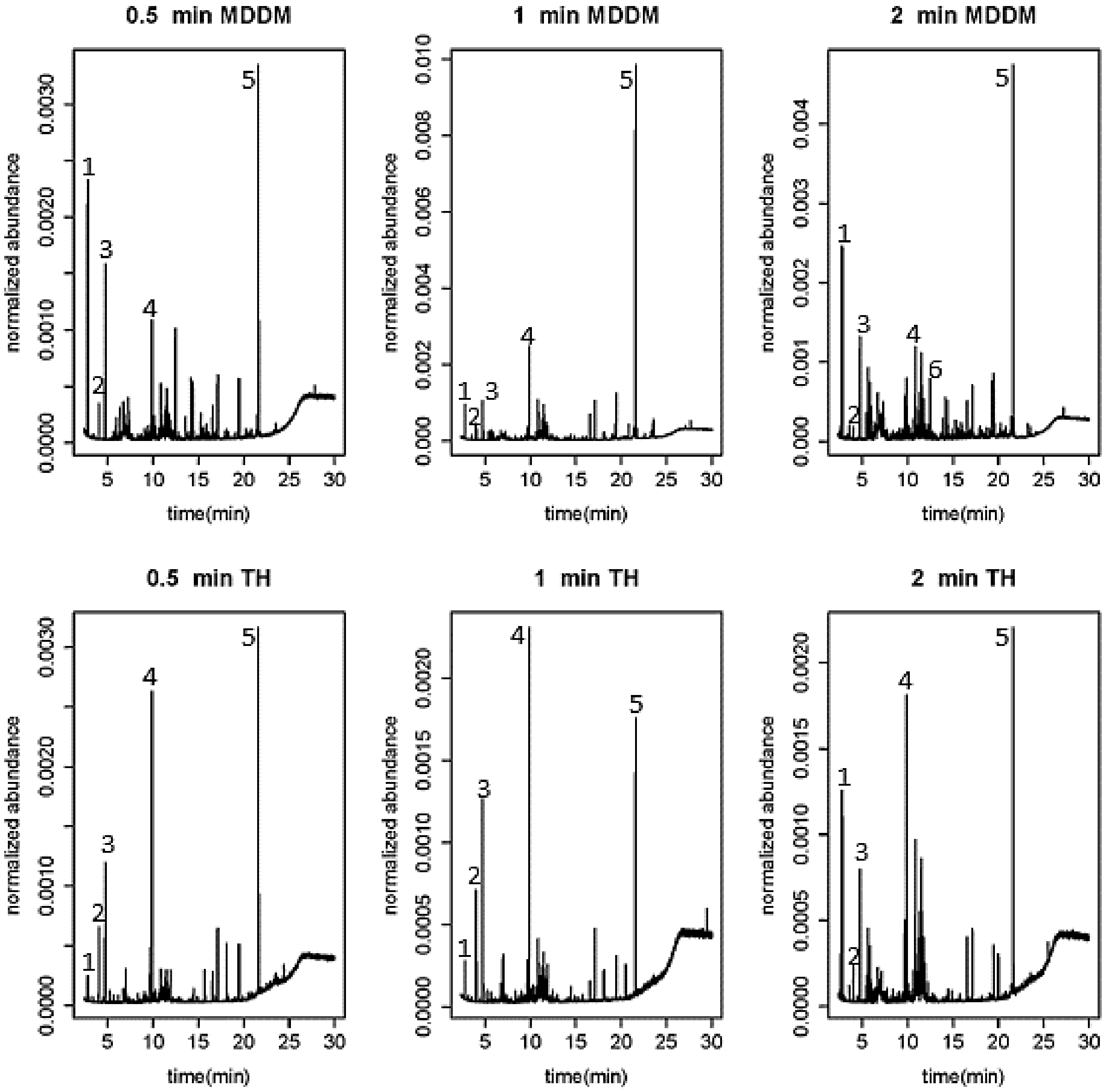


Figure 30: Compounds (1) benzene, (2) methyl isobutyl ketone, (3) toluene, (4) 2-ethyl-1-hexanol, (5) methyl ester hexadecanoic acid, (6) naphthalene

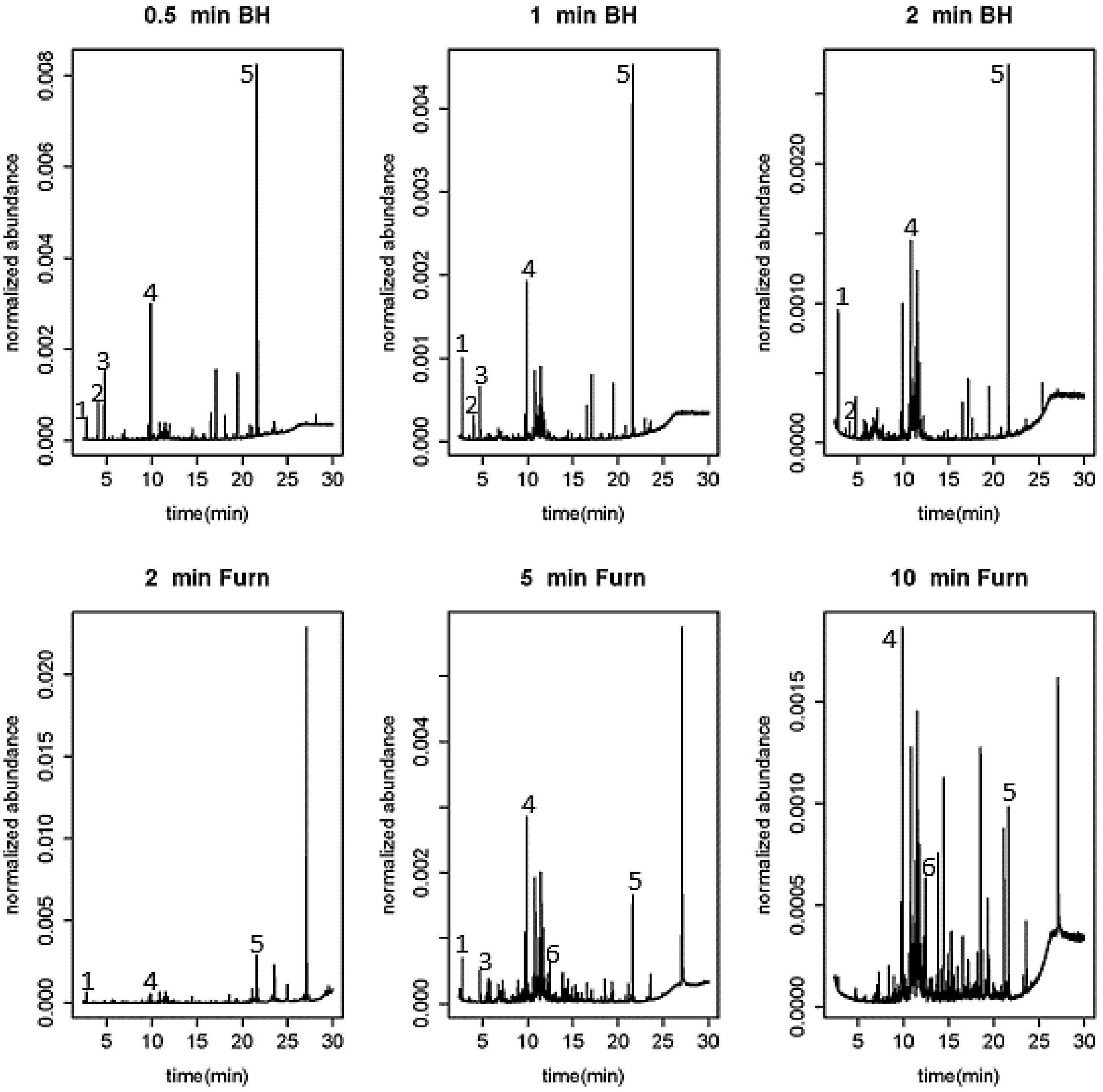


Figure 31: Compounds (1) benzene, (2) methyl isobutyl ketone, (3) toluene, (4) 2-ethyl-1-hexanol, (5) methyl ester hexadecanoic acid, (6) naphthalene

From the above figures, multiple conclusions about the substrate and the laboratory burning methods could be reached. As observed for all discussed carpeting, the MDDM burning method produced the largest number of identified products. Within the MDDM laboratory burns, the 1 min laboratory burn yielded an increase in methyl ester hexadecanoic acid and decrease of volatile components in the TIC. With increase in burn time, TH laboratory burns produced similar pyrolysis/combustion products within the TICs. BH laboratory burns of vinyl flooring produced pyrolysis/combustion products that decrease in abundance with increasing burn time. FURN laboratory burns of vinyl flooring yielded a less volatile, unidentified product at the tail end of the chromatogram with observed retention time of 27 minutes. With increase in burn time, FURN laboratory burns decreased at the tail end of the chromatogram and additional pyrolysis/combustion products were identified in the 10 min laboratory burn chromatographic profile.

Observed pyrolysis/combustion results may reflect different additives that were added during the manufacturing process of vinyl flooring. Methyl ester hexadecanoic acid was the most abundant pyrolysis/combustion product observed within all laboratory burns of vinyl flooring. Methyl ester hexadecanoic acid, or methyl palmitate, was used in the manufacturing of the veneer finishing layer of the vinyl flooring in addition to methyl isobutyl ketone in resin formation and varnish finishing.[57, 58] Different burn method parameters and laboratory burn time affected the chromatographic profile of pyrolysis/combustion products that were produced.

4.8 Laminate Flooring

4.8.1 Projection of Laboratory Burns into Fire Debris Data Sets

Laminate flooring burns were completed using four different laboratory burn methods (MDDM, TH, BH and FURN) with three different burn times and projected into the same principal component space and map of the contour regions used for projection of the *in silico* data. Laboratory burns were compared to LSB and neat IL/SUB principal component spaces. The first three principal components were utilized in the projection of laminate flooring laboratory burn data. Projection of the laminate laboratory burn data into the LSB PCA space is provided in **Figure 32**.

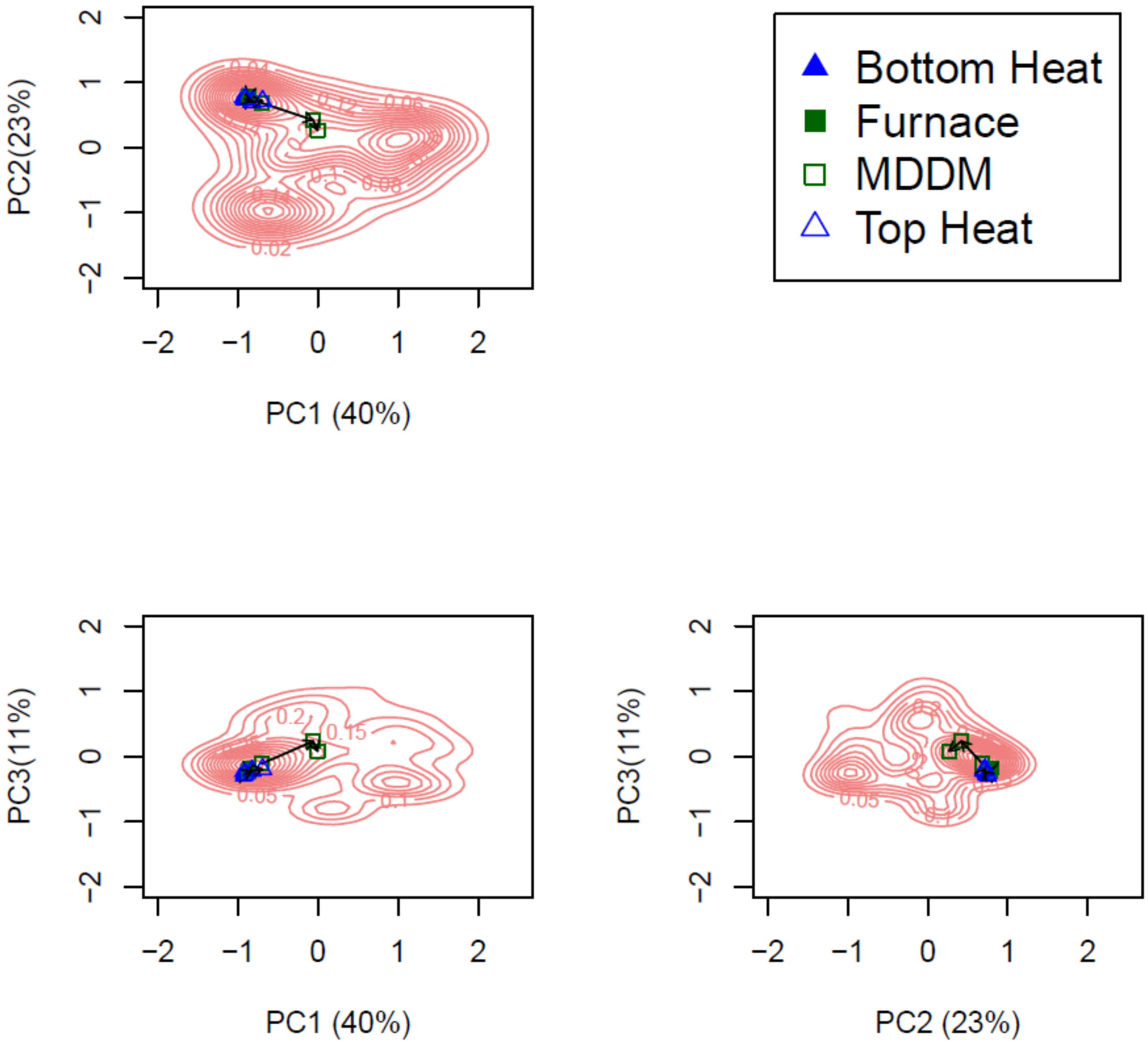


Figure 32: Projection of laminate flooring burns into LSB PCA space

As stated for the previously discussed substrates, BH/TH and MDDM/FURN were grouped together due to their similarities in properties. In the three different orthogonal views covering 74% variance in the data, all laboratory burn data projected into the LSB map of the contour region. Clustering was observed between TH, BH and FURN laboratory burn projections. Shifts in projection of the MDDM laboratory burn data occur away from the clustering of burn points with increase in burn time. Projection of the laminate laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 33**.

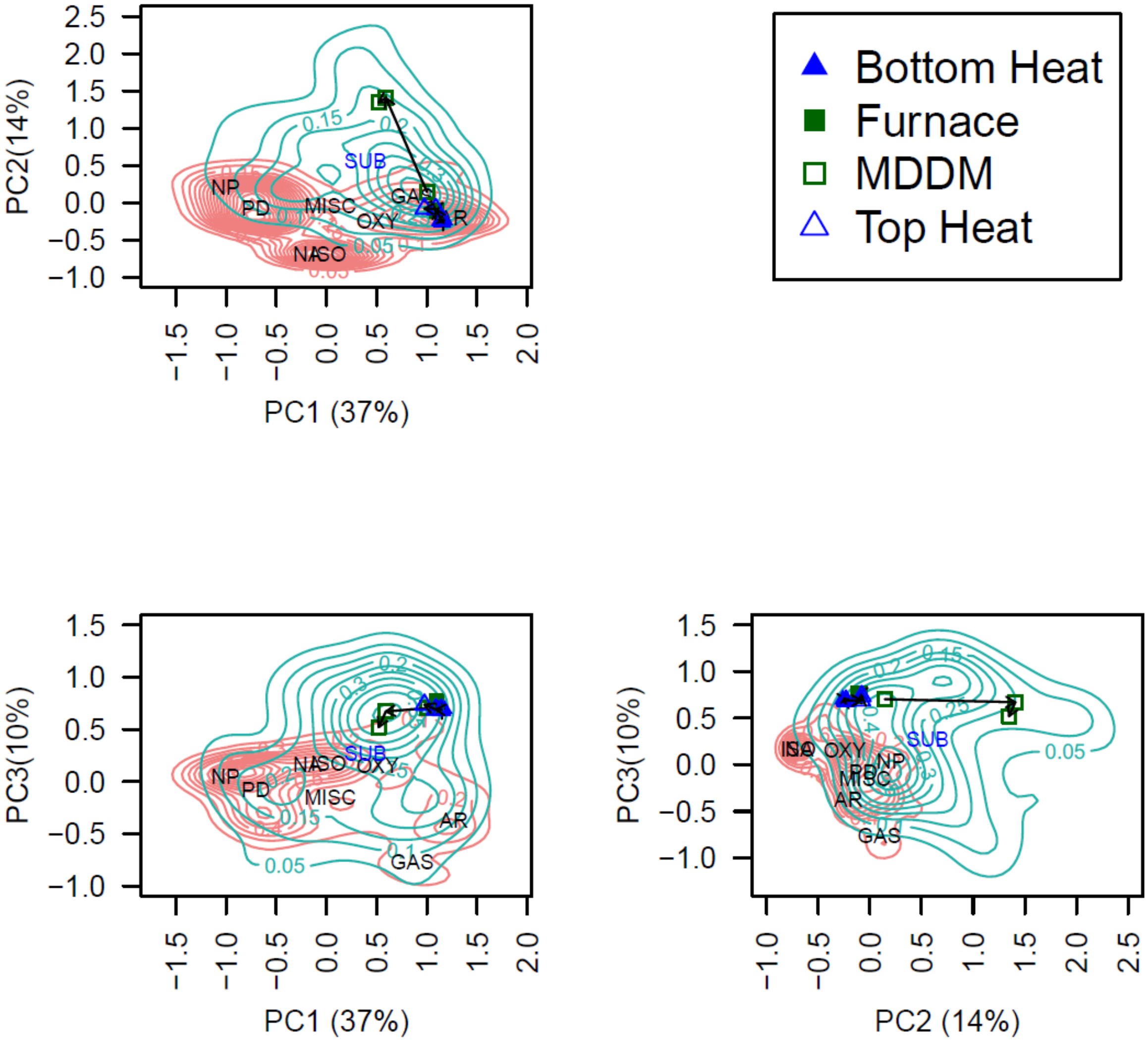


Figure 33: Projection of laminate flooring into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn data of laminate flooring projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burns project within the mapping space, all laboratory burn data for all PCs shown in **Figure 33** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all laminate laboratory burn data projected within the neat IL and SUB PC map of the contour region. Clustering was occurring between TH, BH and FURN laboratory burn projections. MDDM laboratory burn data shifted from the cluster of laboratory burn data with increase in burn time. The 1 and 2 min MDDM laboratory burn projections were noticeably different than the other laboratory burn projections. The laboratory burn data appeared to be similar to the burn data that is contained within the Substrate database. All laminate flooring laboratory burn data projected into the SUB region.

4.8.2 TICs from Laboratory Burns

Laminate flooring was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared between the burns. Major pyrolysis products expected for laminate flooring were produced from the decomposition of poly(melamine-co-formaldehyde) yielding 2-furaldehyde and furfuryl alcohol, which were common cellulosic pyrolysis products. Pyrolysis components were confirmed through mass spectra comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and TH laboratory methods are displayed in **Figure 34**. The TICs from the FURN and BH laboratory methods are displayed in **Figure 35**.

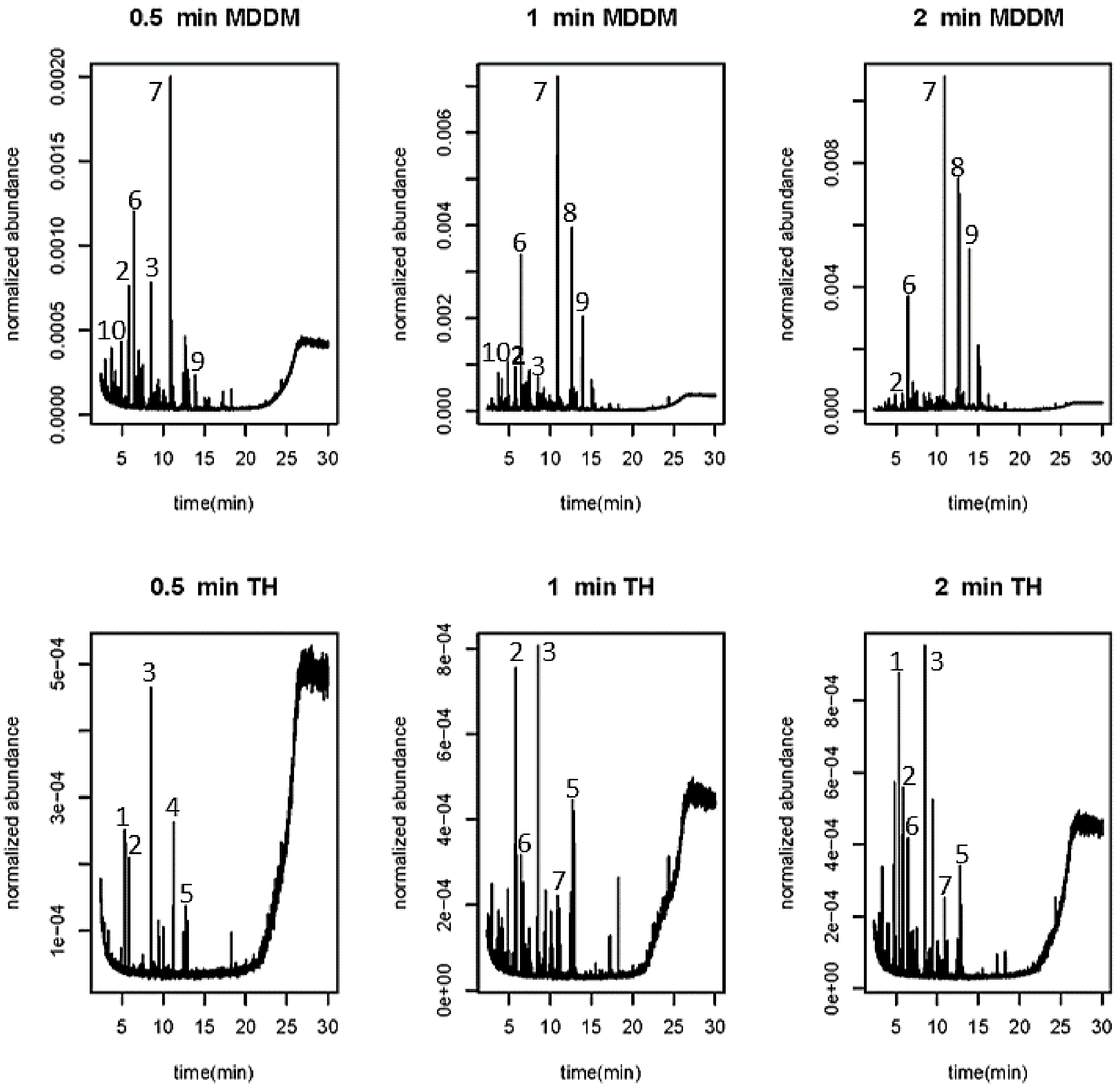


Figure 34: Components (1) hexanal, (2) 2-furaldehyde, (3) benzaldehyde, (4) nonanal, (5) alpha terpinol, (6) furfuryl alcohol, (7) 2-methoxyphenol, (8) 2-methoxy-4-methylphenol, (9) 4-ethyl-2-methoxyphenol, (10) toluene

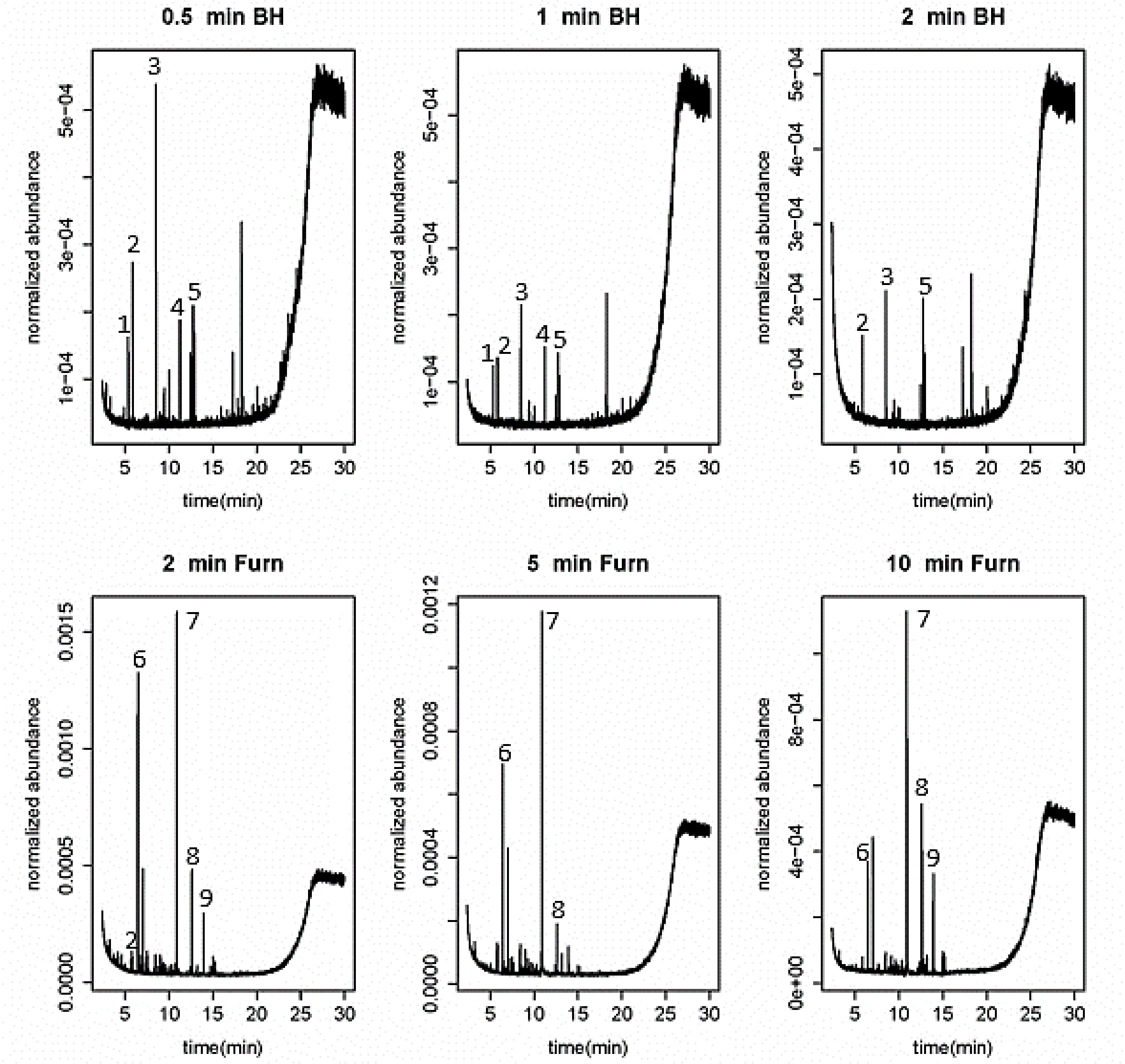


Figure 35: Components (1) hexanal, (2) 2-furaldehyde, (3) benzaldehyde, (4) nonanal, (5) alpha terpinol, (6) furfuryl alcohol, (7) 2-methoxyphenol, (8) 2-methoxy-4-methylphenol, (9) 4-ethyl-2-methoxyphenol, (10) toluene

From the above figures, multiple conclusions about the substrate and laboratory burning methods could be reached. As observed for all discussed carpeting and vinyl flooring, the MDDM burning method produced the largest number of identified products that were formed. With an increase in burn time, MDDM laboratory burn TICs favored less volatile components within the chromatographic profile. MDDM laboratory burns displayed an increase of identified phenolic aromatic pyrolysis/combustion products in 1 and 2 min MDDM burns of laminate flooring. TH laboratory burns displayed an increase in volatile pyrolysis/combustion products with increase in burn time. Additional phenolic aromatic components were identified in the 1 and 2 min TH laboratory burns. BH laboratory burns decreased in abundance with increase in burn time and less identified pyrolysis/combustion products were observed in the 2 min BH TIC. FURN laboratory burns displayed mostly phenolic aromatic components within the chromatographic profiles. With an increase in burn time, FURN laboratory burns displayed a decrease in abundance of pyrolysis/combustion products.

Almost every laminate flooring labotoraty burn, other than the 5 and 10 min FURN burns, displayed the identification of 2-furaldehyde. Another common cellulosic product, furfuryl alcohol, was identified within the 5 and 10 min FURN burns. 2-furaldehyde was one of three common pyrolysis/combustion products observed from the pyrolysis of cellulosic materials. Furfuryl alcohol was identified in MDDM, TH, and FURN laboratory burns of laminate flooring. Within the TH and MDDM laboratory burns, furfuryl alcohol abundance increased with increase in burn time. FURN laboratory burns exhibited decrease of furfuryl alcohol abundance with increasing burn time. Different burn method parameters and laboratory burn time affected the chromatographic profile of pyrolysis/combustion products that were produced.

4.9 Plywood

4.9.1 Projection of Laboratory Burns into Fire Debris Data Sets

Plywood burns were completed using four different laboratory burn methods (MDDM, BH, TH and FURN) with three different burn times and projected into the same principal component space and map of the contour regions that were used for projection of the *in silico* data. Laboratory burn data was compared to LSB and the neat IL/SUB principal component spaces. The first three principal components were utilized for projection of the plywood laboratory burn data. Projection of the plywood laboratory burn data into the LSB PCA space is provided in **Figure 36**.

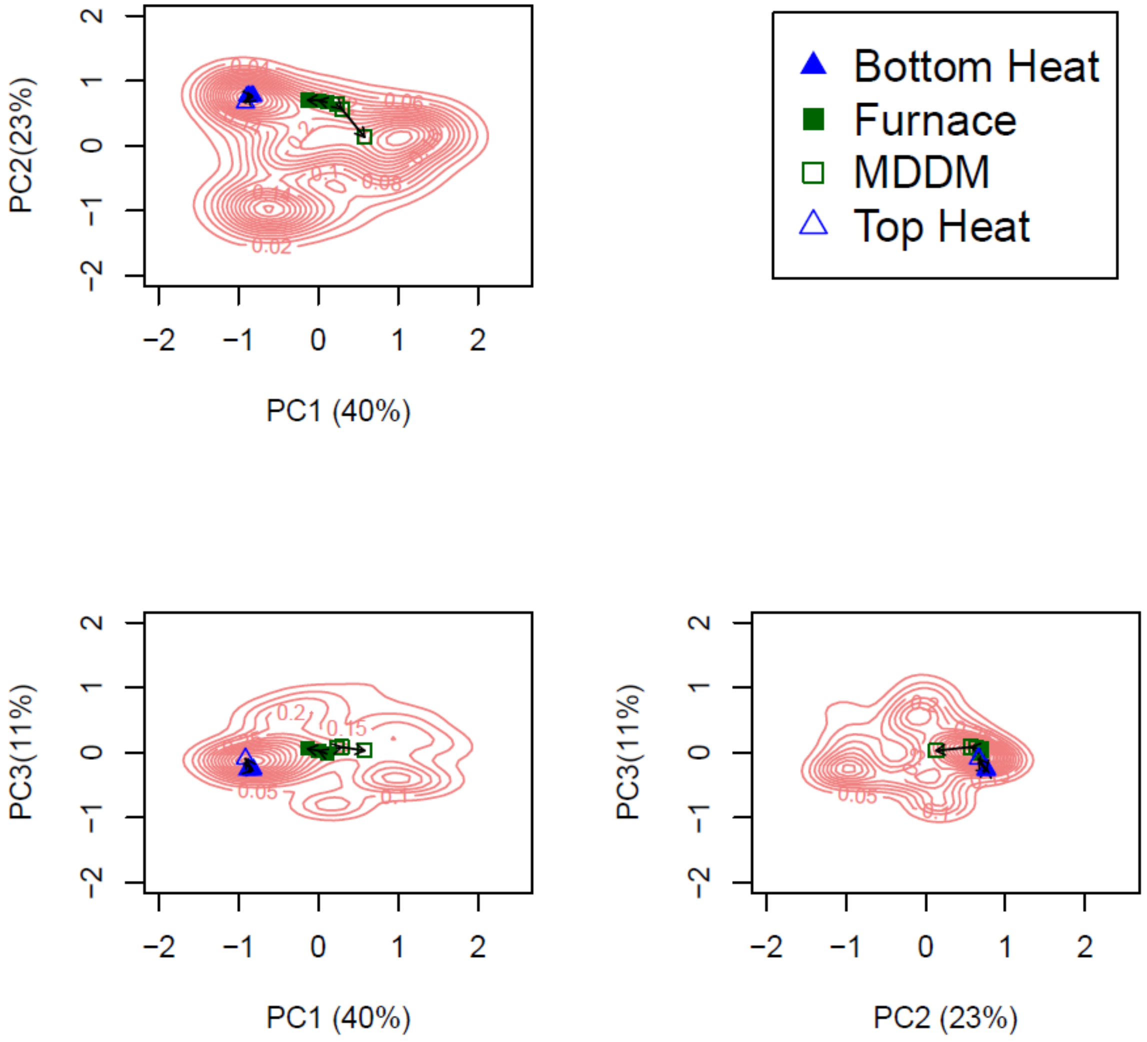


Figure 36: Projection of plywood material into LSB PCA space

As stated for the previously discussed substrates, BH/TH and MDDM/FURN were grouped togheter due to their similarities in properties. In the three different orthogonal views covering 74% variance in the data, all laboratory burn data projected into the LSB map of the contour region. Clustering occurred between the TH and BH laboratory burn projections. Clustering was also occurring between the MDDM and FURN laboratory burn data. There was a shift in projection of the 2 minute MDDM laboratory burn data away from the cluster of MDDM and FURN burn projections with increase in burn time. Projection of the plywood laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 37**.

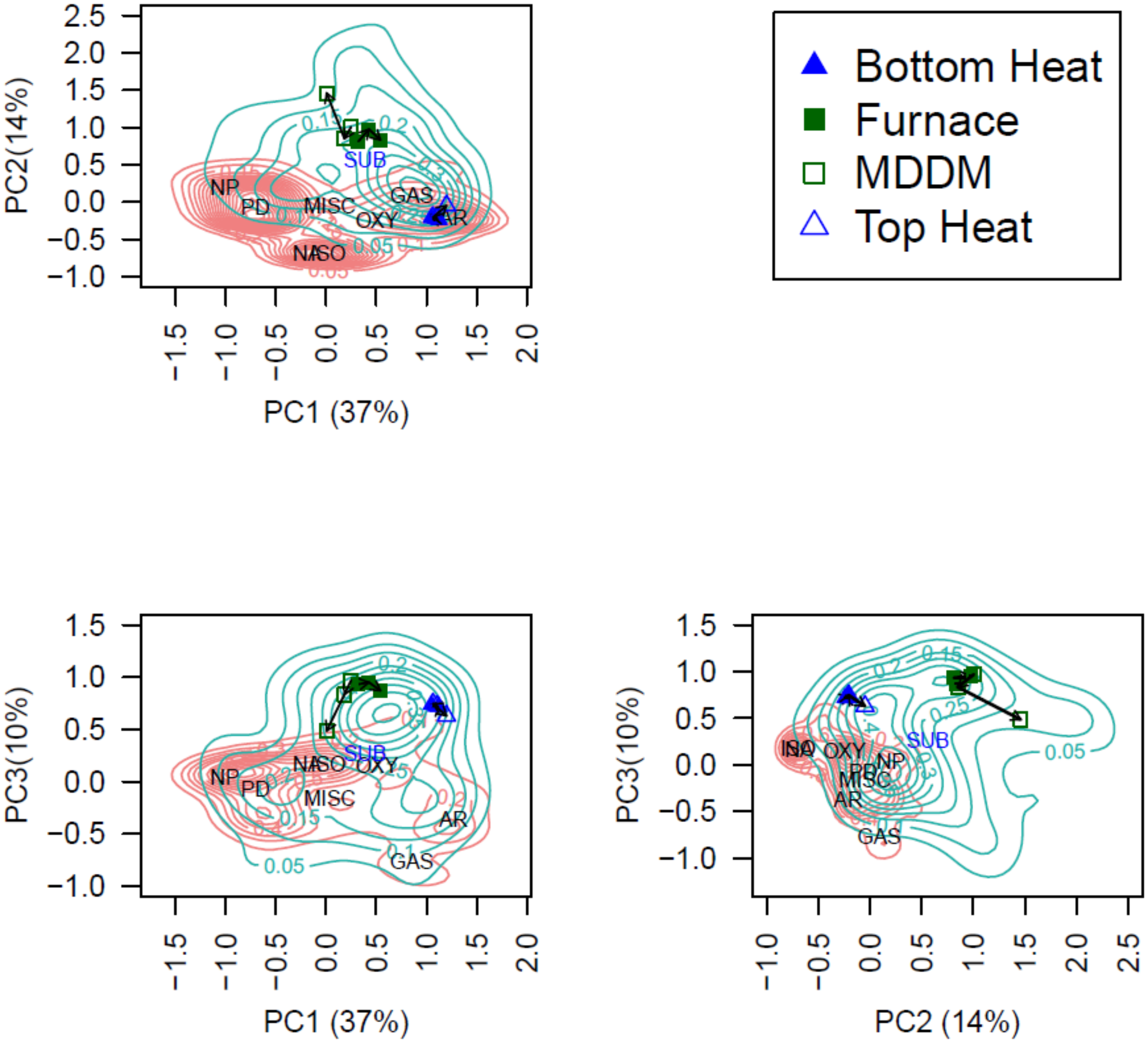


Figure 37: Projection of plywood material into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn of plywood flooring projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burn data project within the mapping space, all laboratory burn data for all PCs shown in **Figure 37** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all plywood laboratory burns projected within the neat IL and SUB PC map of the contour region. Clustering was occurring between the TH and BH laboratory burn projections. Clustering also occurred between the MDDM and FURN laboratory burn projections. The 2 min MDDM laboratory burn data shifted in projection away from the MDDM and FURN laboratory burn cluster. BH/TH and MDDM/FURN laboratory burn data projected separately and were noticeably different within all three orthogonal views. The laboratory burn data appeared to be similar to the burn data that is contained within the Substrate database. All plywood flooring laboratory burn points projected into the SUB region.

4.9.2 TICs from Laboratory Burns

Plywood was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared between the burns. Major pyrolysis products expected for plywood were produced from the thermal degradation of wood that yields cellulosic materials such as 2-furaldehyde, furfuryl alcohol and 5-methylfurfural.[10] Decomposition of wood broke down its three main components due to increasing temperature with decomposition of hemicellulose (180-350˚C), cellulose (275-350 ˚C) and lignin (250-500 ˚C).[29, 61] Observed components were confirmed through mass spectra comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and TH laboratory methods are displayed in **Figure 38**. The TICs from the FURN and BH laboratory methods are displayed in **Figure 39**.

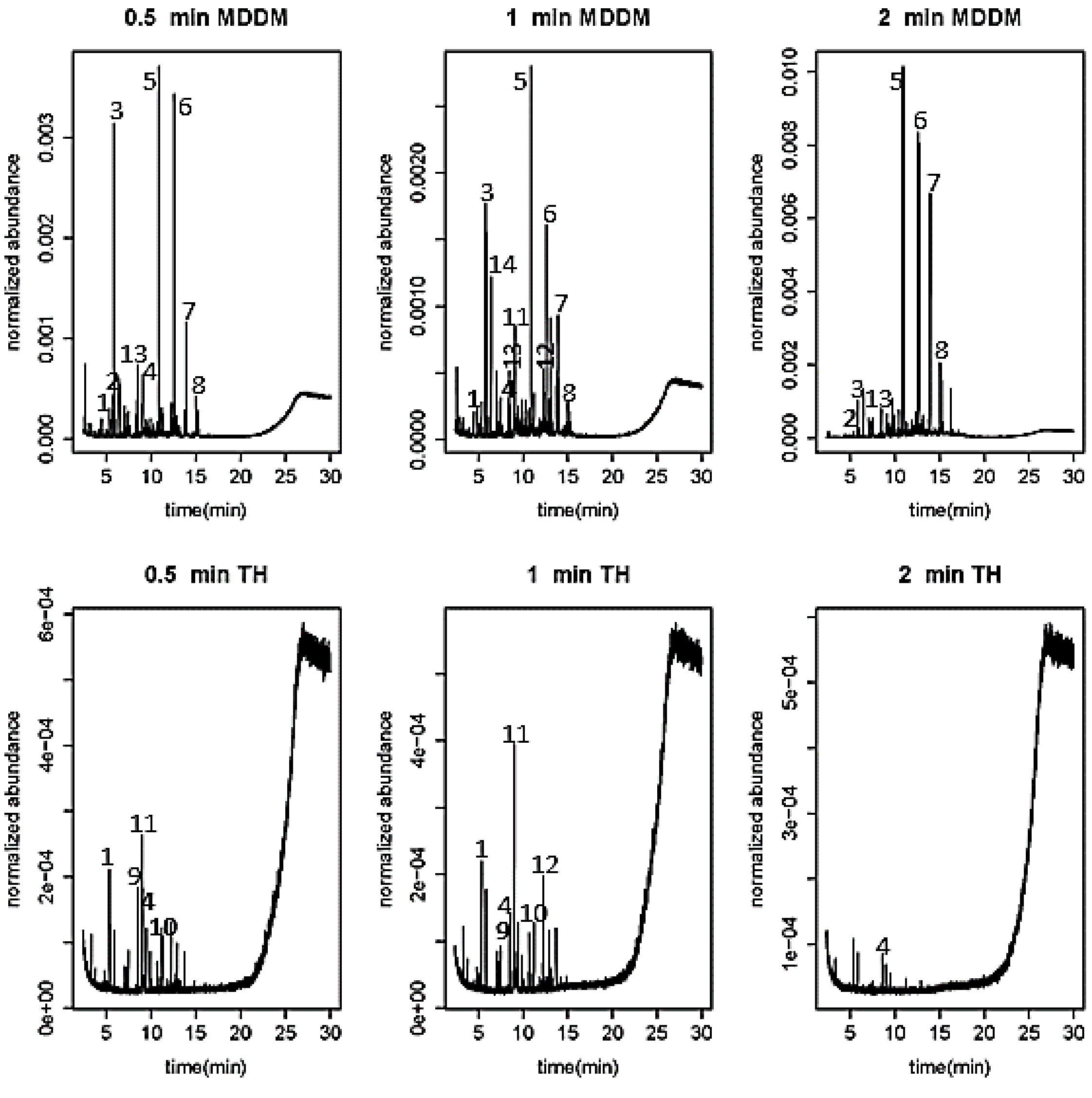


Figure 38: Compounds (1) hexanal, (2) 2-cyclopenten-1-one, (3) 2-furaldehyde, (4) alpha pinene, (5) 2-methoxyphenol, (6) 2-methoxy-4-methoxyphenol, (7) 4-ethyl-2-methoxyphenol, (8) eugenol, (9) benzaldehyde, (10) nonanal, (11) hexanoic acid, (12) octanoic acid, (13) 5-methylfurfural, (14) furfuryl alcohol

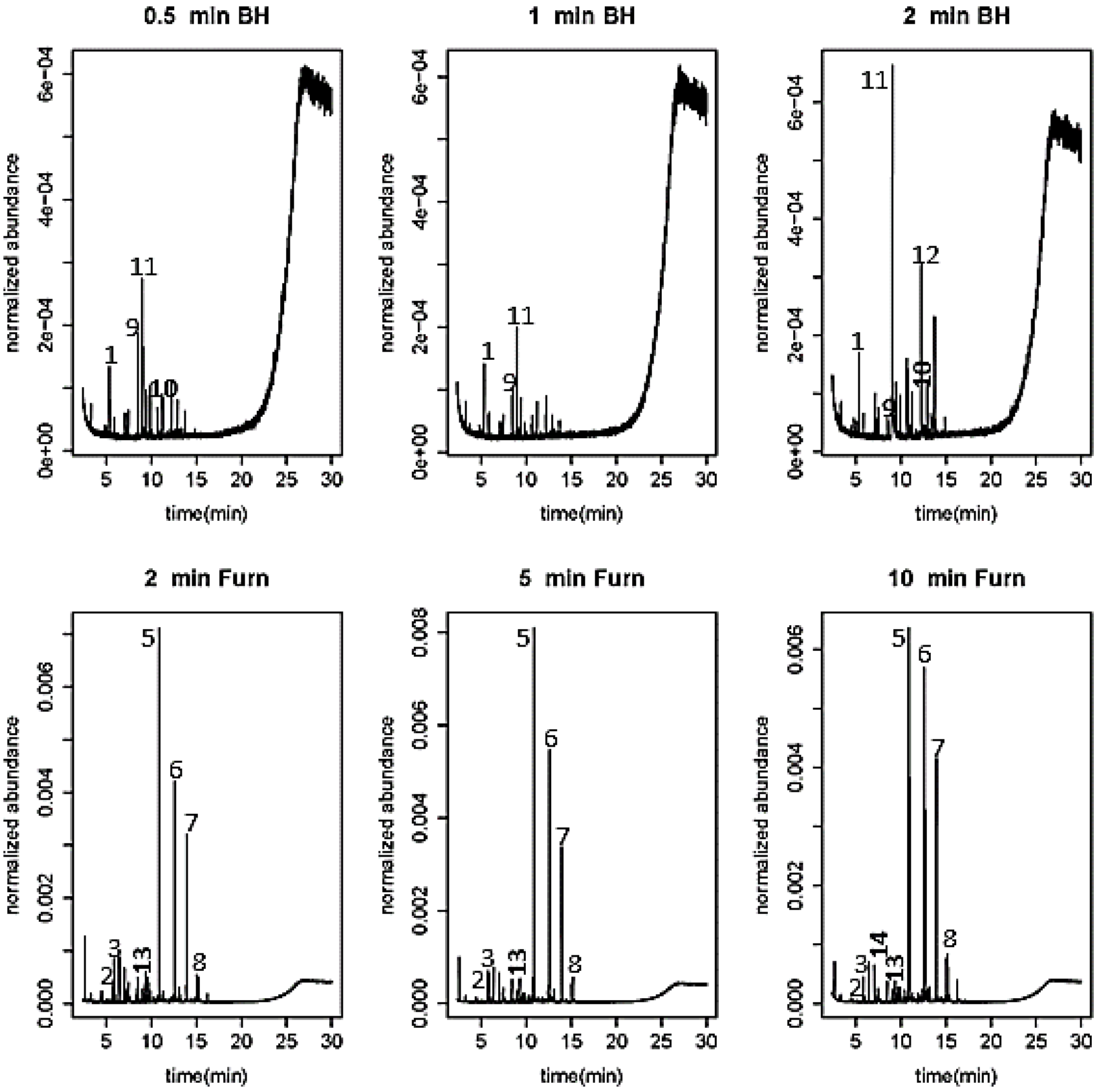


Figure 39: Compounds (1) hexanal, (2) 2-cyclopenten-1-one, (3) 2-furaldehyde, (5) 2-methoxyphenol, (6) 2-methoxy-4-methoxyphenol, (7) 4-ethyl-2-methoxyphenol, (8) eugenol, (9) benzaldehyde, (10) nonanal, (11) hexanoic acid, (12) octanoic acid, (13) 5-methylfurfural, (14) furfuryl alcohol

From the above figures, multiple conclusions about the substrate and laboratory burning methods could be reached. As observed for all sicussed carpeting and processed flooring, the MDDM burning method produced the largest number of identified products. MDDM laboratory burns of plywood decreased in volatile components in the front portion of the chromatographic profile. The 2 min MDDM laboratory burn exhibited an increase of less volatile phenolic aromatic pyrolysis/combustion products. FURN laboratory burns displayed a similar chromatographic profile to the 2 min MDDM laboratory burn with abundant phenolic aromatic pyrolysis/combustion products. TH laboratory burns yielded similar chromatographic profiles with shorter burn times, but only alpha pinene was identified in the 2 min TH burn. BH laboratory burns displayed a similar product pattern to TH lab burns, but the 2 min BH lab burn displayed an increase in abundance in the front portion of the chromatogram. BH and TH laboratory burns exhibited fairly low abundance of pyrolysis/combustion products in all TICs.

The three major cellulosic pyrolysis products were observed. However, only FURN and MDDM laboratory burns displayed the identification of the three major cellulosic pyrolysis products of 5-methylfurfural, furfuryl alcohol and 2-furaldehyde within the TICs. Additional fire retardant or adhesives applied during the manufacturing process could potentially alter the pyrolysis/combustion products for plywood material. Ultimately, different burn method parameters and laboratory burn time affected the chromatographic profile of pyrolysis/combustion products produced.

4.10 Yellow Pine

4.10.1 Projection of Laboratory Burns into Fire Debris Data Sets

Yellow pine burns were completed using four different laboratory burn methods (MDDM, TH, BH and FURN) with three different burn times and were projected into the same principal component space and map of the contour region that were used for projection of the *in silico* data. Laboratory burn data was compared to LSB and neat IL/SUB principal component spaces. The first three principal components were utilized for projection of yellow pine laboratory burn data. Projection of the yellow pine laboratory burn data into the LSB PCA space is provided in **Figure 40**.

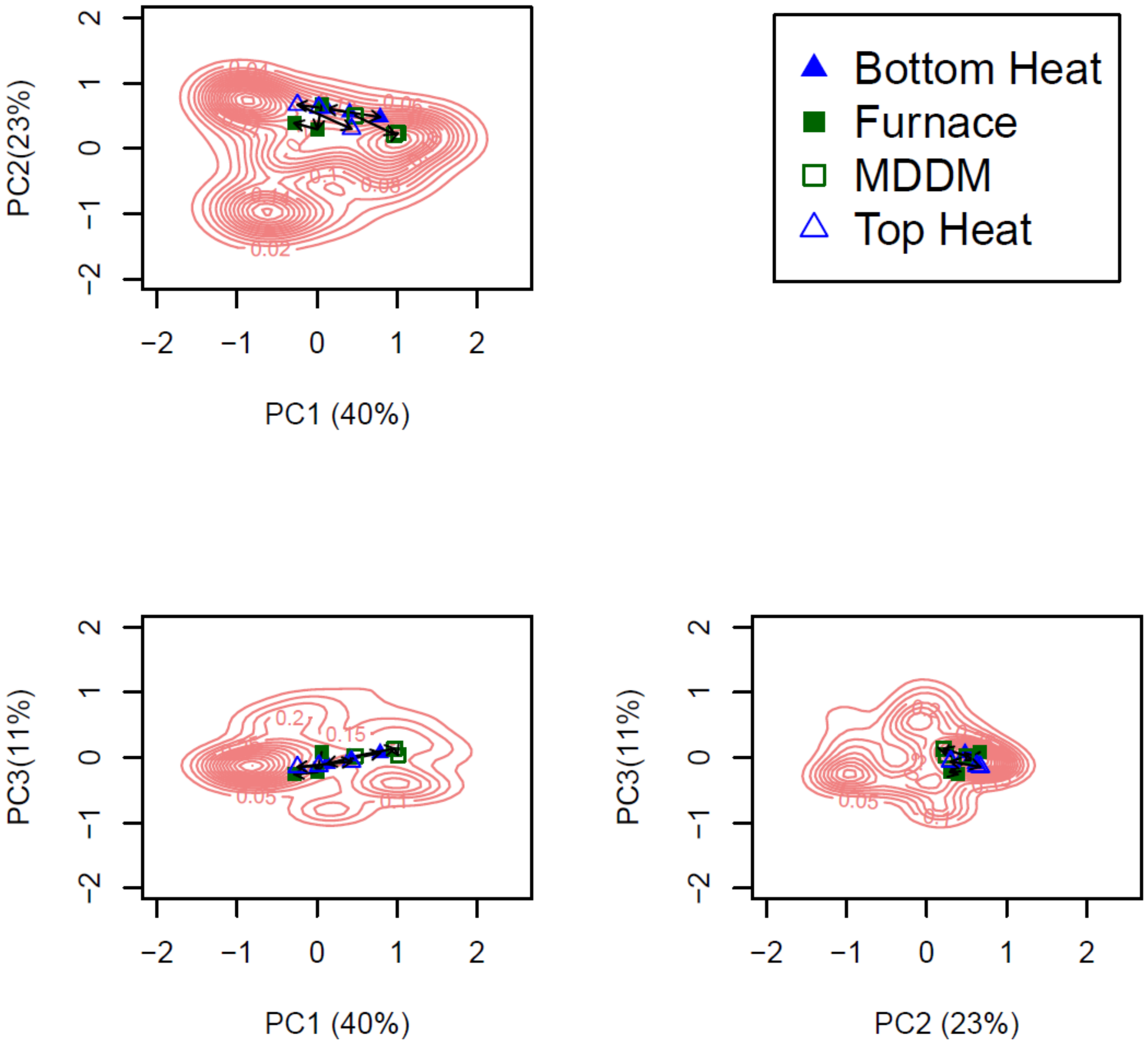


Figure 40: Projection of yellow pine flooring into LSB PCA space

As stated for the previously discussed substrates, BH/TH and MDDM/FURN were grouped together due to their similarities in properties. In the three different orthogonal views covering 74% variance in the data, all laboratory burn data projected into the LSB map of the contour region. Clustering was observed between MDDM, TH, BH and FURN laboratory burn point projections. Slight shifting in projection of the FURN laboratory burn data occurred with increase in burn time. MDDM laboratory burn data shifted in projection with increase in burn time as well. Projection of the yellow pine laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 41**.

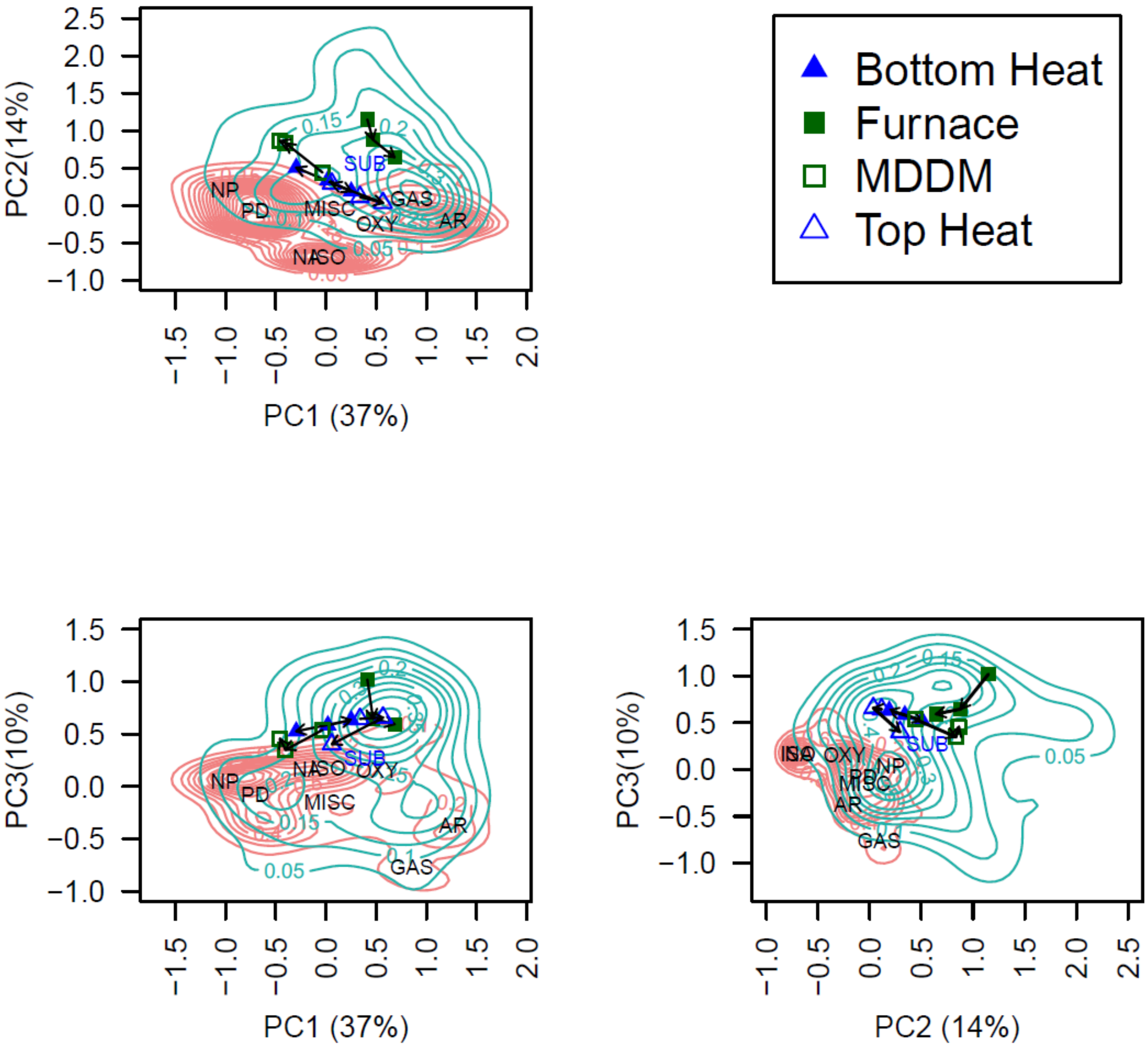


Figure 41: Projection of yellow pine into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burned using the MDDM burn method, it was expected that each MDDM laboratory burn of yellow pine projected within the map of the contour region of neat IL/SUB. Not only did all MDDM laboratory burn data project within the contour space, all laboratory burn data for all PCs shown in **Figure 41** projected within the contour region.

In the three different orthogonal views covering 61% variance in the data, all yellow pine laboratory burns projected within the neat IL and SUB PC map of the contour region. Clustering was occurring between the TH and BH laboratory burn projections. MDDM laboratory burn data projected near the cluster of TH and BH, but shifted away with increase in burn time. FURN laboratory burn data shifted slightly in projection with increase in burn time as well. The laboratory burn data appeared to be similar to the burn data that is contained within the Substrate database. All yellow pine laboratory burn data projected into the SUB region.

4.10.2 TICs from Laboratory Burns

Yellow pine wood was burned using four different burning methods and three burn times for each method. The TICs from the laboratory burns were compared amongst the burns. Major pyrolysis products expected for yellow pine wood were produced from thermal degradation of wood yielding cellulosic materials such as 2-furaldehyde, furfuryl alcohol, and 5-methylfurfural.[10] Decomposition of wood broke down its three main components due to increasing temperature with decomposition of hemicellulose (180-350˚C), cellulose (275-350 ˚C) and lignin (250-500 ˚C).[29, 61] Pyrolysis products were confirmed through mass spectra comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and TH are displayed in **Figure 42**. The TICs from the FURN and BH are displayed in **Figure 43**.

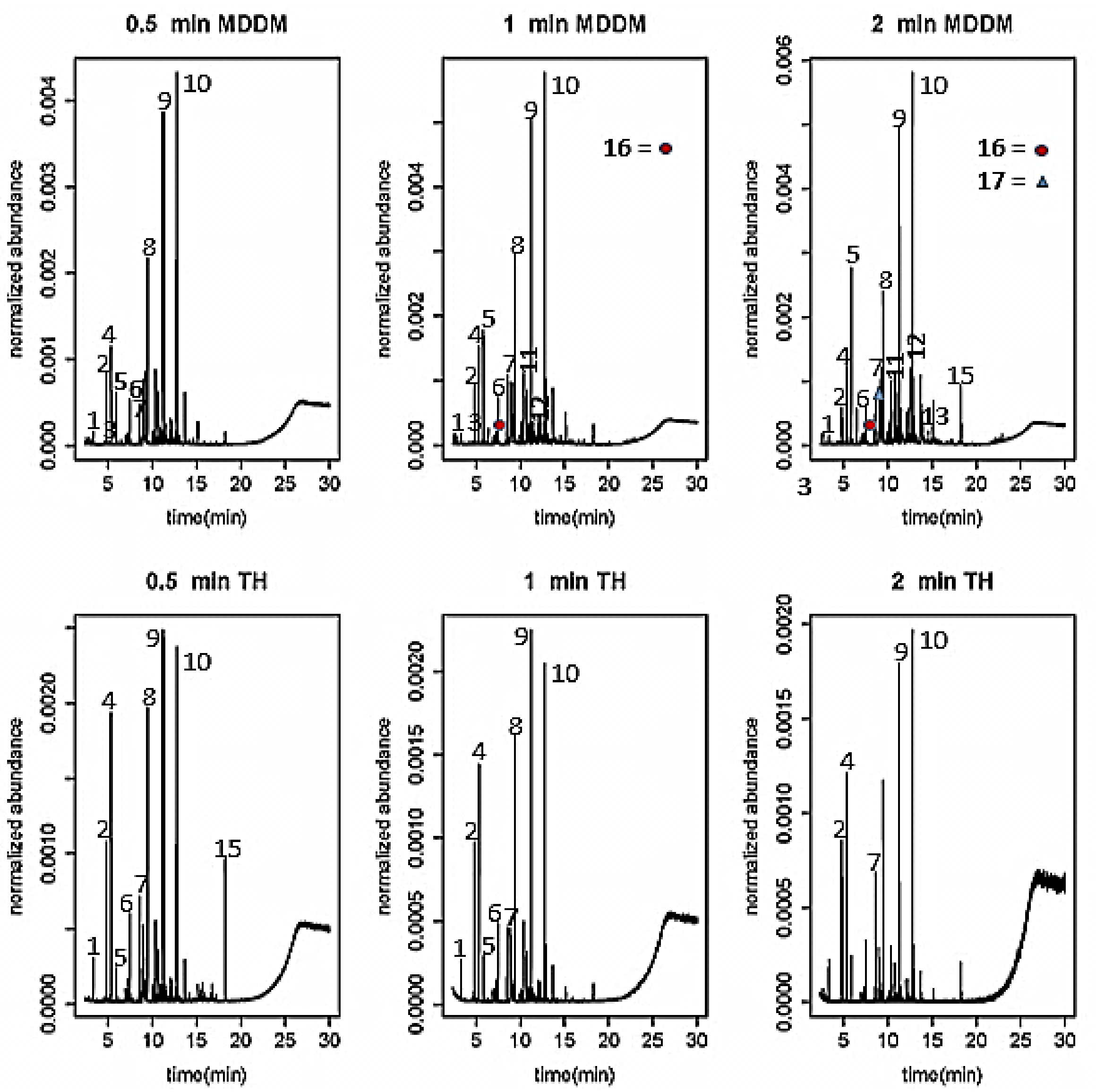


Figure 42: Compounds (1) pentanal, (2) 1-pentanol, (3) toluene, (4) hexanal, (5) 2-furaldehyde, (6) heptanal, (7) alpha pinene, (8) octanal, (9) nonanal, (10) 1-methoxy-4-(2-propenyl) benzene, (11) 2-methoxyphenol, (12) 2-methoxy-4-methylphenol, (13) 4-ethyl-2-methoxyphenol, (15) TXIB, (16) furfuryl alcohol, (17) 5-methylfurufral

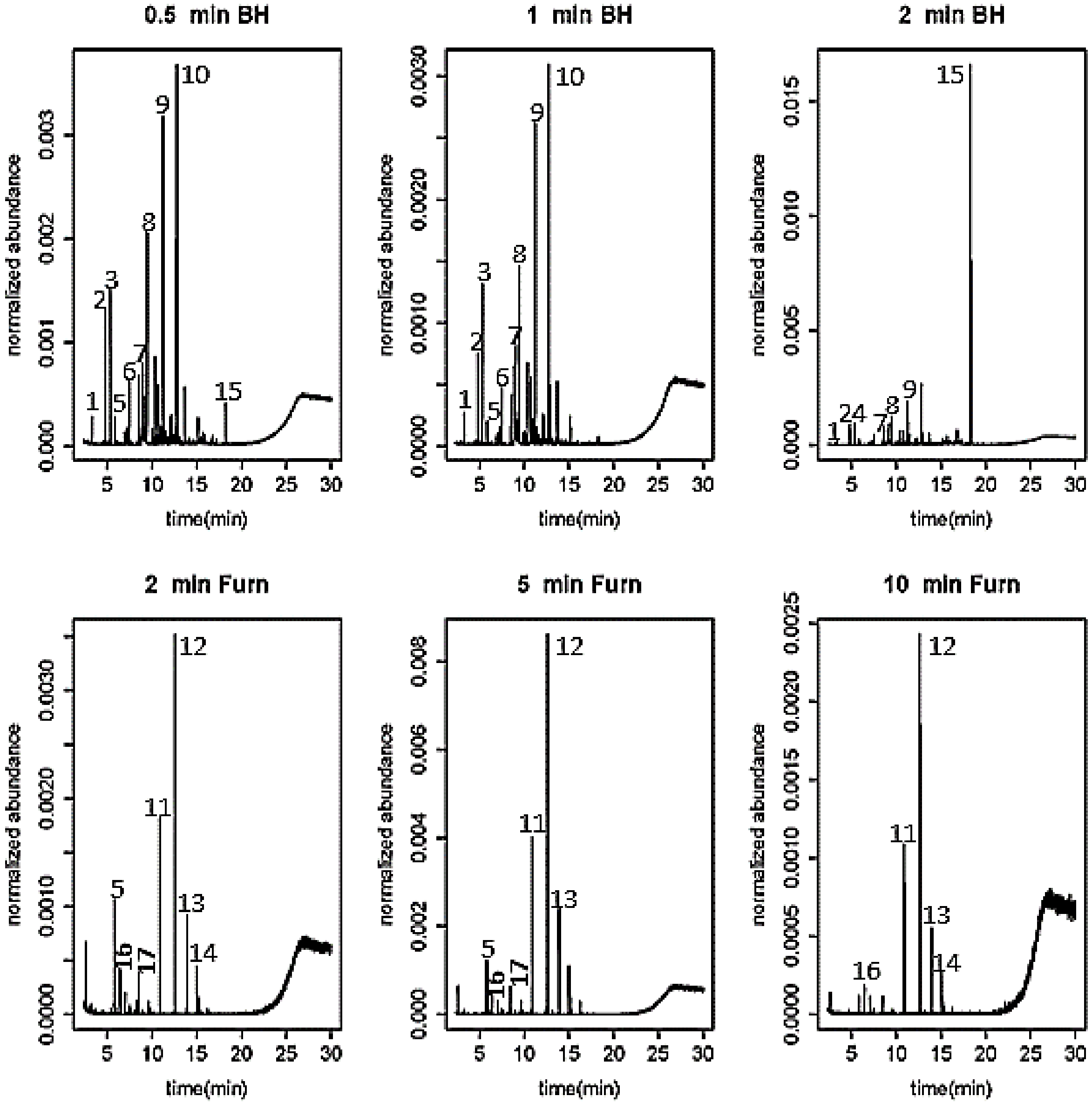


Figure 43: Compounds (1) pentanal, (2) 1-pentanol, (3) toluene, (4) hexanal, (5) 2-furaldehyde, (6) heptanal, (7) alpha pinene, (8) octanal, (9) nonanal, (10) 1-methoxy-4-(2-propenyl) benzene, (11) 2-methoxyphenol, (12) 2-methoxy-4-methyl phenol, (13) 4-ethyl-2-methoxy-phenol, (14) eugenol, (15) TXIB, (16) furfuryl alcohol, (17) 5-methylfurfural

From the above figures, multiple conclusions about the substrate and laboratory burn methods could be reached. As observed for all discussed carpeting and processed flooring, the MDDM burning method produced the largest number of identified products. With increase in burn time, the MDDM laboratory burn TICs of yellow pine increase in volatile pyrolysis/combustion products and additional identified phenolic aromatic products were observed. TXIB, a wood coating commonly used as finishing, was identified in the 2 min MDDM chromatographic profile. TH laboratory burns displayed TXIB identification in the 0.5 min laboratory burn. With increase in burn time, TH laboratory burn TICs were similar in chromatographic profiles, but fewer identified pyrolysis/combustion products were observed in the 2 min TH burn. The 0.5 and 1 min BH laboratory burns displayed similar peak patterns and chromatographic profiles to TH laboratory burns. The 2 min BH laboratory burn exhibited a difference in product profile with identification of the TXIB component. FURN laboratory burns yielded mostly phenolic aromatic components within the TICs. The MDDM and FURN laboratory burns displayed the three major cellulosic pyrolysis/combustion products expected from pyrolysis of yellow pine.

2-furaldehyde was present in almost all laboratory burns of yellow pine, but the abundance varied depending on the burning method and time utilized. 2-furaldeyhde, an aromatic component, was one of the major expected cellulosic pyrolysis/combustion products identified in the degradation of wood. Intensity of abundance of 2-furaldehyde decreased with increasing burn time, but in MDDM laboratory burns, the 2-furaldehyde abundance slightly increased. Different burn method parameters and laboratory burn time affected the chromatographic profile of pyrolysis/combustion products that were produced.

4.11 Polyester Carpet/Carpet Padding

4.11.1 Projection of Laboratory Burns into Fire Debris Data Sets

Polyester carpeting and carpet padding burns were completed using three different laboratory burn methods (MDDM, MDDM with Gasoline, and MDDM with MPD) with three different burn times and projected into the same principal component space and map of the contour regions that were used for projection of the *in silico* data. Chosen ILs utilized for the laboratory burns were a neat gasoline, SRN 105 – Phillips 66 Unleaded Regular Gasoline, and a medium petroleum distillate (MPD), SRN 30 – Klean Strip Odorless Mineral Spirits. Gasoline and petroleum distillate ILs were chosen due to their target products in identification and product pattern that is discernible through observation of the chromatogram. Laboratory burn projections were compared to LSB and neat IL/SUB principal component spaces. The first three principal components were utilized for projection of polyester carpet and carpet padding laboratory burn data. Analysis of projected laboratory burn data yielded information as to the similarities and differences between the utilized MDDM laboratory burn method and the addition of ignitable liquid to the MDDM laboratory burning method. Projection of the polyester carpeting and carpet padding laboratory burn data into the LSB PCA space is provided in **Figure 44**.

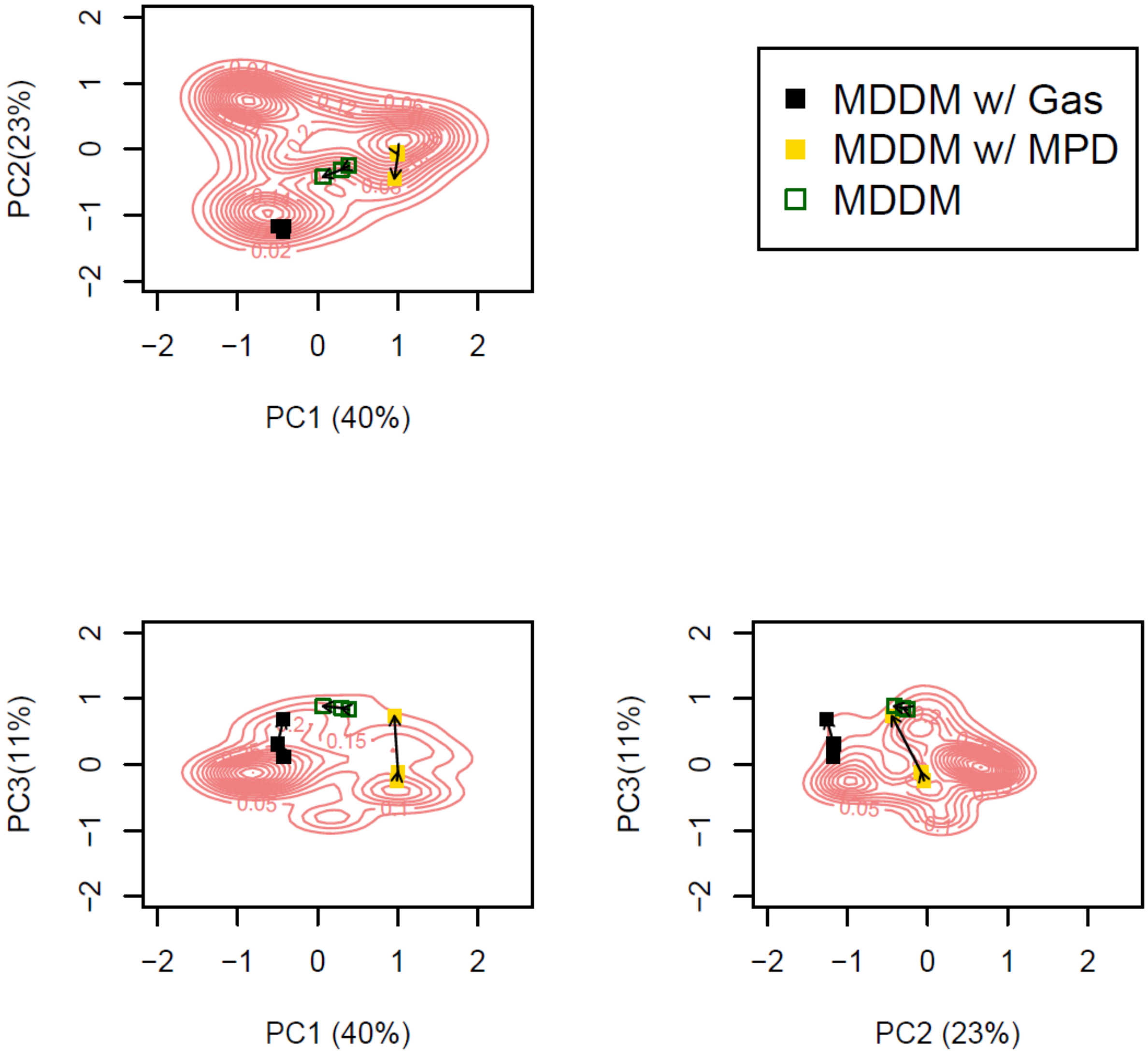


Figure 44: Projection of polyester carpeting and carpet padding into LSB PCA space

Due to similarities in the properties of all three MDDM methods, they were grouped into similar shapes. Different colors denote whether the laboratory burn was performed with or without a particular IL.

In the three different orthogonal views covering 74% variance in the data, all laboratory burn data projected into the LSB map of the contour region. However, there were a few laboratory burn projections that neared the edge of the map of the contour area. With increase in burn time, the MDDM with IL addition laboratory burn data shifted in projection. Clustering was observed between the MDDM without IL addition laboratory burn projections. Projection of the polyester carpeting and carpet padding laboratory burn data into the neat IL/SUB PCA space is provided in **Figure 45**.

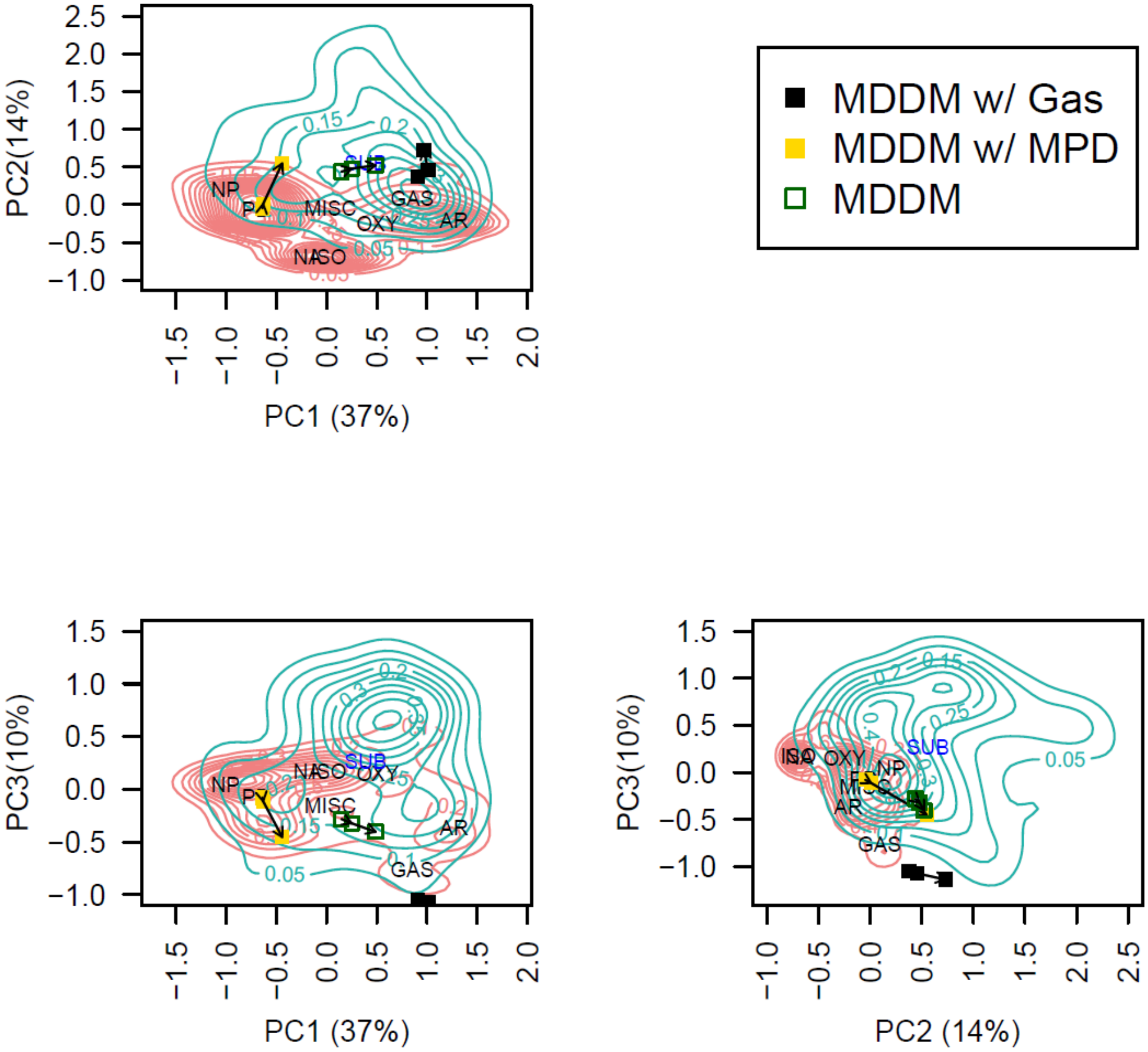


Figure 45: Projection of polyester carpeting and padding into neat IL/SUB PCA space

Because the Substrate Database was composed of substrates burning using the MDDM burn method, it was expected that each MDDM laboratory burn of polyester carpet and carpet padding projected within the map of the contour region of neat IL/SUB. It was also expected that each MDDM laboratory burn with IL addition projected near the respective IL contour regions before evaporation of IL occurred with increase in burn time. Almost all laboratory burn data projected within the contour region for all PCs shown in **Figure 45**. Some MDDM with Gas addition laboratory burn data projected outside of the map of the contour region slightly.

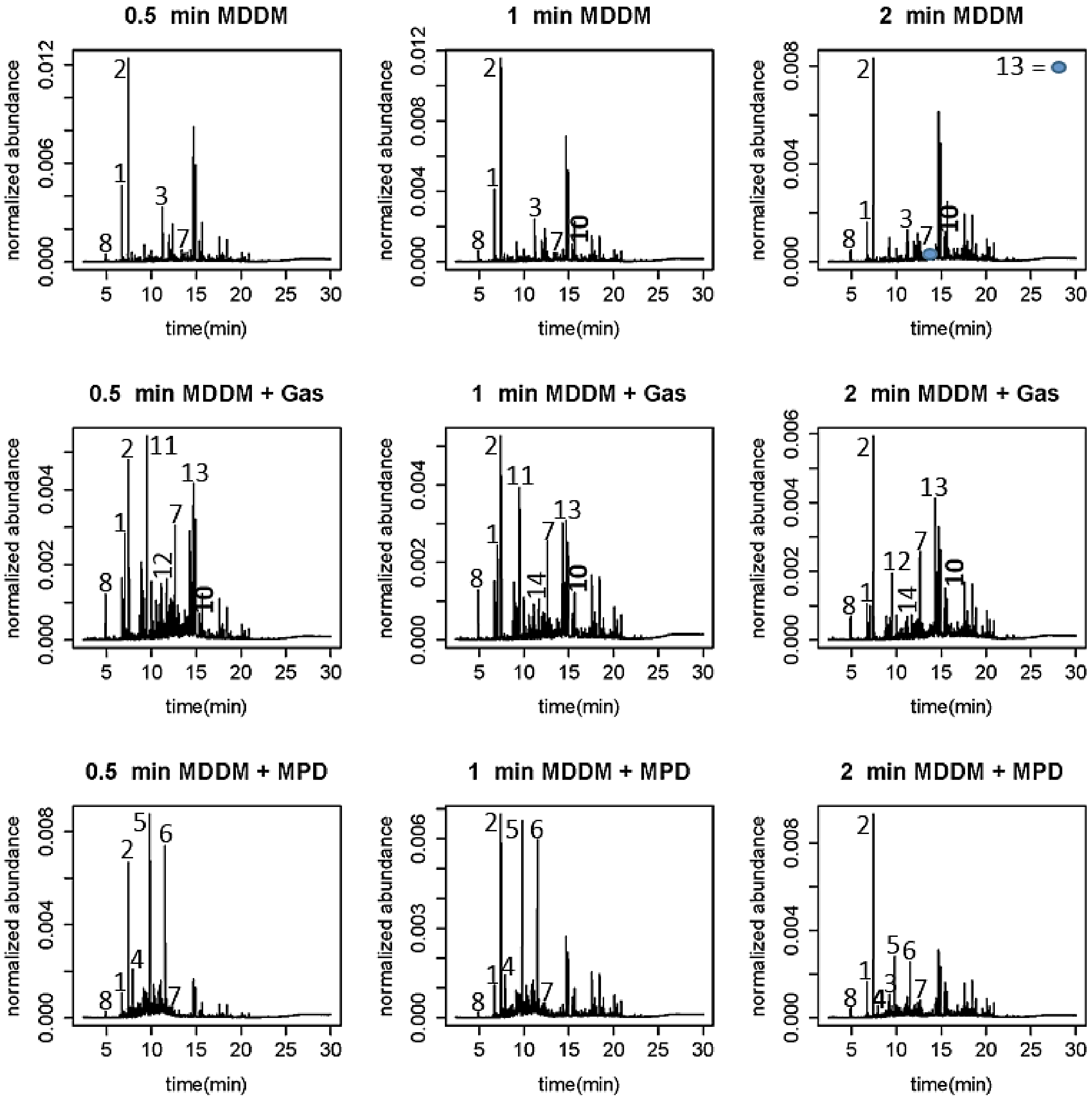
In the three different orthogonal views covering 61% variance in the data, almost all polyester carpeting and carpet padding laboratory burns projected within the neat IL/SUB PC map of the contour region. Therefore, there was a similarity between the MDDM and MDDM with MPD polyester carpeting and carpet padding burn data and the pure ignitable liquid and substrate data contained within the ILRC and Substrate database, respectively. The MDDM with Gas addition projected slightly outside of the contour mapping region. Therefore, there was a slight difference between the MDDM with Gas burn data and the ignitable liquid and substrate data sets. MDDM with no IL addition was clustering together with little shifting occurring with increase in burn time. The 0.5 and 1 min MDDM with Gas laboratory burn points clustered together and shifted with increase in burn time. The 0.5 and 1 min MDDM with MPD laboratory burn projections clustered as well and then shifted with increase in burn time. The laboratory burn data appeared to be similar to the burn data that is contained within the ILRC database. All polyester carpet and carpet padding laboratory burn data projected into the IL region. Analysis of the projections of laboratory burn data into the LSB and neat IL/SUB PC spaces and the TICs of the laboratory burns yielded information regarding the similarities and differences between the different MDDM laboratory burn methods.

4.11.2 TICs from Laboratory Burns

Mixture of polyester carpet and carpet padding with and without IL addition was burned using the MDDM burning method and three burn times for each different addition mixture. MDDM was chosen as the burning method for this experiment because it produced the largest number of identified pyrolysis/combustion products in the chromatographic profile. Polyester carpet was burned with carpet padding directly underneath without any IL addition. Six additional laboratory burns were performed using addition of gasoline or medium petroleum distillate IL to observe how the IL affected the resulting chromatographic profile. It was expected that the product pattern would be reflective of both substrate and ILR pattern.

Major pyrolysis/combustion products expected for polyester carpet are produced from random scission of PET and propylene or polybutadiene backing of the carpet yielding small amounts of oxygenated aromatics like toluene, benzene and styrene. Major pyrolysis products expected for carpet padding are produced from random scission of polyurethane yielding benzene, toluene, alpha methylstyrene, and styrene. The addition of IL provided insight into the possible modification of peak abundances in the scenario where substrate and IL observe similar components in the TICs.

The TICs from the laboratory burns were compared amongst the burns. Pyrolysis products were confirmed through mass spectra comparisons from NIST and ILRC NCFS compiled libraries and retention time comparison. The TICs from the MDDM and MDDM with ignitable liquid additions are displayed in **Figure 46**.



0.5 min MDDM

1 min MDDM

2 min MDDM

0.5 min MDDM + Gas

1 min MDDM + Gas

2 min MDDM + Gas

0.5 min MDDM + MPD

1 min MDDM + MPD

2 min MDDM + MPD

Figure 46: Compounds (1) 2,4-dimethyl-1-heptene, (2) styrene, (3) alpha methylstyrene, (4) n-nonane, (5) n-decane, (6) n-undecane, (7) naphthalene, (8) toluene, (9) 4-phenylbutronitrile, (10) biphenyl, (11) 1,2,4-trimethylbenzene, (12) 1,2,3,5-tetramethylbenzene, (13) 2-methylnaphthalene, (14) 1,2,4,5-tetramethylbenzene

From the above figures, multiple conclusions about the substrate mixture, addition of ignitable liquids and MDDM laboratory burning method could be reached. MDDM with addition of gasoline produced the largest number of identified pyrolysis/combustion products. For the MDDM with gasoline addition laboratory burns, volatile components such as toluene and 2,4-dimethyl-1-heptene decreased with increasing burn time. Target compounds identified within gasoline ILR patterns were identified within the chromatographic profiles of the MDDM with gasoline addition TIC. The target compounds of gasoline identified were: 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene, 2-methylnaphthalene, and 1,2,4,5-tetramethylbenzene.

For MDDM laboratory burns of polyester and carpet padding with addition of MPD, decrease of normal alkane abundace was observed with increase in burn time. Major target compounds identified within MPD ILR patterns were identified within the chromatographic profiles of the MDDM with MPD addition mixture. Major target compounds of MPD identified were: n-nonane, n-dodecane, and n-undecane.

For MDDM laboratory burn of polyester carpet and carpet padding with no addition of IL, increase in the number of identified pyrolysis/combustion products was observed with increasing burn time. It was apparent from the MDDM with no IL addition TICs, that the IL addition yielded a difference of chromatographic profile with an increase in identified ILR. Analysis of laboratory burns without use of IL addition and using that information in attempting to understand the effects of the IL addition was extremely beneficial.

Across all polyester carpeting and carpet padding laboratory burns, 2,4-dimethyl-1-heptene, toluene, naphthalene and styrene were present in all chromatographic profiles. 2,4-

dimethyl-1-heptene, an aliphatic compound, was observed in the previously discussed carpeting and the carpet padding MDDM laboratory burns. Styrene and 2,4-dimethyl-1-heptene were pyrolysis/combustion products from the substrate mixture of polyester carpeting and carpet padding. Toluene and naphthalene were similarly obsvered within laboratory burns of polyester carpeting and carpet padding and have previously been found within ILR patterns of gasoline and MPD. Similarity in composition amongst pyrolysis/combustion products could lead to modification of peak abundances within the chromatographic profiles. IL additions could complicate the chromatographic profile with ILR being present in the TIC. Different burn method parameters and the laboratory burn time affected the chromatographic profile of pyrolysis/combustion and ILR products that were produced.

4.12 Compilation of Laboratory Burns

Eight different substrates were utilized to create the laboratory burns that were analyzed and projected against the substrate and ignitable liquid databases. In this research, 105 laboratory burns were completed and similar pyrolysis/combustion products were observed in the TICs of different flooring substrates. The most commonly observed pyrolysis/combustion products in different substrate laboratory burns using the four different laboratory burn methods have been compiled in **Table 1**. This allows for the percent of observed pyrolysis/combustion products from the burns to be compiled and compared. The majority of flooring substrates chosen for this research were carpeting. Additional tables have been formed to display the most common pyrolysis products observed for the three different types of chosen flooring substrates. The most common pyrolysis/combustion products for carpeting is displayed in **Table 2**, processed flooring in **Table 3** and wood flooring in **Table 4**.

Table 1: Most common pyrolysis/combustion products from laboratory burns

Compound	Occurrence in %
*Benzaldehyde	49.5%
Styrene	43.8%
Toluene	38.1%
2,4-dimethyl-1-heptene	29.5%
*Acetophenone	25.7%
*2-furaldehyde	23.8%
Naphthalene	21.0%
Alpha methylstyrene	20.0%
Benzene	17.1%
*Hexanal	17.1%
*2-methoxyphenol	16.2%
*Nonanal	15.2%
*Furfuryl Alcohol	14.3%

***** Oxygenated component

For carpeting substrates, 57 different carpet burns were compared that included the polyester, nylon and olefin carpets, carpet padding and a mixture of polyester carpet and carpet padding. For synthetic/processed flooring, 27 different burns were compared from the vinyl and laminate flooring substrates. For the wood based flooring, 27 different burns were compared that included yellow pine and plywood. Similarities were observed between the processed and wood flooring pyrolysis products. Both contain mostly oxygenated pyrolysis/combustion products.

Table 2: Common pyrolysis/combustion products for carpet flooring from laboratory burns

Compound	Occurrence in %
Styrene	80.7%
*Benzaldehyde	68.4%
2,4-dimethyl-1-heptene	54.4%
*Acetophenone	47.4%
Toluene	43.9%
Alpha methylstyrene	36.8%
Biphenyl	28.1%
Naphthalene	24.6%
Caprolactam	15.8%
Benzene	12.3%
4-phenylbutronitrile	10.5%
Benzonitrile	8.8%

***** Oxygenated component

Table 3: Common pyrolysis/combustion products for processed flooring from laboratory burns

Compound	Occurrence in %
*Methyl ester hexadecanoic acid	52.2%
*2-ethyl-1-hexanol	52.2%
Toluene	47.8%
Benzene	47.8%
*2-furaldehyde	43.5%
*Methyl isobutyl ketone	39.1%
*Furfuryl alcohol	34.8%
*Benzaldehyde	34.8%
*Alpha terpinol	26.1%
*2-methoxyphenol	26.1%
*2-methoxy-4-methylphenol	17.4%
*Hexanal	17.4%

***** Oxygenated component

Table 4: Common pyrolysis/combustion products for wood flooring from laboratory burns

Compound	Occurrence in %
*2-furaldehyde	65.2%
Alpha pinene	60.9%
*Hexanal	60.9%
*Nonanal	56.5%
*2-methoxyphenol	47.8%
*4-ethyl-2-methoxyphenol	43.5%
*5-methylfurfural	43.5%
*1-pentanol	39.1%
*Pentanal	34.8%
*Eugenol	34.8%
*Octanal	34.8%
*1-methoxy-4-(2-propenyl) benzene	34.8%

***** Oxygenated component

The majority of the highest occurring components from the burning of the different flooring substrates appeared to be oxygenated compounds. Aromatic components were also commonly listed components identified within the chromatographic profiles of the different laboratory burns. Benzaldehyde and styrene were both identified in over 40% of substrate burns within this research. Although wood and processed flooring mostly yielded oxygenated components, carpets yielded more varied pyrolysis/combustion products. The variation observed from the burning and analysis of different types of flooring material was reflective of the variability of fire debris. The expansion of the Substrate Database to include many different substrates will provide analysts with another tool to utilize during the analysis process to identify the presence of ILR in fire debris.

CHAPTER 5: CONCLUSION

A burning method, MDDM, was utilized previously to study pyrolysis and combustion products that were expected to be produced in a fire scene. Those results were compiled to form the Substrate Database. Three additional burning methods, TH, BH and FURN, were established to further study fire debris and pyrolysis effects in a laboratory setting. From the results, it was difficult to replicate casework fire debris, but pertinent information could be gathered from this research. Each substrate that was burned produced a different chromatographic profile with different pyrolysis/combustion products and a different product pattern. Increase in burn time affected each outputted TIC in different ways directly related to the substrate and burn method being utilized. MDDM allowed for observation of many possible pyrolysis/combustion products that could be observed from the burning of a material. However, every possible pyrolysis/combustion product from the burning of a substrate may not be observed in casework fire debris. Additional laboratory burning methods facilitated different possible burn scenarios. This created multiple product profiles of substrates that were observable with the use of GC-MS instrumentation utilizing ASTM E1412 extraction method. One laboratory burning method that was most applicable to real life fire debris could not be chosen. Outputted TIS (total ion spectra), which were projected onto the calculated PCA spaces, displayed the similarities in types of pyrolysis/combustion products. Outputted TICs displayed differences in pyrolysis/combustion products, product pattern, and chromatographic profile for the different burn methods and burn times. The use of both TIS and TICs for comparison of the burn data allowed for the observation of similarities and differences amongst the different laboratory burns.

A few improvements and continuing research could help escalate these studies for the benefit of further understanding fire debris. One suggestion that could be implemented is researching the effects of older substrates versus newer substrates. Understandably, it would be reasonable to burn additional substrates using multiple burn methods to analyze the outputted pyrolysis/combustion products. In terms of the burning methods, the FURN laboratory burn method was not able to be done consecutively. The FURN laboratory method was able to be performed twice at 2 and 5 minutes, then the tube furnace needed to be cooled before performing the next burn. A possible solution could be to perform the MDDM method at a longer burning time in hopes to simulate the FURN laboratory burns. Improving the BH laboratory burning method, that was heated through two layers, would require the use of a paint can lid instead of the tin boat and metal pan for heating. This will allow the heat to be indirectly applied from underneath the material as the flame will only have to go through one layer. Weighing each substrate to ensure consistency for each individual substrate could be beneficial. Another improvement could be to perform additional experimentations similar to the addition of ignitable liquid to carpeting and carpet padding, but on the other various substrates to see the outputted pyrolysis product profiles. All of these improvements would only further add to the overall coverage of the Substrate Database.

Furthermore, the analysis of the many different chromatographic profiles in comparison to casework fire debris and the Substrate/Ignitable Liquid databases were beneficial. TH and BH laboratory burn points consistently clustered together due to condensation. MDDM laboratory burn TICs tended to observe the largest amount of identified pyrolysis/combustion products due to the burn taking place within a container and condensate retained within the paint can. Shifting in projections with increase in burn time was frequently observed for all burn methods. Shifts in location of the projected points corresponded to changes in composition of the samples. The biggest takeaway was observing the similarity between the laboratory burn data and the LSB, ILRC and Substrate data sets. Information regarding the classification was more complex using this study, but a few substrates were very similar to the data contained in the Substrate Database. Indicators present in the product profile could aid the analyst in determining the presence of a particular substrate, such as the major cellulosic products in wood. Investigation of simulated laboratory burns using different burn methods allowed for the observation of the similarities and differences of chemical composition within particular substrates chosen for this research.

The most beneficial aspect to this research was the expansion of the Substrate Database to not only include additional substrates, but additional burning methods that potentially yielded slightly different pyrolysis/combustion products. This updated database could aide analysts in attempting to interpret chromatographic profiles that were analyzed from a fire scene. Certain pyrolysis/combustion products could be linked to a substrate that is burned, while other peaks could be linked to ILR that is from addition of ignitable liquid. The ILRC is currently the largest non-profit Ignitable Liquid and Substrate databases able to be studied by anyone that has internet access. Studying different pyrolysis processes and observing patterns amongst different substrates facilitated further understanding of real world fire debris. Through the optimization of different laboratory burn methods, knowledge about fire debris and sample pyrolysis/combustion interpretation could be obtained.

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